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## Surface-grafted block copolymer gradients: Effect of block length on solvent response<sup>☆</sup>

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### Abstract

We outline a method to fabricate gradient combinatorial libraries that explore architectural parameters of surface-grafted block copolymers (BCs). In addition, we demonstrate the utility of such libraries for the rapid, thorough assessment of the response of grafted BCs to solvent exposure. Our fabrication route uses surface-initiated controlled radical polymerization to produce a tethered polymer block with uniform length (in this case, poly(*n*-butyl methacrylate), PBMA), followed by a graded synthesis that adds a second block that varies in its length over the library (here, poly(2-(*N,N'*-dimethylamino)ethyl methacrylate), PDMAEMA). Our demonstration study maps the response of PBMA and PDMAEMA blocks to hexane and water, and defines regimes of behavior to this respect. Moreover, our study illuminates a narrow BC composition window that exhibits the strongest possible response to water and hexane treatment.

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### 1. Introduction

The advancement of new technologies such as micro- and nano-electro mechanical systems, novel sensors, and new biomaterials, hinges upon precise management of surface chemistry and physical properties to control factors such as adhesion, friction,

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environmental response and biocompatibility [1–3]. However, in many cases, the materials (e.g., silicon) best suited for bulk fabrication, mechanical strength, electronic properties, etc., in these applications offer limited flexibility regarding surface properties.

Surface-initiated polymerization offers a way to shape the surface properties of a variety of materials by adding a layer of end-tethered (grafted) polymer chains [4,5]. In this approach, a monolayer of moieties capable of initiating polymerization are covalently attached to the substrate material, and polymer chains are grown from these sites, forming a so-called polymer “brush”. Recent research in controlled polymer synthesis (a primary example being atom transfer radical polymerization or ATRP) demonstrates that polymer brushes with a huge variety of tailored compositions and architectures can be grafted from surfaces [6–8].

While surface-initiated polymerization routes offer a plethora of possibilities for materials modification, the behavior of grafted polymers is dictated by the same complex set of factors (e.g., grafting density, layer thickness, copolymer composition) that make them attractive [8–13]. Moreover, structure-property data useful for understanding the interaction and effect of these parameters, and for the engineering of these systems, is sparse.

Given this complex parameter space, in this paper we aim to develop and demonstrate combinatorial and high-throughput methods that foster the rapid and thorough assessment of grafted polymer species for surface modification. In this work, we focus on a particular polymer architecture, the diblock copolymer (BC), which consists of two chemically distinct polymer chains covalently bound at one end. Grafted BC systems are interesting because they can form surfaces that respond to environmental conditions, such as exposure to solvents that preferentially interact with specific blocks [14]. However, only certain ranges of BC composition are expected to accommodate the block segment rearrangement necessary for effective solvent-response. To elucidate this behavior, we exploit surface-initiated ATRP, and expand upon gradient methods forwarded by, for example, Genzer and Tomlinson [15,16] and researchers at NIST [17–20], to fabricate libraries that systematically vary BC composition. Our gradient grafted BC library consists of: (1) a “bottom” (i.e.

surface tethered) block of poly(*n*-butyl methacrylate) (PBMA), which is uniform in length, and (2) a “top” (untethered) block of poly(2-(*N,N*-dimethylamino)ethyl methacrylate) (PDMAEMA), which gradually varies in its length as a function of position along the specimen. To demonstrate the utility of this library for surface engineering, we map the response of this BC library to solvent exposure. In particular, through water contact angle measurements, we gauge the extent of block rearrangement induced by exposure to water and hexane. As will be seen below, our gradient library is effective in illuminating both general trends and details of BC surface behavior in this respect.

