Tailoring hydrophobic/hydrophilic binary polymer brushes: controlling grafting and chain length for tunable wetting properties

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Surface-grafted polymer systems can be designed to adapt dynamically to solvent environments, making them ideal for multifunctional interfaces. Exposure to solvents of different polarity can induce significant conformational and compositional changes within polymer layers, leading to tunable variations in surface properties such as wettability, adhesion, and morphology. [1, 2] In this context, binary polymer brushes (BPBs), which are composed of two distinct polymer chains grafted onto the same substrate, represent a promising platform. [3] However, the performance and responsiveness of BPBs critically depend on key structural parameters, notably the grafting density and the degree of polymerization of each constituent polymer. [4] In this contribution, we establish an alternative methodology for the synthesis of BPBs using successive surface-initiated atom transfer radical polymerization (SI-ATRP). Unlike previous approaches, our method combines control over the grafting ratio, achieved from a two-component initiator monolayer on silicon substrates, with optimized polymerization conditions that enable tuning of the polymer chain length, allowing the preparation of BPBs with tailored compositions. The monolayer consists of two mono(ethylene glycol) silanes: one bearing 2-bromoisobutyryl moieties that serve as SI-ATRP initiating sites (MeG-BiB), and the other carrying trifluoroacetate groups (MeG-TFA), which can be hydrolyzed and subsequently functionalized to anchor the second initiator through an acylation reaction. The polymerizations were based on the polarity-contrasting monomers *n* -Butyl methacrylate (BMA) and 2-hydroxyethyl methacrylate (HEMA) to prove the concept and to study the switching wetting properties. The influence of the grafting and polymer chain length ratios on the morphology and wettability upon interaction with solvents of different polarities was investigated. Precise control over these parameters resulted in changes in both surface topography and dynamic contact angle. Additionally, the results suggest that the phase separation (vertical or horizontal) can also be tuned depending on the specific solvent exposure.

Keywords:
Binary polymer brushes, wettability, switchable hydrophobic/hydrophilic polymer surfaces

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