

# Polybenzyl Methacrylate Brush Used in the Top-Down/Bottom-Up Approach for Nanopatterning Technology

Yuhsin Tsai,<sup>1</sup> Wei-Ching Wang,<sup>2</sup>

<sup>1</sup>Division of Polymer Technology, Union Chemical Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

<sup>2</sup>Graduate Institute of Chinese Medical Science, China Medical University, Taichung, Taiwan

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**ABSTRACT:** Atom-transfer radical polymerization (ATRP) of benzyl methacrylate (BzMA) at ambient temperature was applied to step and flash imprint lithography. This process involved the formation of patterned polymeric networks (top-down) and the grafting polymerization of BzMA from these networks (bottom-up) via ATRP. Confocal laser scanning microscope and scanning electron microscope were used to de-

termine the change in line-to-line separation (width) resulting from poly BzMA brush. The increase in line width at 400 nm could be maximized given a reaction time of 2 h. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1953–1957, 2006

**Key words:** surfaces; atom-transfer radical polymerization (ATRP); graft copolymers; lithography; nanotechnology

## INTRODUCTION

Fabrication of precise nanoscale structures is essential for nanotechnology. The ability to fabricate on a nanometer scale guarantees a continued miniaturization of functional devices. New advanced fabrication technologies have enabled the lateral dimensions of devices to be reduced to well below 100 nm. Basically, fabrication techniques can be divided into two broad categories, namely “top-down” approaches and “bottom-up” approaches.<sup>1</sup> Top-down approaches include micro fabrication techniques including photolithography, dip-pen nanolithography, e-beam patterning, nanoimprint lithography,<sup>2</sup> step and flash imprint lithography,<sup>3</sup> and microcontact printing.<sup>4</sup> Meanwhile, bottom-up approaches include the use of self-organizing materials that can undergo pattern formation at the nanoscale levels to provide technologically interesting structures.

One bottom-up approach, which has received considerable attention recently, is surface-initiated polymerization reaction (grafting-from), which enables the modification and control of the surface properties of materials to a considerable extent. Various surface-initiated “living” polymerization including cationic,<sup>5</sup> anionic,<sup>6</sup> ring-opening,<sup>7</sup> atom-transfer radical polymerization (ATRP),<sup>8–12</sup> nitroxide-mediated radical polymerization,<sup>13</sup> and reversible addition/fragmentation chain transfer<sup>14,15</sup> have been successfully used to

produce surface-grafted polymers under controlled growth conditions. Among the different methods used to date, surface-initiated free-radical polymerization is a versatile method since it permits the synthesis of various functional brushes with controlled molecular weight and molecular weight distribution.

Recently, a top-down/bottom-up approach for manipulating the size and chemistry of nanoscopic features using a combination of step and flash imprint lithography (top-down process) and controlled-radical polymerization (bottom-up process) has been developed.<sup>16</sup> The proposed approach involves a photopolymer containing an imbedded initiating fragment, which was molded into patterned features followed by UV curing process to form patterned network (step and flash imprint lithography). A secondary reaction step involves the growth of polymer brushes from the surface of the patterned network via controlled-radical polymerization. Consequently, various nanoscopic structures with different feature sizes and functional groups can be grown from the original molded template.

To date, most controlled-radical polymerization reactions on surfaces have been conducted at fairly raised temperatures, mostly between 90 and 120 °C. Owing to practical considerations, the patterned polymeric features from the original molded template (top-down process) should not be destroyed during atom-transfer radical grafting reaction (bottom-up process) in the top-down/bottom-up approach. High reaction temperature and long reaction time cause patterned polymeric features to become deformed or peeled off from the substrate by the swelling effect of

Correspondence to: Y. Tsai (ytsai@itri.org.tw).

monomer or solvent. Grafting reaction from the patterned polymers to a certain thickness should be completed rapidly and under ambient temperature. This study reports a top-down/bottom-up approach for nanoimprint, in which benzyl methacrylate is selected as the monomer for surface-initiated polymerization because of its rapid polymerization rate at ambient temperature.<sup>17</sup>