## 2. Experimental procedures<sup>1</sup>

### 2.1. Materials

2-(*N,N*-Dimethylamino)ethyl methacrylate (DMEAMA, 99%) was purchased from Polysciences. Copper(I) bromide (CuBr, 99%, Aldrich) was purified according to the literature procedures [21]. Copper(II) bromide (CuBr<sub>2</sub>, 99%), 2,2'-bipyridyl (bpy, +99%), *n*-butyl methacrylate (BMA, 99%), methylene chloride (99.9%, HPLC grade), hexane (98.5% ACS grade), dimethylformamide (DMF, 99.8%, HPLC grade), acetone (99.5%, ACS grade), and anhydrous toluene (99.8%) were purchased from Aldrich. Isopropanol (J.T. Baker) was HPLC grade. Water was purified through a Millipore Rios 16 system. Polished silicon (1 0 0) wafers were purchased from Wafer World, Inc.

### 2.2. Preparation of initiator functionalized substrate [22]

The initiator, 11-(2-bromo-2-methyl)propionyl-oxyundecanyltrichlorosilane, was synthesized according to literature procedures [23], and a solution of the initiator (0.5 mmol/L) in anhydrous toluene was

<sup>1</sup> Certain commercial equipment or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

prepared. Next, a silicon substrate ( $1.2\text{ cm} \times 8\text{ cm}$ , cleaned with acetone and a 30 min exposure to UV-ozone) was immersed in this solution overnight to form a self-assembled monolayer (SAM) of initiator on the surface. Finally, the specimen was rinsed with toluene and acetone, and then dried with nitrogen.

### 2.3. Preparation of polymerization solutions

CuBr (19.2 mg), CuBr<sub>2</sub> (3.3 mg), bpy (49.2 mg), and a stir bar were placed in a flask, which was capped with a septum. After three cycles of vacuum and argon backfill, 4.5 mL degassed isopropanol, 0.5 mL degassed H<sub>2</sub>O, and 5 mL degassed monomer (BMA or DMAEMA) were sequentially syringed into the flask. Solutions were stirred for 1 h.

### 2.4. Synthesis of the BC brush gradient

Fig. 1 outlines our route for surface-initiated ATRP of PBMA/DMAEMA BCs, which is similar to the solution polymerization reported by Matyjaszewski and co-workers [21]. First, a uniform PBMA brush layer was polymerized on the initiator-modified

silicon substrate. The substrate was placed in a flask sealed with a rubber septum. Following three cycles of vacuum and backfilling with argon, the flask was quickly filled with the BMA polymerization mixture to immerse the substrate. After a 1 h polymerization at room temperature, the substrate was removed from the reaction mixture, thoroughly rinsed with DMF, and dried with nitrogen. To synthesize the BC brush gradient, the PBMA functionalized substrate was placed upright in a flask, sealed with a rubber septum and followed by three cycles of vacuum and argon backfill. The PDMAEMA polymerization solution was transferred into a 10 mL syringe mounted on a programmable syringe pump (BS-8000, Braintree Scientific Inc.). The polymerization solution was pumped into the reaction flask along its sidewall at a rate of 100  $\mu\text{L}/\text{min}$ . Accordingly, the time of PDMAEMA polymerization gradually increased from the bottom of the substrate to the top. After a total of 2 h, the specimen was removed from the flask, rinsed with DMF, and dried with nitrogen. Spectroscopic ellipsometry (J. A. Woollam Co. Inc.) was used to map the thickness of the polymer brush before and after the PDMAEMA block was added. The spot size of the

