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Terraced and Smooth Gradient Polymer Brushes via a Polymer-Single-Crystal-Assisted-Grafting-To Method

*Shan Mei and Christopher Y. Li**

Abstract: Gradient polymer brush provides a spatial gradient change in molecular characteristics of the brush and such a change can be utilized to study structure-property relationship in a combinatorial fashion. In this study, we present a bottom-up method to synthesize gradient polymer brushes with predesigned and precisely controlled grafting density gradient and brush pattern. A polymer-single-crystal-assisted-grafting-to (PSCAGT) method was employed where end-functionalized polymers were grown into two-dimensional polymer single crystals. The latter were chemically coupled to a solid substrate to form well-defined polymer brushes. To tune the grafting density, end-dissimilar polymers were used to co-crystallize into one single crystal. Programmed single crystal growth was introduced to synthesize brushes with two different gradient architectures, i.e. terraced and smooth gradient with pyramid patterns. Our work demonstrates that the PSCAGT method offers a unique means to tune polymer brush nanostructure.

Polymer brushes have drawn significant attention in scientific community because these densely tethered chains exhibit unique properties.[1] A unique brush structure is called gradient polymer brush, which is characterized with gradual/controlled change in physical or chemical properties such as chain grafting density (σ, chains/nm^2), chain length, and/or chemical composition, along one or more directions on the substrate.[2] Gradient polymer brushes have found applications in biosensors, matter transport and high throughput analysis.[1c, 2a, 3] From a synthesis standpoint, it is challenging to achieve controlled gradient for polymer brushes, particularly on a submicron length scale. A few elegant approaches have been reported. For example, Genzer *et al.* employed controlled diffusion of the vapor phase initiators followed by back filling of inert molecules to generate a density gradient of the initiator on the surface, and the gradient polymer brush was subsequently prepared by surface initiated polymerization.[4] Polymer chain length was also controlled by a draining method.[5] The initiator gradient can also be obtained by applying an electrochemical gradient potential and back filling with initiators.[6] Modified controlled radical polymerizations are used to generate chain length gradient.[7] Top-down lithography methods have also been widely utilized in generating gradient and patterned polymer brushes.[8] In this work, we report the design and synthesis of gradient and patterned polymer brushes using a "bottom-up" approach by taking advantage of polymer single crystal (PSC) templating, which allows for precise σ and gradient architecture control. Polymer brushes exhibiting both terraced and smooth gradient architectures with pyramid micropatterns were successfully synthesized.

PSCs have been extensively studied in the past few decades and they can be used as templates to fabricate functional materials.[9] The recently reported crystallization driven block copolymer self-assembly work highlights the versatility of using crystallization to guide complex molecular assembly.[10] Most recently, we showed that polymer-single-crystal-assisted-grafting-to (PSCAGT) can be used for the synthesis of polymer brushes with precisely controlled σ and tethering point.[11] In this method, end-functionalized polymers were pre-assembled into 2D PSCs before coupling the end functional groups onto the substrates. A crucial factor for PSCAGT synthesis is integral folding of the chain in PSCs, which enables the functional chain ends to be exposed on the PSC surface. The functional chain ends serve as the brush tethering point after binding to the substrate. The surface areal density of the functional groups on PSC surface determines final σ. In this work, we hypothesize that co-crystallizing *end-dissimilar* crystalline polymers with different molar fractions into *one* PSC allows us to precisely tune σ. By programming the growth of such PSCs, patterned gradient polymer brushes can be readily synthesized. Poly(ethylene oxide) (PEO) is chosen as the model polymer in this study since PEO brushes have been widely used in antifouling and biomedical applications.[1c, 1d]