## EXPERIMENTAL

### Materials

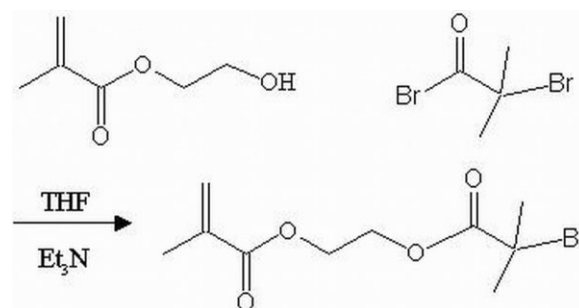
Benzyl methacrylate (BzMA) and tetrahydrofuran (THF) from Aldrich were dried over  $\text{CaH}_2$  and distilled under reduced pressure. *N*-Vinyl pyrrolidone (Aldrich), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (TMPA) (Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Aldrich), pentamethyl-diethylenetriamine (PMDETA, 99%) (Aldrich), and 3-methacryloxypropyl trichlorosilane (UCT) were used as received. Patterned silicon molds with desired features were made by e-beam lithography. Glass substrates were soaked in a concentrated sulfuric acid solution and rinsed extensively with deionized water. The glasses were then dried in an oven. An adhesion promoter, 3-methacryloxypropyl trichlorosilane, was then vapor-deposited on the glass under a saturated stream of dry nitrogen.

### Instrumentation

Surface topographical images were obtained by KeyenceVK-8550 confocal laser scanning microscope (CLSM). Electron micrographs were recorded on a Hitachi S-4700 scanning electron microscope (SEM). Gel permeation chromatography (GPC) was performed on a Waters chromatograph (four Waters Styragel HR columns HR1, HR2, HR4, and HR5E in series) connected to a Waters 410 differential refractometer with THF as the eluent. Molecular weight standards were narrow polydispersity polystyrenes.

### Synthesis of 2-methacryloxyethyl-2'-bromoisobutyrate

A three neck flask containing 100 mol of dry THF, 2.12 g (16.3 mmol) of 2-hydroxyethyl methacrylate, and 1.15 g (16.3 mmol) of triethylamine was equipped with a stir bar and cooled to 0 °C in an ice bath. Using an addition funnel, 4.37 g (19.0 mmol) of 2-bromoisobutyryl bromide was added drop-wise. Upon complete addition, the mixture was brought to room temperature and stirred for 18 h. The product was washed with 100 mL of  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ , and the solvent was evaporated. The remaining pale yellow oil was distilled under reduced



Scheme 1

pressure (200 mTorr) at 75 °C, and the product (5.94 g, 65.2%) was collected.

### Pattern formation

The photopolymer solution consisted of the following formulation: ethoxylated bisphenol-A dimethacrylate (20%), *N*-vinyl pyrrolidone (30%), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (25%), 2,2-dimethoxy-2-phenylacetophenone (5%), 2-methacryloxyethyl-2'-bromoisobutyrate (20%). This solution was filtered onto a cleaned and 3-methacryloxypropyl trichlorosilane treated glasses and spun at 3000 rpm for 1 min. The patterned silicon molds with desired features was brought into contact with the glasses, and pressure was applied. The glasses were exposed using 365-nm light (14 mW/cm<sup>2</sup>) for 1 min, and then the mold was peeled off leaving an inimer-embedded network replica layer on the surface of the glasses.

