COMMUNICATION

Formation of surface-grafted copolymer brushes with continuous composition gradients

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We report on a simple methodology that facilitates the generation of surface-grafted assemblies comprising block copolymers with tunable composition and molecular weight gradients along flat solid substrates.

Formation of surface-anchored macromolecular assemblies on solid substrates has received much attention recently.[1] The technologies utilized to fabricate surface-grafted polymers with high grafting densities are based typically on decorating material surfaces with monolayers of polymerization initiators followed by polymerization carried out from such surfaces ("grafting from"). While most of the early work concentrated on growing layers of in-plane homogeneous surface-anchored homopolymers, papers reporting on preparing di- and triblock copolymers have also appeared.[2–4] Most recently, techniques of patterning polymer layers grafted to the substrate have also been developed that included both homopolymer[5–11] as well as copolymer[12] brushes. In this Communication we describe a simple technique for generating surface-tethered block copolymer assemblies whose composition varies gradually along a flat solid substrate.

Continuous material gradients represent the chief tools for combinatorial chemistry and materials science. Systematic variation of at least one physico-chemical property enables multivariant exploration of the broad parameter space, improved efficiency, and lower cost.[13] Our group has pioneered a simple methodology for generating polymer assemblies with a gradual variation of polymer grafting densities on flat solid substrates.[14] Using this setup we probed the characteristics of the mushroom-to-brush transition in neutral polymers[14,15] and monitored the effect of the external salt and pH on the behavior of weak poly(acrylic acid) brushes as a function of their grafting density and molecular weight.[16] Recently, we have developed a technique for creating substrate-anchored polymer assemblies with a gradual variation of molecular weight.[17] In this Communication we describe a method for generating surface-tethered poly(hydroxyl ethyl methacrylate-b-methyl methacrylate) block copolymers (PHEMA-b-PMMA), whose composition varies gradually along the substrate.

A silicon wafer is cut into 1×5 cm rectangles and its surface is exposed to the ultraviolet–ozone treatment (UVO) for 15 minutes. The UVO produces a large number of surface-bound hydroxyl groups that serve as attachment points for the polymerization initiator, [11-(2-bromo-2-methylpropionyloxy)undecyl]trichlorosilane (BMPUS). BMPUS, synthesized following the recipe given in the literature,[2] is deposited from toluene solutions at -10 °C and forms an organized self-assembled monolayer (SAM) on the silica-covered substrate.[18] Measurements using variable angle spectroscopic ellipsometry (VASE, J. A. Woollam, Co.) confirmed that only a monolayer of BMPUS was formed and that BMPUS molecules were homogeneously distributed on the substrate. The bromo-isobutyric terminus in BMPUS acts as an initiator for atom transfer radical polymerization (ATRP). A custom-designed polymerization chamber is flushed with nitrogen and the bottom of the chamber is charged with solution comprising 37.45 g of HEMA, 25.5 g of methanol (MeOH), 7.0 g of deionized water (DIW), 2.33 g of bipyridine (BiPy), 0.66 g of CuCl and $CuCl_2$

(amount to be specified later). BMPUS-covered substrate is lowered vertically into the solution and the polymerization of HEMA takes place at room temperature only on those parts of the substrate that are in contact with the reaction mixture (*cf.* Fig. 1). Length of polymer chains grown at a given point on the substrate is proportional to the time for which that point remains in contact with the reaction mixture. A micropump attached to the bottom of the chamber gradually empties the reaction vessel of polymerization medium, thus slowly lowering the level of the solution along the substrate and creating a gradient in molecular weight of HEMA along the length of the substrate (arrow A in Fig. 1). The variation of the brush molecular weight gradient may be tuned by adjusting the solution drain rate and/or the $CuCl_2/CuCl$ ratio.[17] After polymerization, the substrate is thoroughly washed with MeOH, DIW, and blow-dried with nitrogen. VASE is used to determine the PHEMA dry thickness as a function of the position on the substrate. In ATRP, the growing end of the chain is protected by the halogen atom; it can be easily reinitiated in the presence of another monomer, thus
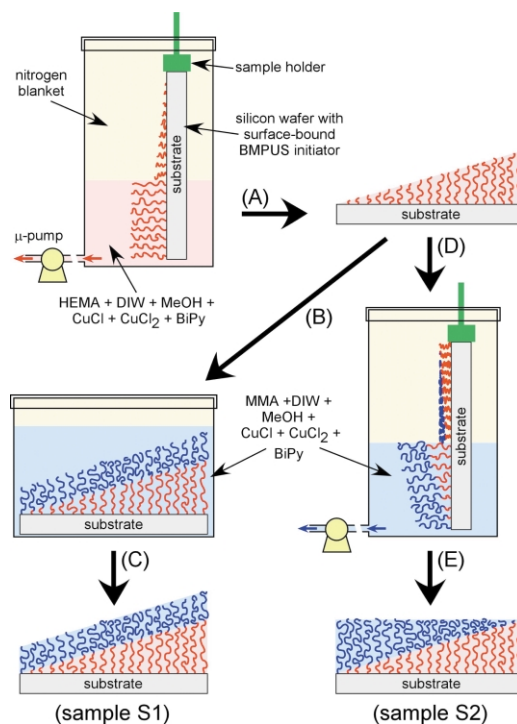

Fig. 1 Schematic illustrating the technological steps leading to the formation of surface-anchored PHEMA-b-PMMA assemblies with a gradual composition variation along the substrate. A custom designed apparatus is used to decorate the sample surface with a grafted PHEMA having a gradient in molecular weight (arrow A). While polymer immersed in the polymerization solution is fully expanded, macromolecules on the dry part of the substrate are collapsed. Surface-grafted PHEMA acts as a macroinitiator for the polymerization of the PMMA block that has either a constant molecular weight (arrow B) or a variable molecular weight (arrow D). The overall process results in PHEMA-b-PMMA block copolymers with a constant PMMA length and a variable total length (arrow C) or a gradual PMMA length and a constant total length (arrow E).

forming a copolymer. We use the PHEMA block as a macroinitiator for polymerization of methyl methacrylate (MMA). We have devised several methods that lead to PHEMA-b-PMMA block copolymers with various composition designs. In this Communication, we will outline strategies for generating PHEMA-b-PMMA copolymers with a variable PHEMA block length and either a constant (sample S1) or variable (sample S2) PMMA block length.

