Manipulation of Surface-Tethered Helical Polypeptide-Based Nanostructures with Localized Chemical Functionalities

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Abstract:

Polymer brushes are polymer chains with one end covalently anchored to a surface. Due to the unusual molecular arrangements and surface attachments, these densely grafted polymer brushes have exhibited unique mechanochemical properties and thus have gained wide interest from the polymer science community. Potential applications of such thin film could be biosensors, photovoltaic devices, organic electronics, and biomimicry surfaces. It was previously reported that the arrangement of polymer brushes could be organized via an integrated process of electron beam lithography, surface-initiated synthesis, and post-processing treatments. In this work, the customizability of such polymer nanostructure was further enhanced by end-point functionalization and vapor annealing process.

Summary of Research:

Polymer brushes have demonstrated various responsive behaviors towards external stimuli such as solvents [1], pH [2], temperature [3], and ionic strength [4]. It has been found that polymer brushes can display novel behaviors when subjected to nanoconfinement [5]. Previously, we reported a nanopatterning process of making "spiky" nanoarrays of polypeptide rod brushes on silicon substrates which have resulted in interesting "bridging" morphology governed by the localized chain-chain interactions (Figure 1 and 2) [6]. However, the characterization and manipulation of the chain arrangement in these nanostructured brushes can be challenging due to the extremely small feature sizes (less than 100nm) and highly confined structure.

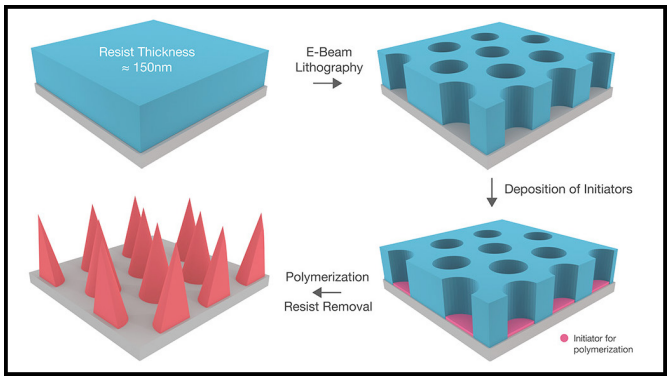

Figure 1: Schematic illustration of the fabrication process of nanopatterned brushes.

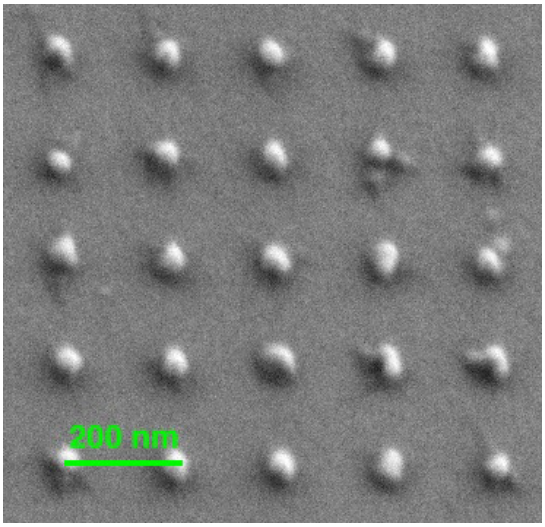

Figure 2: SEM image of the patterned PBLG rod brushes.

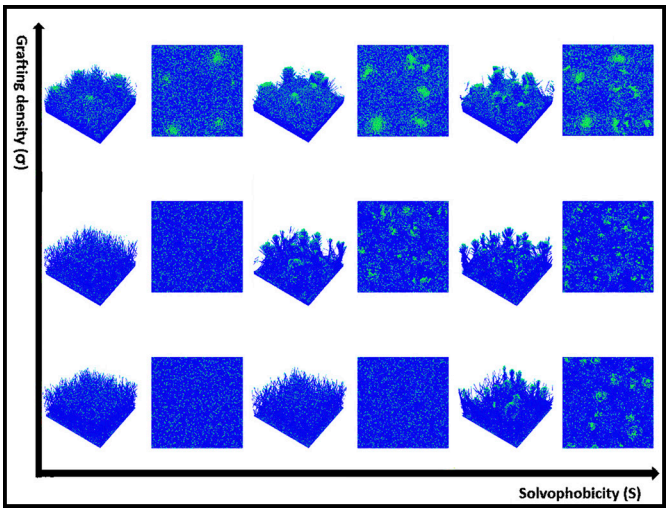

Figure 3: Computational simulation of rod brushes in various conditions.