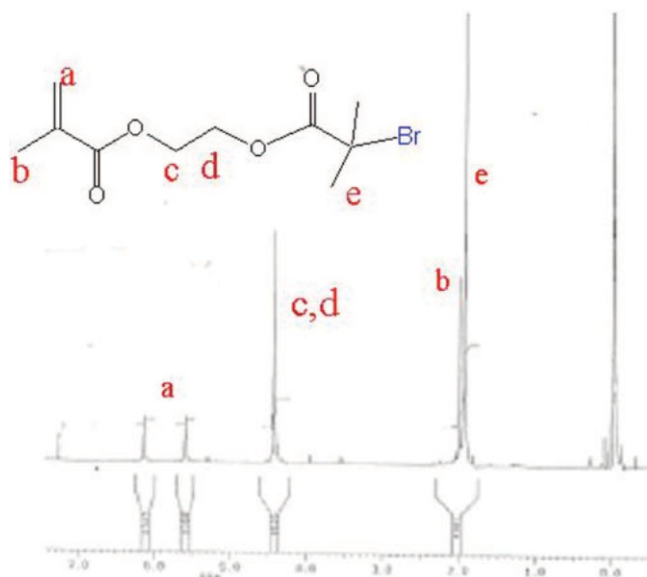
### Graft ATRP from patterned network

A glass coated with a cured thin film network was added to a Schlenk flask containing 10.2 mg (7.1–10.5 mol) of CuBr and a stir bar. BzMA (2.50 mL) and PMDETA (10.0–30.5 mol) were added via syringe. The flask was purged of oxygen via three cycles of freeze-pump, thaw, and backfilling with  $\text{N}_2$ . The reaction was performed at room temperature. The glass was removed from the flask and rinsed with excess of acetone and THF. Any physisorbed polymer was removed by exhaustive extraction with THF in a Soxhlet apparatus.

## RESULTS AND DISCUSSION

### Synthesis of 2-methacryloxy-2'-2-bromoisobutyrate

Methacryloxy-2'-bromoisobutyrate is synthesized from 2-hydroxyethyl methacrylate and 2-bromoisobutyryl bromide in dry THF at room temperature in the presence with triethyl amine as catalyst, as shown in Scheme 1. Methacryloxy-2'-bromoisobutyrate is used as an inimer (with both initiator and monomer frag-



**Figure 1**  $^1\text{H}$  NMR spectrum of methacryloxy-2'-bromoisobutyrate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ments) in this work. The double bond of 2-methacryloxy-2'-bromoisobutyrate is reactive to UV generated radical process, and is shown at 6.1 and 5.5 ppm in the  $^1\text{H}$  NMR spectrum (Fig. 1). This reactive feature provides a pathway for film formation on the substrate following UV curing. This study also observes the hydrogen chemical shift of methylene oxide and methyl at 4.3 and 2.0 ppm, respectively. Tertiary bromide is an essential group for initiating sites of ATRP, and is the site from which polymer brush grows.

#### Surface-initiated ATRP of poly(BzMA) brush on a flat substrate

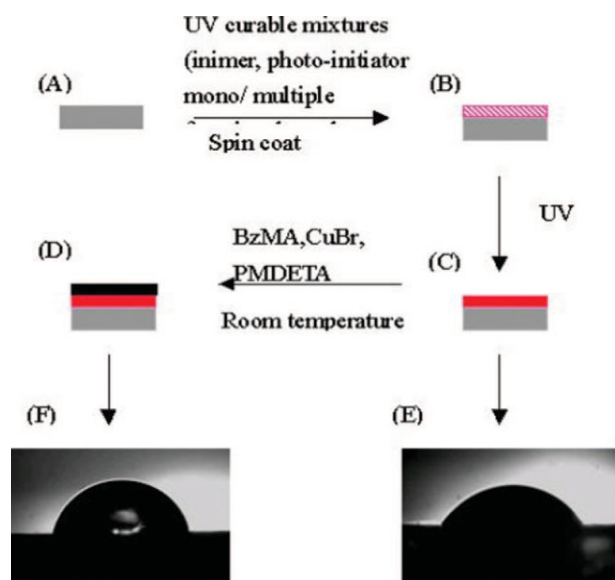
The feasibility of surface-initiated polymerization of inimer-embedded networks is examined, before applying to step and flash imprint lithography. The embedded inimer network are obtained from a UV curable solution containing 2-methacryloxy-2'-2-bromoisobutyrate (inimer), *N*-vinyl pyrrolidone, 2-ethyl-2-hydroxyethyl-1,3 propanedol trimethacrylate, and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), through exposure to UV radiation. This solution is spun at 3000 rpm for 1 min on 3-methacryloxypropyl trichlorosilane treated glass and then exposed to 365-nm light ( $14 \text{ mW}/\text{cm}^2$ ) for 1 min [see Figs. 2(A)–2(C)]. 3-Methacryloxypropyl trichlorosilane promotes adhesion between the glass surface and the forming polymeric film during UV curing.

