

Abstract

The experimental results summarized and described within the series of publications forming the basis of this dissertation present innovative concepts inspired by the principles of "green chemistry", for the synthesis of polymer brushes grafted from flat surfaces *via* atom transfer radical polymerization (ATRP) and activator regeneration, allowing a reduction in the concentration of the catalytic complex used. Among the modified materials, inorganic substrates were distinguished, i.e. silicon wafers acting as a model substrate, and organic surfaces, such as polyetheretherketone (PEEK) sheets used for bone implants production. As a result of the carried out experimental work, a number of solutions were proposed to allow environmentally friendly, controlled synthesis of functional polymer brushes grafted from a previously brominated surface of a modified substrate. In the context of grafting polymer brushes from the silicon wafers, it was shown that the addition of sacrificial initiator significantly accelerates polymerization in comparison to a system initiated only from the inorganic surface, while obtaining materials with hydrophilic and amphiphilic characteristics.

One of the breakthroughs presented in this work are a significantly simplified procedure for the synthesis of pH-sensitive polymer brushes using microliter volumes of reaction mixture per cm² of functionalized surface, and the possibility of carrying out modifications directly on the laboratory bench, without the need to provide an anaerobic atmosphere. For this purpose, a methodology for controlled radical polymerization was developed, in which only the monomer played the role of the reducing agent of the deactivated complex to the activator. The versatility of the developed procedure means that it can be successfully applied to the functionalization of a wide range of organic and inorganic materials containing a covalently attached ATRP initiator on the surface. The novel aspect of the work involved not only the use of an environmentally friendly solvent (water or water-ethanol mixture), but also an ATRP controlled by external (blue light) and internal (sugars) factors.

Another innovative idea realized within the scope of the dissertation is the development of a concept for the synthesis of gradient polymer brushes by the diffusion-controlled *SI-se*ATRP technique at the microliter scale, using a simplified two-electrode reaction system, in an air atmosphere. The author's experimental setup enable to obtain gradient brushes with a pattern dependent on the shape and topography

of the working electrode used, thus creating opportunities for designing hybrid materials with a wide range of specialized industrial applications.

In addition, a procedure for the polymerization of monomers that do not mix with water, using a miniemulsion made with dry wine containing the addition of antioxidants (ascorbic acid and sodium sulfite) was proposed. This antioxidants according to the ATRP mechanism, can act as an internal reducing agent, allowing the activator to regenerate cyclically. In this case, ascorbic acid plays the role of a reducing agent according to the ATRP concept with activator regeneration by electron transfer (ARGET), while the sulfites present in the wine participate in polymerization according to the supplemental activation and reducing agent ATRP mechanism.

The above examples represent a selected range of material, and the entire series of works is, in a way, a guide to the pathways inspired by the principles of "green chemistry" for the synthesis of hybrid materials with the desired physicochemical properties. With a view to simplifying the synthetic procedure and reducing its toxicity, the work proposes a number of methods that can successfully provide a sustainable alternative to current technological solutions used in the plastics industry and biomedicine, for example, as intelligent systems for the release of bioactive substances.