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Sonja Neuhaus

POLYMER MICRO- AND NANOGRAFTING

Micro & Nano Technologies Series

Polymer Micro- and Nanografting

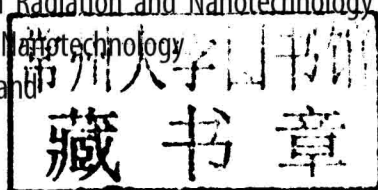
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Polymer Micro- and Nanografting

Preface: Polymer Structures on Polymer Substrates

Modern synchrotrons are radiation sources built and operated in order to provide high-quality and -intensity photon beams in a very wide range of photon energies. Synchrotron beamlines are usually set up for specific analytical applications ranging from spectroscopic, scattering, and diffraction methods to various types of microscopy and tomography. In addition, a few beamlines have been constructed to perform lithographic structuring, particularly in hard x-ray and more recently in the extreme ultraviolet range. In 2003, we took the unique opportunity to do test exposures on pristine and uncoated fluoropolymer films at the extreme ultraviolet interference (EUV-IL) beamline at the Swiss Light Source (SLS) to create patterns of radicals at their surface. The samples were then treated in a monomer solution at typical conditions to perform graft polymerizations. Analysis of the samples after this reaction indicated that we had a unique method in hand to produce high-resolution patterns of polymer brushes on polymer surfaces. The method appeared attractive because it allowed us to locally endow an inert polymer foil with flexible and functional structures. In the following years, we explored this technology in detail, with emphasis on the influence of reaction parameters on achievable resolution, the formation of polymer brushes and hydrogels, grafting and characterizing polyelectrolyte systems, the production of biofunctional structures, and chemical modification of grafted brush structures in order to introduce additional functionalities.

Furthermore, we widened the scope and potential application fields using different activation methods. Low-pressure and atmospheric-pressure plasma sources as well as vacuum UV lamps were used for large area exposures and, in combination with shadow masks, to produce patterns in the micrometer to millimeter range. Exposures at LIGA beamlines were used to produce bulk structures and electron beam writers to generate arbitrary high-resolution structures.

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CHAPTER 1

Functional Polymer Structures

Materials with a multitude of functionalities have been introduced in our daily lives and are used without thinking much about their origin and way of production. Examples include magnetic, electrical, optical, and biological functions, and many of them are implemented in polymeric or polymer-based systems. This chapter focuses on the chemical properties and related functionalities that can be introduced to polymer systems using different methods. Main emphasis is placed on polymer brushes, which are extremely versatile and interesting for the functionalization of surfaces and which are accessible on polymers using grafting technology.

1.1 POLYMER SYSTEMS: INERTNESS VERSUS FUNCTIONALITY

Polymers are the most promising materials for current and future applications due to their special properties: They have low densities, exhibit relatively high specific strength and flexibility, and in some cases display remarkable chemical inertness (e.g., fluoropolymers and polyaryletherketones). For many applications, the chemical inertness of polymers provides a substantial advantage. Chemically inert polymers are long-lasting and stable, resistant to weathering, and show very low sorption of water. To benefit from these properties, polymeric coatings are often used as the finish for surfaces of daily life goods, applied in order to achieve (chemical) inertness and stability.

In contrast, other classes of polymers are not inert. They may interact strongly with the environment and adopt special functions. Examples include specific interactions with molecules and ions exploited in separation and purification techniques; electrical and optical properties used in polymer solar cells, organic light emitters, and optical elements; as well as properties relevant for bio-applications, such as anti-biofouling properties and specific binding of proteins.

Adding locally defined functionality to inert surfaces is interesting for many applications. For instance, integration of small sensing elements that could—actively or passively—monitor the freshness of packed goods is of great interest to the packaging industry. With current structuring and patterning technologies, length scales can be addressed which are interesting for studying interactions with cells. Such studies are of importance for the functional design of polymeric implants. Further developments of patterning technology to reach dimensions of the size of single protein molecules are in progress, which will be beneficial for constructing ultrasensitive bioanalytical devices.