In our design, the formation of patterned gradient polymer brushes relies on two key factors. The first is programmable growth of PSCs, which has been demonstrated in earlier work.[12] The second factor is co-crystallization of end-dissimilar polymers with functionalized and unfunctionalized chain ends. σ is mainly dependent on the functional group areal density on the PSC surface, which can be 'diluted' by co-crystallizing end-dissimilar polymers (see Figure 1a). To demonstrate this, we chose PEO with the same molar mass (number average molar mass M_n = 5 kg/mol) and polydispersity index ($\mathit{Đ} = 1.06$) but different chain ends. Triethoxysilane was used as the functional group for reactive PEO (PEO–SiOR), which can chemically couple with glass surface via silane reaction (Supplementary Information, SI, and Figure S1). Hydroxyl-terminated PEO (PEO–OH) was utilized as the inert polymer. A series of PEO_{114}–SiOR and PEO_{114}–OH (subscript denotes degree of polymerization) mixtures with different molar ratios (PEO_{114}–SiOR : PEO_{114}–OH = 1:0.25, 1:0.5, 1:1, 1:2 and 1:4) were used to grow PSCs in pentyl acetate (PA). Polymer brushes were prepared from blend PSCs following the method reported previously,[11] and σ were determined using atomic force microscopy (AFM, see SI for procedures and calculation). The AFM images and the height profiles of the PSCs (before washing) and the corresponding brushes (after washing) are shown in Figure 1. All the PSCs have similar crystal thickness h of ~ 9.5 nm (Figure 1b-c show

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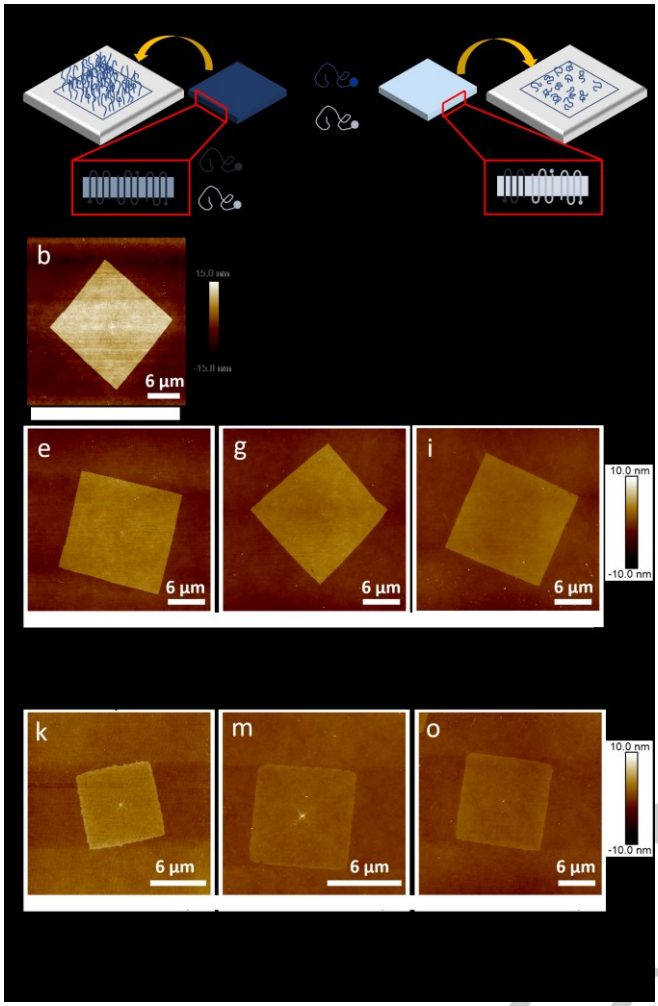

Figure 1. Control of σ by co-crystallization end-dissimilar polymers. a) Synthesis procedure. b,c) AFM image and height profile of a PEO_{114}–SiOR single crystal. d) Dependence of brush thickness and σ on PEO_{114}–SiOR content. e-p) AFM images and height profile of PEO brush prepared from different PEO_{114}-SiOR/PEO_{114}-OH ratios: e,f) 1:0 g,h) 1:0.25 i,j) 1:0.5 k,l) 1:1 m,n) 1:2 o,p) 1:4.