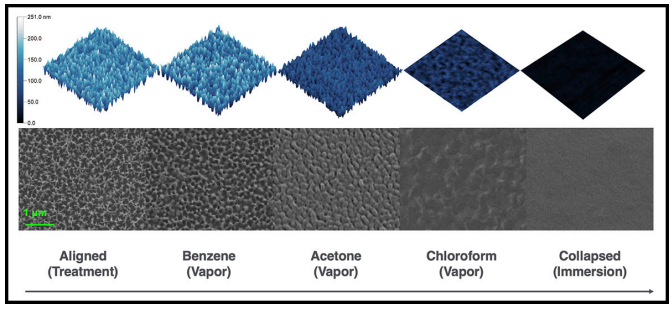

Figure 4: The SEM and AFM characterizations of PBLG brushes undergoing different treatments.

In this study, the organization of polypeptide rod brushes was examined via an integrated study of computational simulations and fluorescent dye-functionalized rod brushes. Chain-end functionalization of the brush tip was realized by chemically modifying the end groups with fluorescent probes — the fluorescence properties of the resulting brush film were found to be sensitive to the chain arrangement due to the aggregation-induced mechanism of the fluorophores. Coarse-grained rod polymer models, in conjunction with a density field-based energy function, were built to analyze the influence of various factors on the chain orientation, end-point density, and overall brush morphology (Figure 3).

Moreover, the potential of polypeptide rod brushes to serve as recognition elements in sensing devices for volatile organic compounds (VOCs) has been explored. The film's response to different VOCs, including benzene, chloroform, and acetone, was analyzed using an *in-situ* monitoring system based on reflectometry for real-time monitoring of vapor responses. It has been found that the brush exhibited reversible swelling-collapsing behavior when exposed to different VOCs such as benzene, chloroform, and acetone. Subsequently, a vapor treatment technique was developed to fine-tune the morphology of PBLG brushes, which has the potential to produce customizable nanostructured surfaces in combination with nanolithography (Figure 4).

In addition to nanolithography, we have demonstrated that polymer nanostructures can be further customized by chemical modification of the chain-ends and vapor-phase annealing process. The distribution and molecular arrangements of these active chain-ends can be examined by the behavior of the attached fluorescence molecules and controlled by vapor-phase treatment. In the future, we plan to explore the possibility of functionalizing these nanostructures with bioactive compounds for biomimicry surface and modeling study. We also plan to introduce mixed rod-coil brushes in the same system for binary and stimuli-responsive surface functionalities.

References:

[1] C.-T. Yang, Y. Wang, C. W. Frank, and Y.-C. Chang, "Chemoresponsive surface-tethered polypeptide brushes based on switchable secondary conformations," Rsc Adv, vol. 5, no. 105, pp. 86113-86119, 2015, doi: 10.1039/c5ra15839g.

[2] G. A. Eken, Y. Huang, Y. Guo, and C. Ober, "Visualization of the pH Response through Autofluorescent Poly(styrene-alt-Nmaleimide) Polyelectrolyte Brushes," Acs Appl Polym Mater, vol. 5, no. 2, pp. 1613-1623, 2023, doi: 10.1021/acsapm.2c02066.

[3] X. Wang, et al., "Temperature-Responsive Hierarchical Polymer Brushes Switching from Bactericidal to Cell Repellency," ACS Appl. Mater. Interfaces, vol. 9, no. 46, pp. 40930-40939, 2017, doi: 10.1021/acsami.7b09968.

[4] C.-H. Lin and S.-C. Luo, "Combination of AFM and Electrochemical QCMD for Probing Zwitterionic Polymer Brushes in Water: Visualization of Ionic Strength and Surface Potential Effects," Langmuir, vol. 37, no. 42, pp. 12476-12486, 2021, doi: 10.1021/acs.langmuir.1c02230.

[5] W.-L. Chen, M. Menzel, O. Prucker, E. Wang, C. K. Ober, and J. Rühe, "Morphology of Nanostructured Polymer Brushes Dependent on Production and Treatment," Macromolecules, vol. 50, no. 12, pp. 4715-4724, 2017, doi: 10.1021/acs.macromol.7b00714.

[6] Y. Huang, H. Tran, and C. K. Ober, "High-Resolution Nanopatterning of Free-Standing, Self-Supported Helical Polypeptide Rod Brushes via Electron Beam Lithography," Acs Macro Lett, vol. 10, no. 6, pp. 755-759, 2021, doi: 10.1021/acsmacrolett.1c00187.