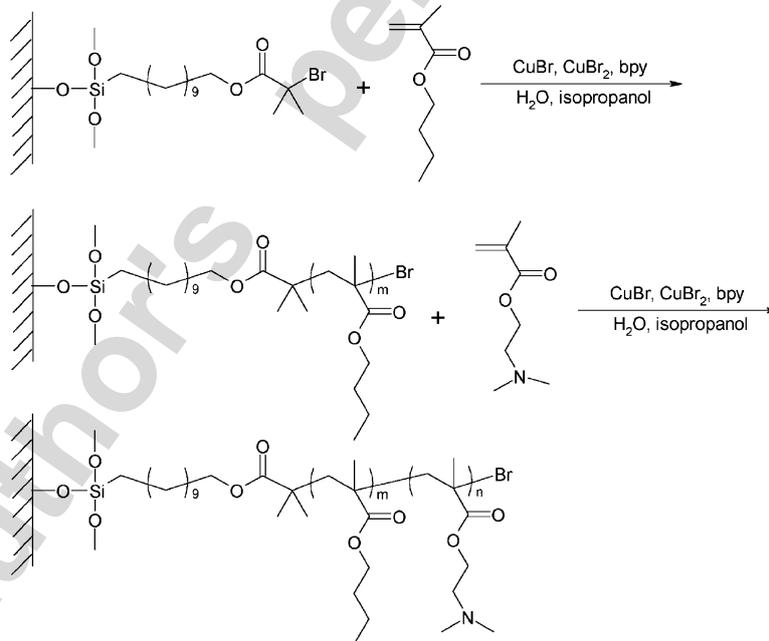


Fig. 1. Synthesis scheme for surface-initiated ATRP polymerization of BC brushes of PBMA and PDMAEMA. Acronyms for chemical species are defined in the text.

light used in the ellipsometry measurement was  $\sim 1.5$  mm. The standard uncertainty in these measurements is approximately  $\pm 0.4$  nm. We note that this BC library was fabricated in about the time necessary to synthesize a single-case specimen.

### 2.5. Solvent response measurements

We examined the BC brush library response to hexane and water. To facilitate the rearrangement of the copolymer segments, the brushes were treated to a series of “intermediate” solvents: methylene chloride, acetone and methanol. That is, before the sample was treated to water, it was sequentially immersed in methylene chloride, acetone, and methanol. Before hexane treatment, the reverse sequence was applied. Each solvent immersion lasted 30 min. Immediately after final solvent treatment, samples are quickly dried with nitrogen to prevent gross segmental rearrangement of the brushes during solvent the removal process. Static water contact angle ( $\theta_w$ ) measurements along the gradient library were immediately performed with a Krüss G2 instrument. In a typical measurement, the water droplet spread less than 2 mm. Our  $\theta_w$  measurements have an approximate standard uncertainty of  $\pm 3^\circ$ .

## 3. Results and discussion

### 3.1. Characterization of the BC brush library

As discussed above, the BC brush gradient was synthesized in two steps. First, a uniform PBMA brush was synthesized. As shown in Fig. 2, the PBMA layer was measured to be  $\approx 10$  nm thick across the entire substrate. Second, a graded polymerization of DMAEMA from the PBMA layer resulted in a BC brush gradient. After the second block was added, ellipsometry measurements show that the thickness of the PDMAEMA layer ranges linearly from  $\approx 0$  nm to  $\approx 12$  nm across the library (Fig. 2). This system is schematically illustrated in Fig. 3 (top).

### 3.2. Solvent response

Using our library, we mapped the response of the BC brush to water and hexane as a function of

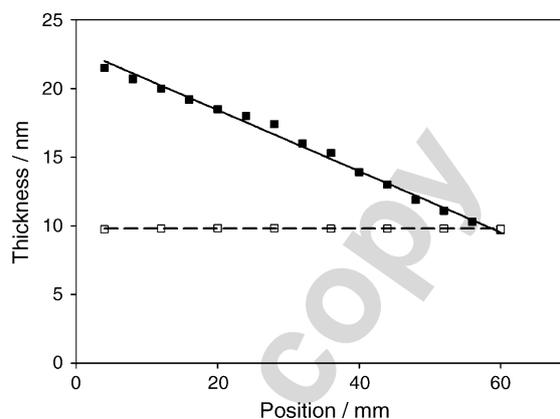


Fig. 2. Thickness profile of BC brush gradient library: (□) after polymerization of the PBMA block, (■) after addition of the PDMAEMA block.