one example), indicating that PEO_{114}–SiOR and PEO_{114}–OH have the same chain folding number (each chain folds twice in the PSC, see SI) and the chain ends did not affect polymer crystallization. After washing away free polymers, all the resultant polymer brushes showed smooth surface and uniform thickness (Figure 1e-p), indicating that PEO_{114}–SiOR and PEO_{114}–OH uniformly co-crystallized in one PSC and the silane groups were evenly distributed on the PSC surface. The sample thickness also decreased after the washing process. AFM measurements revealed that the thicknesses of the polymer brushes h from different PEO_{114}-SiOR/PEO_{114}-OH ratios are 3.5 nm, 3.0 nm, 2.2 nm, 1.5 nm and 0.9 nm, corresponding to the σ of 0.52, 0.44, 0.33, 0.22 and 0.13 nm^{-2}, respectively (see SI). Compared with polymer brushes prepared from PEO_{114}-SiOR homopolymer, which has an h of 4.5 nm and a σ of 0.66 nm^{-2}, the σ prepared from the mixed polymer samples decreased linearly with the decrease of PEO_{114}–SiOR content (Figure 1d), which confirms that the PEO_{114}–OH 'diluted' the –SiOR group surface density in the PSCs. This result enabled the preparation of gradient brushes using the co-crystallization method.

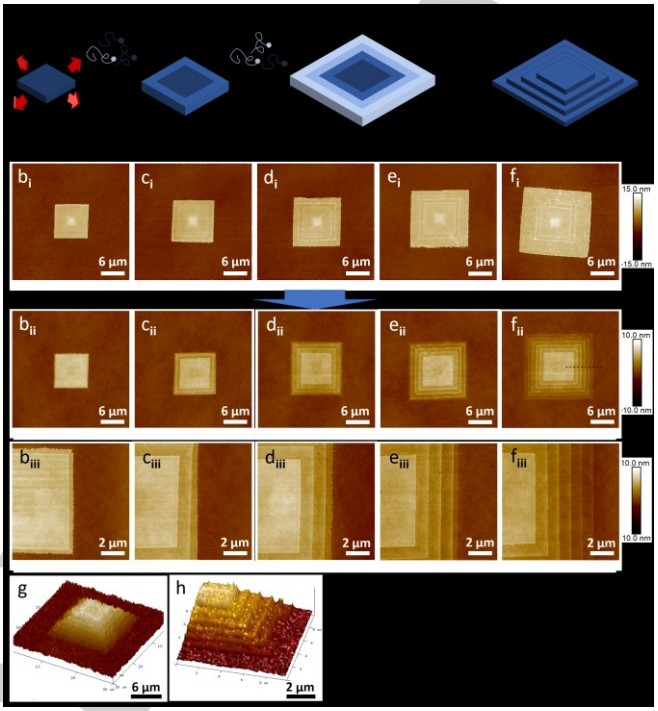

Figure 2. Terraced gradient PEO polymer brush. a) Synthesis procedure. b_i-f_i) PEO single crystal with 1-5 concentric bands; b_{ii}-f_{ii}) PEO brushes with 1-5 concentric bands. b_{iii}-f_{iii}) are enlarged images of b_{ii}-f_{ii}). g,h) 3D images of the terraced gradient PEO brush with five bands. i) height profile and the corresponding σ, measured from dash line area in f_{ii}.

To test the hypothesis of synthesizing patterned brushes using the PSCAGT method, a terraced gradient brush pattern was firstly prepared (Figure S2), where σ change followed a quantized fashion as shown in Figure 2a. Such morphology resembles a nanoscale terrace farmland, and terraced gradient brush is therefore used to describe this brush architecture. In this design, PEO_{114}–SiOR were firstly used to grow PSCs in PA via the self-seeding solution crystallization method (Figure $2a_i$, SI).PEO_{114}–SiOR/PEO_{114}–OH mixed solution with a molar ratio of 1: 0.25 was added to the 8µm x 8 µm PEO_{114}–SiOR PSCs to grow the first PEO_{114}–SiOR/PEO_{114}–OH (1:0.25) band around the PEO_{114}–SiOR crystals (Figure $2a_{ii}$, b_i). After a predetermined growth time, polymer solution with mix ratio of 1: 0.5, 1:1, 1:2 and 1:4 were subsequently added to form more concentric PEO_{114}–SiOR/PEO_{114}–OH bands where the end group composition in each band is determined by the feeding ratio of the two polymers (Figure 2 a_{ii-iii}). Figure $2b_i$-f_i show these PSCs with multiple bands. In these PSCs, these bands exhibit the same thickness despite the difference in compositions, and no terrace features are seen (Figure S3), while the boundaries between adjacent bands are observed due to thickening of PSC edges (arrows in Figure S3). After washing with DI water, PEO_{114}–OH were removed from the PSCs and polymer brushes were obtained.

