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Polyacrylamide polymer brushes synthesized with "grafting through"approach: scaling factor and characterization

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Polymer brushes represent a class of surface coatings consisting of macromolecules attached to a surface. This class of structures owns unique features such as elongated conformation of polymer chains, possibility to polymer modification and so on, so that they can be utilized in various fields of science and industry. For instance, polymer brushes are used as efficient lubricants with ultralow friction, smart coatings responsive to external triggers, protective coatings, etc. Also polymer brushes are actively used in specific polymer passivation of chemically inert surfaces for single-molecule studies.

There are several strategies for the solution synthesis of polymer brushes which have their advantages and limitations: widely applied and well investigated "grafting to"approach, consisting in the chemisorption of functionalized polymer chains to the target groups on the surface, and in some sense opposite "grafting from" approach, based on a controllable linear growth of polymer chains from the surface. The intermediate "grafting through"approach, in which the surface itself takes part in polymerization reaction due to deposited on the surface reactive groups, has attracted an increasing interest in recent years. "Grafting through"may be treated as a combination of the "grafting to"and "grafting from"approaches, so this approach partially inherits the advantages of both "grafting to"(simplicity) and "grafting from"(relatively high grafting density, variability of the synthesis components, relatively low cost) approaches. "Grafting through"technique has already proved itself in the field of nanocomposites and it has a great potential in the other areas of application. However, processes that occurs in the "grafting through"system as polymer brush grows are not well known, as most of the efforts during the last decades were targeted at "grafting to"and "grafting from"approaches, so this work is an attempt to reveal new knowledge about this technique.

The objective of our study is the analysis of the structure, quality of the polymer film and its chemical composition. The brushes were synthesized in three steps: surface activation, surface modification by grafting the anchor monomers, and attachment of the growing polymer chains to the surface. Chemical composition of such layers at each step of preparation was proved by X-ray photoelectron spectroscopy and fourier-transform infrared spectroscopy and their morphology was analyzed by atomic-force microscopy. It was shown that the thicknesses of the dried brush obtained with the method of X-ray reflectometry can be tuned by varying the polymerization temperature, since it affects the length of macromolecules. The scaling dependence of the brush thickness on the polymer length was obtained by the comparison of the sizes of attached and free polymer chains, which corresponds to an intermediate grafting density between a mushroom-like or a fully stretched polymer brush. Increasing of the polymer molecular weight does not result in a significant decrease of the grafting density, estimated from molecular masses of attached polymer chains. The long-term exposure of modified surfaces to water demonstrated that they are more stable than similar coatings not covalently attached to the substrate.

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