The embedded inimer film is characterized using water contact angle measurements to determine its surface properties. Following initial surface characterization, the thin films were subjected to ATRP poly-

merization conditions. The embedded inimer coated glass is immersed into a Schlenk flask with BzMA, CuBr, and pentamethyldiethylenetriamine (PMDETA) under a nitrogen atmosphere at room temperature [see Figs. 2(C) and 2(D)]. After 1 h reaction, the glass is extensively rinsed. The differences in water contact angles for both the films containing the embedded inimers before and after grafting reactions are shown in Figures 2(E) and 2(F), respectively. These results indicate that polymer brush was formed on the surface of embedded inimer film via ATRP, since poly-(BzMA) is less hydrophilic than embedded inimer film.

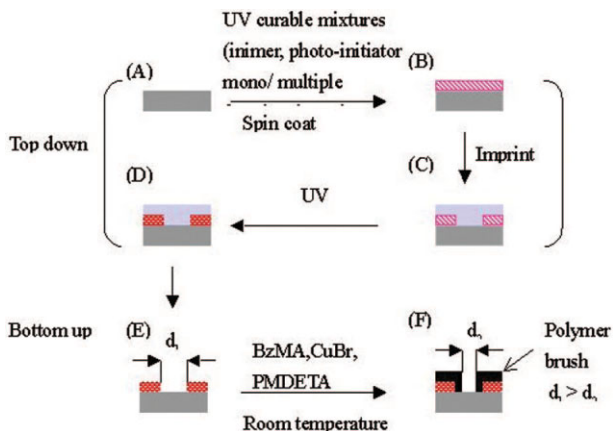
#### Poly(BzMA) brush for step and flash imprint lithography

Figure 3 shows the combination of step and flash imprint lithography (top-down) and controlled-radical polymerization (bottom-up). The top-down step is the preparation of a polymeric network with patterned features using the imprinting and UV curing process [step and flash imprint lithography; see Figs. 3(A)–3(C)]. This study uses 3-methacryloxypropyl trichlorosilane treated glass as the substrate and patterned silicon as the mold in this step. Several molds with various width pattern features were prepared via e-beam and ranged from 2 to  $20 \mu\text{m}$ . A UV curable solution containing 2-methacryloxy-2'-2-bromoisobutyrate (inimer), *N*-vinyl pyrrolidone, 2-ethyl-2(hydroxyethyl)-1,3 propanedol trimethacrylate, and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) was prepared and filtered.



**Figure 2** Outline of surface-initiated ATRP of poly(BzMA) brush on a flat substrate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



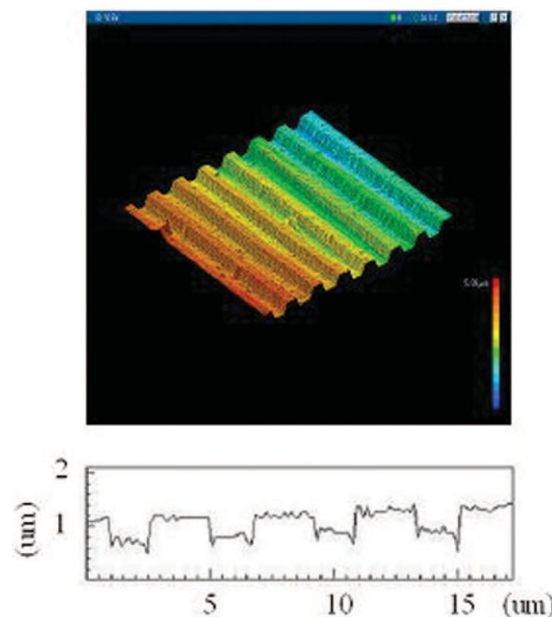


**Figure 3** Outline of the top-down/bottom-up process employed to grow polymer brushes from patterned polymeric network. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

This solution was spun at 3000 rpm for 1 min on the treated glass surface, and then imprinted into patterned features followed by exposure to 365-nm light ( $14 \text{ mW/cm}^2$ ) for 1 min. A polymeric network with patterned features was formed and peeled from the mold. The patterned polymers with inimer-embedded fragments (tertiary bromide groups) are capable of grafting from reactions via ATRP.