In polymer systems, the combination of properties of different components is achieved in a multitude of ways. For example, polymer layers of different functionalities are applied on a polymer substrate by spraying, casting, dip coating, or spreading with a doctor blade. Polymer coatings can be combined with layers of nonpolymeric materials applied from solutions or suspensions of the coating material or precursors thereof, or deposited via vapor phase using physical and chemical vapor deposition.

To achieve structures in deposited layers, screen printing, stamping, and ink-jet printing are very well-established and commercially used technologies. Current and future applications based on such technologies include polymer solar cells [1] and polymer electronics [2]. Polymeric optical waveguide structures on polymer substrates, which require high precision in structure definition, may for instance be produced with micromolding techniques [3]. Taking advantage of the mechanical flexibility of many polymers, developments also aim at elastomeric light-emitting devices and displays [4] or molecularly stretchable electronics [5].

Grafting techniques present an approach on the molecular level for anchoring functionalities on surfaces. The term “grafting” is used in analogy to the biological grafting of a branch from a tree or bush onto the trunk of another closely related species in order to combine the properties of the tree (e.g., the growth of high-quality fruit that in many cases cannot be grown from its own seeds) with the properties of the trunk (e.g., easy to grow and resilient against various insects). In polymer grafting, chemical links are formed between the polymer chains of one material, typically a polymer film, to the chains of another polymer.

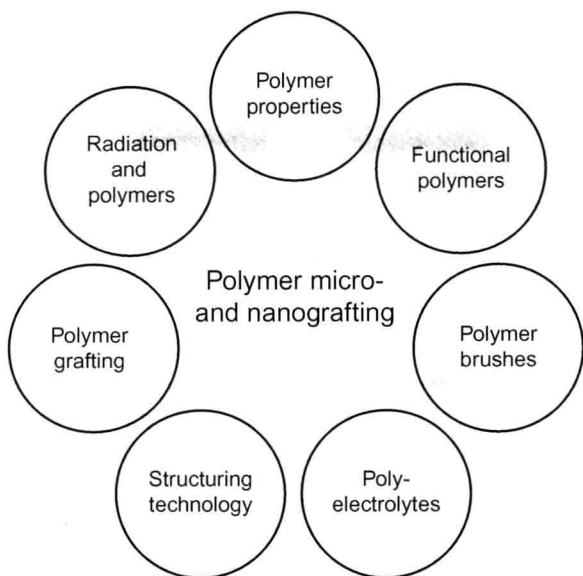


Figure 1.1 *Polymer micro- and nanografting in the context of related fields.*

In comparison to the methods of layer formation discussed previously, the covalent anchoring of grafted polymer layers intrinsically circumvents adhesion problems that are frequently encountered between different polymers. In addition, grafting techniques offer particular flexibility on the molecular level. A large variety of chemically different monomers and polymers may be grafted, and their strong anchoring allows further functionalization and chemical modification to widen the range of accessible functional properties of the modified polymer surface. Furthermore, polymer chains attached on one end to the surface and grafted in high density usually adopt a so-called polymer brush configuration providing interesting properties as outlined later.

Polymer micro- and nanografting combines grafting techniques with structuring. It is related to a number of fields of science and technologies, as schematically summarized in Figure 1.1. *Polymer materials* provide the substrates for the micro- and nanografting process, which aims at local introduction of specific properties and functionality using *structuring technologies*. Functionality is provided, for instance, by *polymer brushes* or *polyelectrolytes*. Aspects of functional polymer surfaces are summarized in the following section in the context of polymer brushes and are further detailed in Chapter 4. Understanding the

impact of *radiation* on polymers in terms of radical formation after ionization and bond-breaking events is fundamental for radiation grafting, which is discussed extensively in Chapter 2. Finally, different aspects of *graft polymerization reactions* are important for successful formation of functional structures starting from either radiation-generated radicals or immobilized initiators, which are discussed in Chapters 2 and 3, respectively.

1.2 POLYMER BRUSHES

Polymer brushes have attracted a tremendous amount of attention in recent years because they enable tailoring of physical, chemical, and biochemical properties of various material surfaces. These brushes are densely packed arrays of polymer chains tethered at one chain end to the surface. At high packing density and in the presence of a good solvent, the chains are forced to elongate perpendicular to the surface. Polymer brushes can be considered as extended interfaces between the polymer surface and the surrounding environment. Due to the flexibility of polymer chains, small molecules are able to penetrate and interact with the chains or with other species embedded within the brush. The term “polymer brush” is not limited to flat surfaces of solid materials; it is also applied to systems in which polymers are densely grafted at the surfaces of nanoparticles, micelles, or even chains of another polymer. The following summary focuses on brushes and brush structures grafted on solid supports.