From center to the edge of each brush sample, because of the increased PEO_{114}–OH content, the remaining PEO_{114}–SiOR that can form brushes in each band decreased. σ therefore decreased accordingly and a terrace structure appeared, seen from both AFM 2D (Figure 2b_{ii}-f_{ii}, b_{iii}-f_{iii}) and 3D images (Figure 2g,h), with the latter resembles a terraced farmland. h of each band (Figure 2i) is the same as the corresponding polymer brush with the same PEO_{114}–SiOR/PEO_{114}–OH blend ratio in Figure 1. Note that the width of each band can be precisely controlled by the amount of added polymer, rendering the whole brush structure hierarchical.

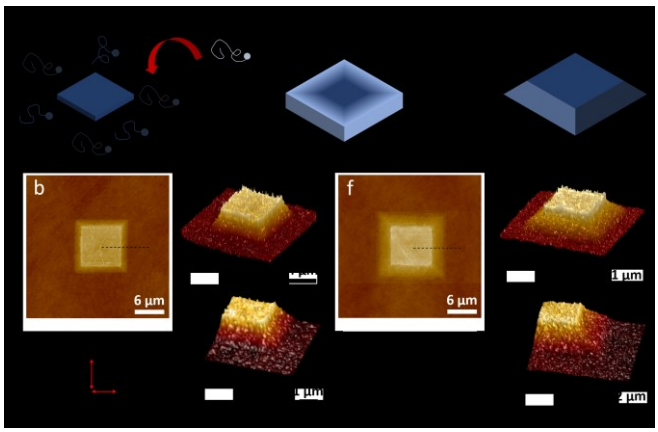

Figure 3. Smooth gradient brush. a) Synthesis procedure. b,f) 2D, d,e,h,i) 3D AFM images and c,g) height profiles with two different slopes, measured from dash lines in b and f, respectively.

To further demonstrate the versatility of the method, we synthesized smooth gradient polymer brushes with continuous σ change. The synthetic route is illustrated in Figure 3a and the crystal growth temperature profiles are shown in Figure S2. First, PEO_{114}–SiOR PSCs was used as the 'seeds'. Instead of adding PEO_{114}–SiOR/PEO_{114}–OH mixture solutions with fixed ratios to form bands with pre-determined σ, the composition of the PSCs was *continuously* varied. PEO_{114}–SiOR solution was firstly introduced to the 8μm x 8 μm PEO_{114}–SiOR PSC seeds. Then PEO_{114}-OH solution was charged to the system with a 30 s interval for 15 min. The latter was chosen as the overall growth time because the crystallization of the added PEO_{114}–SiOR free polymers completes within 15 min. The final PSCs were immobilized on glass slides as described previously to obtain polymer brushes. Figure 3b-e show that from the edge of the central plateau to the edge of the entire brush structure, h and σ gradually decrease from 4.6 nm to 0 nm and 0.66 to 0 nm^{-2}, respectively. The smooth gradient brush can be quantitatively described using gradient slope k, defined as the $k = \frac{\Delta h}{\Delta w}$, where Δh and Δw are the thickness and width change of the gradient brush (Figure 3c). k in Figure 3b-e can be estimated to be ~3.5×10^{-3}. Since Δh is relatively fixed (~ a few nm), k can therefore be tuned by changing Δw. Figure 3f-i show that by increasing Δw, similar smooth gradient brush with $k = 1.2 \times 10^{-3}$ can be achieved. Note that in literature, the gradient brushes from most of the top-down methods lead to a relatively shallower slope of ~10^{-4}.[7, 8e]