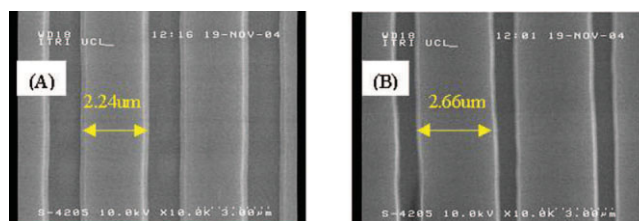
Mild reaction conditions and rapid polymerization rates are required to avoid the patterned polymeric features deforming or peeling from the substrate during the atom-transfer radical grafting reaction. BzMA was selected as the monomer for atom-transfer radical grafting reaction, because of its very rapid reaction rate at ambient temperature compared with that of other acrylic monomers. Under specific ligand ratio, its number average molecular weight can reach more than 100,000 g/mol within decades of minutes at ambient temperature.<sup>17</sup>

The grafting reaction from patterned polymer was performed via regular bulk ATRP [Figs. 3(E) and 3(F)]. The UV-cured patterned polymer was immersed in a reactor containing BzMA, pentamethyldiethylenetriamine, and CuBr under nitrogen atmosphere at room temperature. After a certain reaction time, the sample was removed and rinsed with excess acetone and THF. Exhaustive extraction with THF in a Soxhlet apparatus was conducted to remove physisorbed poly(BzMA). The molecular weight of the polymer grafted from the embedded inimers was reported to be a good approximation of the polymer isolated from solution.<sup>12</sup> The molecular weight and molecular weight distribution of poly(BzMA) brush were determined by isolating the free polymer grown concurrently in solution and followed by GPC. In this study, the molecular weight and molecular weight distribution of poly(BzMA) brush for a reaction of 2 h were about 650,000 g/mol and 1.20, respectively.

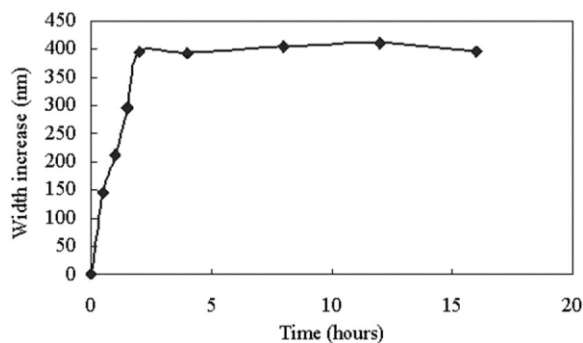


**Figure 4** A typical CLSM image and polymer brushes width profile growth from patterned polymeric networks. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Moreover, the width of the patterned polymer was analyzed using CLSM and SEM. Figure 4 shows a typical CLSM image of the pattern features and its corresponding width trace. Figure 5 shows the width increase of the patterned polymeric features (corresponding to a decrease in line-to-line separation), which resulted from the grafting of poly(BzMA). The increase in line width for the patterned feature size versus time is plotted in Figure 6. The polymerization appears well controlled for a reaction time up to 2 h, as indicated by the line width increasing linearly with reaction time. This observation is consistent with previous reports of surface-initiated ATRP, which demonstrate the growth of polymer brushes being slow down at longer reaction times. This trend suggests loss of active chain ends or increased steric interference to chain growth for longer brushes.<sup>18,19</sup> The maximum increase in width was 400 nm, which was reached



**Figure 5** SEM images of imprinted lines before (A) and after (B) ATRP brush growth. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Plots of the increase in width versus time for ATRP of BzMA.

after a reaction time of 2 h. Although no thickness change data are available for the patterned polymeric features, the increase in width can be expected to be proportional to the thickness increase.<sup>16</sup> Compared with the growth rate of PMMA brushes at ambient temperature (35 nm thickness in 12 h), the growth rate of poly(BzMA) was rapid.<sup>18</sup>

### CONCLUSIONS

ATRP of BzMA at ambient temperature was successfully applied in step and flash imprint lithography. This process involves the formation of patterned polymeric networks followed by grafting polymerization of BzMA from them. Poly(BzMA) brushes are grown from the surface of the patterned network via surface-initiated ATRP. CLSM and SEM were used to determine the change in line-to-line separation (width), which resulted from poly(BzMA) brush. Results indicate that the maximum increase in width is 400nm for

a reaction time of 2 h. This may result from the rapid polymerization rate of BzMA.

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