PDMAEMA block length (i.e. thickness, hereafter  $h_{PD}$ ). In relative terms, water is a “selective” solvent for PDMAEMA (the more hydrophilic block), while hexane is selective for PBMA (the more hydrophobic block). Selective solvents bias the surface expression of polymer segments by swelling the block they are selective for and drawing it to the surface, while collapsing the other block and burying it within the brush layer. Water contact angle ( $\theta_w$ ) measurements were used to gauge this solvent-response. Homopolymer brushes of PBMA and PDMAEMA, prepared

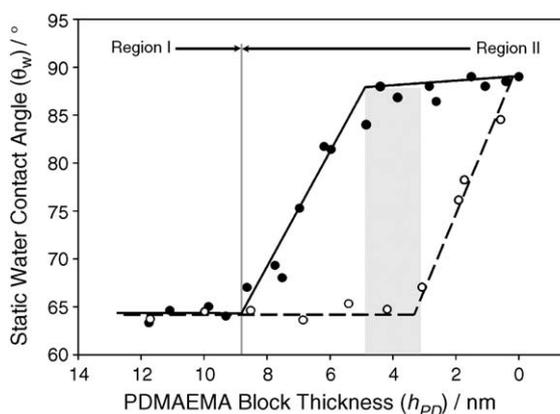


Fig. 3.  $\theta_w$  measurements collected across the BC brush gradient library after solvent treatment: (○, dashed line) after water, (●, solid line) after hexane. Lines are added to guide the eye. The gray line divide the data, the regions discussed in the text. The gray box highlights an approximate window of BC compositions that give the largest response to solvent treatment.

by routes similar to those described above, exhibit  $\theta_w$  values of approximately  $89^\circ$  and  $65^\circ$ , respectively. In our discussion, these  $\theta_w$  values are taken to be nominally characteristic of homogenous PBMA or PDMAEMA surfaces.

Fig. 3 summarizes  $\theta_w$  measurements collected across the BC brush library. Fig. 4 schematically illustrates posited brush morphologies to guide the discussion. In both of these figures,  $h_{PD}$  decreases from left to right. Unfilled circles (○) in Fig. 3 track the response of the brush library to water treatment. For PDMAEMA block thickness down to  $h_{PD} \approx 3$  nm, the surface exhibits a  $\theta_w$  characteristic of a homogenous PDMAEMA surface. Below  $h_{PD} \approx 3$  nm, the  $\theta_w$  value increases to that characteristic of pure PBMA. Accordingly, above  $h_{PD} \approx 3$  nm, the PDMAEMA block completely shields expression of PBMA segments at the surface. Below this critical thickness, PBMA segments are expressed increasingly at the surface in spite of the relative PDMAEMA affinity for water.

Filled circles (●) in Fig. 3 track the BC library response to hexane treatment. Down to  $h_{PD} \approx 9$  nm, the  $\theta_w$  is close to that of pure PDMAEMA. Between

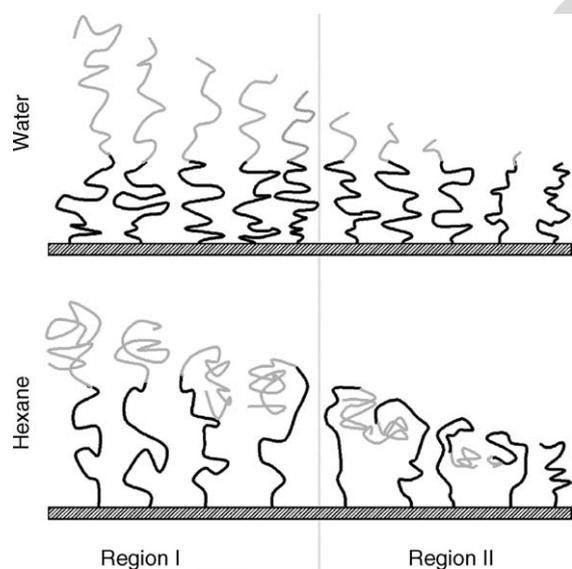


Fig. 4. Schematic illustrations of the BC brush gradient library. Black lines: PBMA block. Grey lines: PDMAEMA block. The top illustration shows the brush response to water; the bottom to hexane. The gray lines delineate regions of response behavior discussed in the text.