1.2.1 Formation of Polymer Brushes on Surfaces

Polymer chains may be attached to surfaces by using “grafting-to” or “grafting-from” techniques (Figure 1.2). “Grafting-to” means that pre-formed polymer chains are bound at one end to the surface or to surface-bound linker molecules via chemical reactions. One intrinsic problem of grafting-to methods is that the bound polymer restricts the diffusion of further chains to the surface, often resulting in low grafting densities. In the “grafting-from” approach, the polymer chains are grown from initiators bound to the surface. Therefore, the term *surface-initiated polymerization* is also used for the same process [6,7]. Typical initiators for free radical polymerizations are azo- and peroxide compounds [8], which are cleaved to reactive radicals under polymerization reaction conditions. In grafting-from processes, only relatively small monomer molecules diffuse to reaction sites at the end

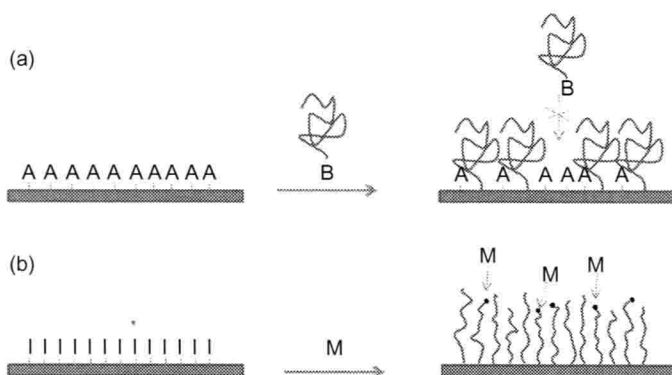


Figure 1.2 **Functional polymer layers on surfaces produced with (a) “grafting-to” and (b) “grafting-from” strategies.** (a) In grafting-to processes, preformed polymer chains containing a linker group (B) are chemically bound to anchor groups (A). (b) In grafting-from, polymerization of a monomer (M) is started from initiators (I) bound to the surface.

of the growing chains; consequently, a higher density of grafted chains can be achieved.

The high polydispersity of grafted chains is one particular drawback of grafting-from techniques based on free radical polymerization to produce polymer brushes. This is often observed and interpreted as a result of poor control over the propagation and termination reactions. In order to circumvent this problem, living radical polymerization schemes such as nitroxide-mediated polymerization (NMP) [9], atom transfer radical polymerization (ATRP) [10,11], reverse ATRP [12,13], or reversible addition–fragmentation chain transfer (RAFT) [12,14,15] have been used, resulting in a significantly lower polydispersity and better control over the chain length.

The previously discussed principles of grafting-to and grafting-from can also be applied for the modification of polymer surfaces with polymer brushes. However, the binding of linkers and polymerization initiators to polymer surfaces is not as straightforward as it is for oxidic inorganic materials. Thus, dedicated pretreatments are usually necessary. These may include rather harsh reaction conditions due to the chemical inertness of many polymers (see Chapter 3). Alternatively, radiation treatment of polymers (to form radicals) followed by exposure to air may be used to form peroxides and hydroperoxides, which can be directly used as initiators for thermally or ultraviolet-induced graft polymerizations [16,17] (see Chapter 2).

1.2.2 Responsive Polymer Brushes

Responsive polymer materials—polymers engineered to change structure and properties in response to environmental influence—are promising materials for biomedical devices, chemical sensors, microfluidic devices, drug-delivery systems, and self-regulating colloids, as reported in a series of books and reviews [18,19]. Examples of adaptive properties include surfaces switching between (super)hydrophilic and (super)hydrophobic properties upon exposure to different solvents [20], and photo- or voltage-induced conformational changes of valve-like systems in artificial membranes [21,22]. Polymer brushes are particularly suitable for the preparation of responsive systems [23,24].