In order to generate sample S1, the substrate covered with the PHEMA surface-tethered block is immersed in a solution containing MMA (= 32.7 g), DIW, MeOH, CuCl, CuCl$_2$ (= 0.0846 g), and BiPy (arrow B in Fig. 1). After about 2 hours, the substrate is removed from the bath, washed thoroughly with DIW and MeOH, and blow-dried with nitrogen. The resulting copolymer (arrow C in Fig. 1) has a variable PHEMA and a constant PMMA block length. Alternatively, PHEMA-b-PMMA can be formed that has a constant total length and a gradual composition variation along the substrate ranging from pure PHEMA to pure PMMA homopolymers (sample S2). In order to achieve this, the polymerization chamber is filled with a solution containing MMA (= 33.6 g), DIW, MeOH, CuCl, CuCl$_2$ (= 0.0480 g) and BiPy. The substrate covered with the PHEMA brush having a molecular weight gradient is lowered into the chamber with the side containing the shorter PHEMA block pointing down (arrow D in Fig. 1). The polymerization bath is pumped out from the chamber, which leads to the formation of a PMMA "reverse" molecular weight gradient on top of the PHEMA molecular weight gradient (arrow E in Fig. 1). After emptying the polymerization chamber, the sample is removed, washed with MeOH, acetone, DIW, and blow-dried with nitrogen. VASE is used to measure the total PHEMA-b-PMMA thickness as a function of the position on the specimen.

Following the design principles described in Fig. 1, we first covered the substrate with PHEMA block having a gradient in molecular weight. The PHEMA block was synthesized using the amount of reagents described earlier and either 0.101 g (sample S1, Fig. 2a) or 0.050 g (sample S2, Fig. 2b) of CuCl$_2$. The solution drain velocity (with respect to the position on the wafer) was adjusted to be 0.27 and 0.062 mm min^{-1} for samples S1 and S2, respectively. In Fig. 2a and 2b we plot the variation of the dry thickness of the PHEMA block (squares) and the PHEMA-b-PMMA copolymer (circles) in samples S1 and S2, respectively. The dry thicknesses were evaluated from the
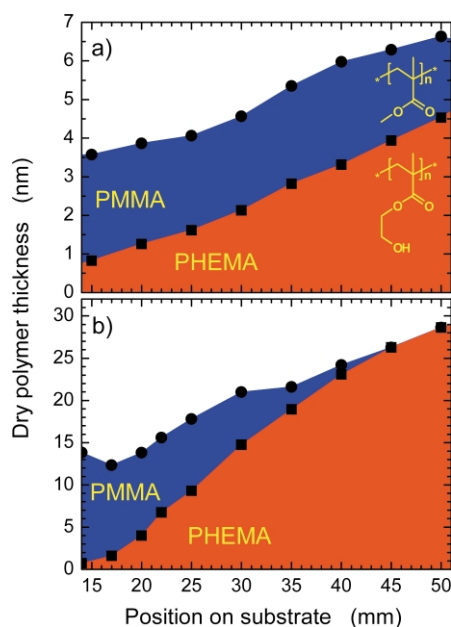
VASE measurements using the tabulated values of the refractive index of PHEMA (n_{PHEMA} = 1.512) and PMMA (n_{PMMA} = 1.491).[19] The data in Fig. 2 illustrate that the thickness of PHEMA varies linearly along the substrate. As expected, the smaller amount of CuCl$_2$ and the slower drain rate of the HEMA polymerization solution in sample S2 resulted in faster PHEMA polymerization (and thus a thicker PHEMA layer) and a steeper PHEMA gradient. The PHEMA-containing gradient block was either immersed in a polymerization bath containing MMA, DIW, MeOH, CuCl, CuCl$_2$ and BiPy (sample S1) or was subjected to a drainage-based polymerization procedure in reverse geometry using the above reagents (sample S2). The data in Fig. 2a illustrate that the PMMA block in sample S1 has a uniform thickness regardless of the length of the PHEMA macroinitiator. In contrast, the PMMA thickness in sample S2 increases with decreasing PHEMA length. While this behavior is expected, Fig. 2b demonstrates that the total PHEMA-b-PMMA thickness does not stay constant across the sample. In order to achieve a constant PHEMA-b-PMMA thickness, the length of the PMMA block needs to be increased by either reducing the drain rate of the MMA polymerization solution from the reaction vessel, or by increasing the MMA polymerization rate by reducing the amount of CuCl$_2$.[17] More work is currently underway that aims at fine-tuning the copolymer composition and studying the ability of the copolymer brush to switch to different surface morphologies upon exposure to block-selective solvents.[20] We envisage that surface-tethered copolymer assemblies with compositional gradients along the substrate will find a multitude of applications in the field of sensors, multi-variant studies of copolymer phase behavior, and morphological exploration of multiblock copolymers.

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Fig. 2 Dry thickness of PHEMA (squares) and PHEMA-b-PMMA (circles) in samples a) S1 and b) S2. The S1 and S2 PHEMA-b-PMMA copolymers have been prepared following the route A→B→C and A→D→E, respectively, depicted in Fig. 1.