MOLECULAR BUILDING OF DIBLOCK AND TRIBLOCK COPOLYMER BRUSHES FROM THE PLANAR SURFACES

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Obtaining of smooth multifunctional polymer nanolayers tethered to surface of metals, ceramics, nanofibers or porous materials still faces the lack of universal chemical methods. The controllability of dielectric/conductive, hydrophobic/hydrophilic, thermo-responsive/pH-responsive, and other functional properties is a challenge especially for nanoscale thin films. Covalently tethered polymer brushes are the often choice for solving these issues, as by controlling concentration, temperature, solvent quality, reaction time, nature of monomers, it is possible to adjust a thickness of the layer, grafting density, surface morphology, and degree of surface coverage.

In this work, we investigated a new method of polymer brushes synthesis, by usingthe reactive oligomers possessing peroxideend groups as surface initiators for polymer brushes growing of different nature: dielectric, polyelectrolyte, hydrophilic, and with combined properties.We showed that reactive peroxideend fragment embedded into the structure of polymer brushes during their growing from the surface, provides an ability for layer-by-layer building of multifunctional polymer brushes with enough thickness, high grafting density, and low surface roughness.

The studied polymer brushes were analyzed by ellipsometry, contact angle analysis, TOF-SIMS, AFM, and impedance spectroscopy. The AFM images show a presence of large island-like structures (up to 200 nm in diameter), and smooth background between them,after the first surface modification. These structures were chemisorbed from the polymer solution, as the grafted polymer is likely to agglomerate even at relatively low concentrations. However, their fraction on the surface does not exceed 15%. Most of the substrate surface is covered by smooth thin film of 12 nm with surface roughness of 2.7 nm. This first layer of oligomer brushes were used for surface-initiated radical polymerization with/without a chain transfer agent. The film thickness of polymer brushes reaches 62 nm, while the surface roughness decreases to less than 1 nm after second modification. There isa clear tendency for a reduction of surface roughness after each next modification, but it depends on the nature of grown polymer brushes too.The wetting properties are also different before and after modification on each step, and it varies for polymer brushes of different nature. The water contact angle (WCA) reduces from 85° down to 57° after synthesis of hydrophilic polymer brushes, and increase in the thickness of polymer brushes correlates with WCA reduction. The forming of hydrophilic polymer brushes leads to an increase of the surface free energy on $\Delta 16$ mJ/m^2. The analysis of impedance spectra shows a dielectric behavior of the formed films and strong dependence on the substrate nature. In the low frequency range as well as in the range of 10^2-10^6 Hz, it is found a little reduction of the surface resistance after the growing of polymer brushes.

All described results indicate that the synthesis of polymer brushes of the diblock and triblock structure was successful. The small corrections on methodology of the synthesis should be made, but the potential of the proposed approach is obvious. We think the new method of the growing of multilayered polymer brushes have a potential application for surface modification in the field of energy storage applications, microfluidic devices, biology, corrosion resistance.