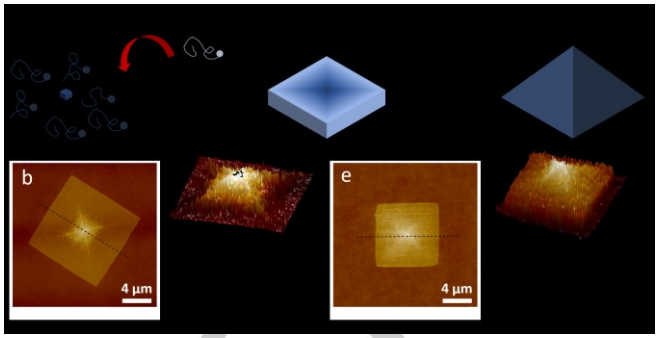

Figure 4. Pyramid polymer brushes. a) Synthesis procedure. b) 2D, c) 3D AFM image and d) height profile of a narrow pyramid brush. e) 2D, f) 3D AFM image and g) height profile of a wide pyramid brush. The height profiles in d and g are measured from dash line in b and e, respectively.

The smooth gradient brushes in Figure 3 have a plateau in the center. We further synthesized smooth gradient patterns with no central plateau, which resemble Egyptian pyramids. The synthetic procedure is illustrated in Figure 4a and SI. Instead of 8μm x 8 μm PEO_{114}–SiOR PSCs, sub-micron PEO crystal nuclei obtained from the self-seeding method were used as the seeds. PEO_{114}–OH solution was slowly added to the PEO_{114}–SiOR solution right after seeding. In this case, the free PEO_{114}–OH and PEO_{114}–SiOR polymers in the solution simultaneously grew from the PEO_{114}–SiOR nuclei. The composition of the two polymers in the PSCs gradually changed during the growth of the PSCs because the polymer ratio in the solution was continuously varied by adding PEO_{114}–OH. The AFM results of the resultant gradient brushes are shown in Figure 4b-g. The gradient begins from the center of the crystal and the brush resembles a nanoscale pyramid. The slope of the gradient can also be tuned. Simply by changing the rate of PEO_{114}–OH addition, we obtained the pyramid with different Δw, and thus different slopes. Fast addition of PEO_{114}–OH (within 5 min) resulted in a narrower pyramid (Figure 4b-d), with a steeper slope of $k = 1.8 \times 10^{-3}$. While slow addition (within 30 min) resulted in a wider pyramid (Figure 4e-g) with a less steep slope of $k = 4 \times 10^{-4}$. In Figure 4b-d, the pyramid brush has a ~ 5 μm wide plateau at the edge while this plateau is absent in Figure 4e-g. This is because for fast addition (Figure 4b), PEO_{114}–SiOR were not completely consumed after 5 mins. The remaining PEO_{114}–SiOR continued to co-crystallize with PEO_{114}–OH to yield the plateau. In the slow addition case (30 mins, Figure 4e), PEO_{114}–SiOR were completely consumed before 30 mins, the edge plateau therefore was not observed. Note that the molar mass of the PEO used in this work is relatively low and our future work will be conducted to synthesize gradient brushes with higher molar mass and different semicrystalline polymers.

In conclusion, we have developed a facile bottom-up method to synthesize patterned gradient polymer brushes with precisely controlled σ and gradient architecture. These unique brushes were obtained by programmable growth of end-dissimilar polymers followed by solid state grafting-to reaction. The final polymer brushes also possess well-controlled and tunable patterns, including terraced and smooth gradient, and the gradient slope can be readily tuned. We envisage this bottom-up

method opens a gateway for the synthesis of gradient polymer brushes with well-defined nanopatterns.

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Keywords: polymer brush • gradient brush • nanopatterened brush • polymer nanostructure • polymer crystallization

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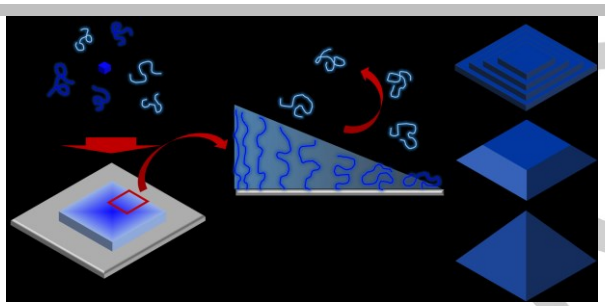

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