$h_{PD} \approx 9$  nm and  $h_{PD} \approx 5$  nm, the  $\theta_w$  increases from the value characteristic of PDMAEMA to that of PMBA. So, in spite of the fact that hexane is selective for PMBA, PDMAEMA layers above  $h_{PD} \approx 9$  nm completely suppress expression of PMBA segments at the brush surface. Moreover, PDMAEMA layers as thin as  $h_{PD} \approx 5$  nm mediate the expression of PMBA at that surface.

According to these results, our BC brush library exhibits two regimes of response with respect to water and hexane exposure. These regimes are delineated roughly in Fig. 3 (vertical gray lines) and schematically illustrated in Fig. 4. In Regime I, the block segments do not rearrange to the extent that they observably affect the surface chemistry. In contrast, Region II represents a range of BC compositions that give a measurable response to the considered solvents. Since the BC library varies  $h_{PD}$  systematically and continuously, Region II represents a parameter map useful for tuning the solvent-response of the brush by tailoring the BC composition. Moreover,  $\theta_w$  data from our gradient library illuminates a window of BC compositions (highlighted by the gray box in Fig. 3) that give the strongest response to solvent treatment. That is, for a narrow range of PDMAEMA block thickness ( $h_{PD} \approx 5$  nm to  $h_{PD} \approx 3$  nm), water or hexane exposure results in the  $\theta_w$  values characteristic for PDMAEMA or PBMA, respectively. Accordingly, in this window, the brush rearranges under solvent treatment to express nearly pure PBMA or PDMAEMA. By identifying this window of optimal response, the utility of the gradient library is clear, since it would be difficult (and time consuming) to observe such a narrow range of BC compositions through the single specimen fabrication and testing paradigm.

While our library explores one aspect of BC architecture ( $h_{PD}$ ), generally the delineation of regions I and II, and the optimal response window, will depend on a variety of other factors. For example, the relative lengths of the top and bottom blocks, the total BC length, the block order (top versus bottom), and the grafting density will likely shift, expand or eliminate response regimes. Also, the solvent removal process after the solvent treatment may affect the boundary of the regions. To broaden our understanding of the solvent behavior of BC brushes, we are currently fabricating and screening gradient libraries that will elucidate the effects of these factors.

#### 4. Summary and conclusions

In summary, we employ a graded surface-initiated ATRP method for fabricating combinatorial gradient libraries of surface-grafted block copolymers. Our BC gradient library exhibits a bottom block of uniform thickness and a top block that gradually and continuously changes in its thickness. We demonstrate this method by fabricating a BC library where PBMA is the constant bottom block and PDMAEMA is a linearly changing top block. Ellipsometry measurements confirm this gradient brush architecture. Moreover, we use the gradient library to map the response of the BC brushes to treatment by water and hexane, which are selective for PDMAEMA and PBMA, respectively. After the specimen was exposed to each solvent, segment rearrangement and segment surface expression was inferred via water contact angle measurements. The solvent-response map indicates the range of composition for which the BC is responsive (or not responsive) to a solvent environment. Furthermore, data from the library neatly illuminates a narrow range of block composition that gives the strongest possible change in surface chemistry by varying the solvent. In this composition window, water exposure results in complete surface expression of PDMAEMA segments, while hexane treatment results in a nearly pure PBMA surface. This kind of detailed information holds great potential for the precision engineering of responsive, “intelligent” surfaces for sensors, biotechnology and nanotechnology applications. Accordingly, our study clearly demonstrates the advantage gradient libraries of this sort present for the rapid, thorough analysis of grafted polymer layers.

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