For instance, weak polyelectrolyte brushes (discussed later) are highly interesting responsive systems because they react with conformational rearrangement to changes in pH and ionic strength [25–27]. As another example, the potential of introducing photoactive moieties such as azobenzenes or spiropyranes into molecular systems in order to remotely influence their properties with light has been widely recognized. Under illumination, these molecules undergo (reversible) changes in configuration, thereby influencing the local chemical environment [28]. Flexible attachment of the photosensitive moieties, which can be achieved particularly well within polymer brushes, is a key for their functionality [29]. In mixed polymer brushes or brushes made up of block copolymers, the responsiveness is often based on the fact that the characteristics of the layer are dominated by either of the two components under different conditions [30,31].

1.2.3 Polyelectrolyte Brushes

Polyelectrolytes (PELs) are polymers that carry charges within their backbone or in side chains. Usually, discrimination is made between weak and strong PELs. Weak PELs are polymers with weakly acidic or basic groups, which are protonated or deprotonated depending on the pH of the surrounding medium, resulting in a pH-dependent charge density. In contrast, the charge density in strong PELs is not influenced by the pH.

Polyelectrolyte brushes exhibit interesting characteristics with respect to both theoretical and practical aspects because their behavior is fundamentally different from that of uncharged polymer brushes [32,33]. In the case of strong PEL brushes, in which the charge density

is independent of the pH, the molecular structure and properties are dominated by electrostatic interactions. Mutual repulsion between charged polymer segments strongly influences the physical properties of the grafted layers. In weak PEL brushes—in which the charge density of the chains depends on their protonation level—the chain conformation depends on the pH of the solution. In particular, the swelling of weak PEL brushes in different solvents was extensively studied due to its importance for responsive polymer systems. Swelling depends on the nature of the solvent system, as well as its pH and the concentration and chemical nature of other ions in the solution [34,35]. Furthermore, interactions with selected counterions can be used to tune the wettability of surfaces with anchored PEL brushes [36,37].

1.2.4 Biofunctional Brushes

The discrimination between specific and nonspecific binding on surfaces is a key issue in most biotechnological applications. Polymer brushes have been investigated for binding of proteins via electrostatic interaction, covalent binding, or via metal affinity binding, as well as for the prevention of nonspecific binding, which is often realized with brushes of poly(ethylene glycol) (PEG) derivatives [38].

Due to their extension and flexibility, polymer brushes can accommodate functional proteins at a substantially higher density compared to what is achieved by protein immobilization on flat surfaces. Furthermore, depending on their chemical composition, brushes may provide a mild environment in which the protein is not degraded [39]. In particular, many types of brushes of PELs are interesting candidates for the accommodation of biomolecules because they are swellable in water and provide an ideal chemical environment for maintaining the activity of enzymes and other proteins. The extent of protein binding via electrostatic interaction in PEL brushes is dependent on the sign of charge of the protein and of the PEL, respectively, as well as the ionic strength of the solution [40,41].

1.2.5 Patterned Polymer Brushes

Surfaces that are patterned on the nano- and microscale with responsive polymer brushes are promising for applications in sensing and actuation, as well as for bioanalytical devices [42,43]. Structures of brushes, for instance, are obtained by patterning of preformed brushes using specific etching protocols or by patterning of initiators before the

grafting reaction. Fabrication of patterns by the combination of top-down lithography and surface-initiated polymerizations has been recently reviewed [44]. For instance, photolithography combined with lift-off or etching techniques results in a chemical contrast between exposed and nonexposed areas. This contrast is then transferred into patterns of polymerization initiators [45]. Alternatively, deposited initiator layers can be locally activated or deactivated by lithographic exposures using, for example, a focused electron beam [46–48]. Deposition of polymerization initiators by microcontact printing was also employed to directly deposit patterns of initiators on surfaces [49,50].

To a certain extent, these techniques to obtain structured brushes, which were originally established on solid supports such as silicon, glass, or metal surfaces, can be transferred to polymer surfaces. Such approaches are summarized in Chapter 3. Alternatively, and uniquely accessible on polymer surfaces, locally defined radiation grafting may be applied as discussed in Chapter 2.

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