# Polymer Brushes

## Synthesis, Characterization, Applications

*Edited by*
*Rigoberto C. Advincula,*
*William J. Brittain,*
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*Jürgen Rühe*

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# Contents

# Preface

Amongst others, notably industrial coatings, barriers, packaging, laminates, and lubricants, have been associated with the modification of the surface of an object so as to have a specific interaction or non-interaction towards an external environment. These terms have mostly implied the use of organic polymer, surfactant, and resin type materials. While a large body of academic and technical literature associated with bulk films and coatings already exists, development of ultra thin coatings of the sub-micron order has recently become of great interest, spanning a new field of surface engineers in the last decade. In the area of organic and polymer thin films, one may be familiar with the more common industrial techniques like spin-coating, dip-coating, doctor blade coating, and roll-to-roll coating processes. At the few nm thickness regimes, the application of both self-assembly and directed-assembly methods becomes fascinating. Some of the more "nanostructured" assemblies include: Langmuir-Blodgett films, self-assembled monolayers (multilayers), alternate polyelectrolyte (sequential) deposition, and thermal and molecular beam epitaxy methods of evaporated organic molecules. To these examples, one can now add the method of thin films by *polymer brushes*.

The study of polymer brushes has long been dominated by physicists because of their interest in investigating macromolecule phenomena in confined environments. From the theoretical standpoint, end-tethering of polymers reduces the degrees of freedom for different macromolecule conformations such that it is possible to define a "stretch" conformation for a neutral polymer. From the experimental side numerous innovative surface sensitive spectroscopic and microscopic methods have been developed and applied as a result of this interest. Grafting density, surface concentration, osmotic pressure, solvent quality, interaction parameters, etc. are important factors to consider in experimental methods. Due to the predominance of "physisorption" models in the formation of these confined polymers, not much focus has been given yet on chemically grafted polymers, which are more thermodynamically robust. For a while, chemisorption methods were popular, but very soon, it was realized that significantly higher grafting densities are not achievable with this method. In the area of polymer grafting, a lot of previous work can be cited on particle modification and the use of plasma or irradiation initiated polymerizations.

With the recent advances in polymer synthetic methodologies and their adaptation to surface chemistry, it has become possible for synthetic chemists to reclaim this field. The contribution of late is evident. In a technique called "grafting from", a highly cited term from the first papers by Rühe and Prücker, it is possible to associate the formation of polymer brushes as a type of surface initiated polymerization. Contributions to this field are numerous and we have tried to include in this book the works by Brittain, Huck, Menzel, Fukuda, Matyjaszewski, Bruening, Minko, Stamm, Müller, Luzinov, Dyer, Advincula, Seery, Quirk, Stamm, Tsukruk, Zauscher, Boyes, Baker, Ballauf, Caster, Genzer, Faust, their co-authors and many others (see list of contributors). However, this field is growing and is indeed very interdisciplinary.

The book starts with an introduction and overview of the field by Rühe. The subsequent chapters are then grouped into three major parts: Synthesis, Characterization, and Applications. Each division begins with a review chapter by the editors. This is followed by individual contributions and reviews from invited authors. In Synthesis, an overview in Chapter 1 gives the highlights of recent advances in synthetic methodologies. Efforts have been made to include living free-radical polymerization (Chapters 2 and 3), ring-opening polymerizations (Chapter 4 and 5), cationic polymerization (Chapter 6), and hyper branched polymer synthesis (Chapter 9). Other polymerization mechanisms are reviewed in Chapter 1. In Characterization, it was helpful to outline the different methods for polymer brush analysis on both flat film substrates and particles (Chapter 10). The characterization of particles and flat surfaces is exemplified in Chapters 11, 12 and Chapters 13, 14, 15, 16, respectively. Lastly in the application part, the review in Chapter 17 gives an excellent overview of the myriads of possibilities in applications of polymer brushes: from microelectronics to bio-applications. The contributions include patterning (Chapter 18, 19), mixed polymer brushes (Chapter 20, 21), nano-object movement (Chapter 22), and photochemical strategies in applications (Chapter 23). More chapters could have been included but this collection should well suffice to whet the appetite of the readers. A number of reviews have been written but this work should be the most comprehensive yet. It is hoped that this book will be a valuable reference and resource to scientists, engineers, and technologists in this rapidly evolving field.

June 2004

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# Polymer Brushes: On the Way to Tailor-Made Surfaces

*Jürgen Rühe*

## Abstract

In recent years, the synthesis of polymer brushes through surface-initiated polymerization reactions has received significant attention. In this overview, several different synthetic strategies for the generation of polymer brushes are reviewed. The unique physical properties of polymer brushes that arise from the covalent anchoring of the polymer chains to the solid substrate are discussed and compared to the properties of polymer layers deposited by other techniques of thin film generation. Finally, examples are provided that highlight some recent developments aimed at strategies for the functionalization of surfaces with polymer brushes, at ways of realizing smart surfaces with switchable properties, and at the generation of micro- and nanostructured polymer monolayers.

## 1

## Growth of Polymer Molecules at Surfaces: Introductory Remarks

Thin coatings applied to the surface of materials can improve the properties of objects dramatically as they allow control of the interaction of a material with its environment. This has been known more or less empirically to man for several thousand years. Lacquer generated from tree sap was used in China some 7000 years ago as a protective coating for wooden objects. Cold process coatings were also used around 3000 BC, where Egyptian ship builders used beeswax, gelatin and clay to produce varnishes and enamels and (later) coatings from pitch and balsam to waterproof their ships. The early Greeks and Romans, as well as the ancient Asian cultures in China, Japan and Korea, used lacquers and varnishes applied to homes and ships for decoration and as protective measures against adverse environmental conditions. In modern times, the coatings industry is a multi-billion dollar business and – especially if the value of the protected objects is considered – a very important contribution to the world economy. Today, however, the application range of coatings extends much beyond the simple decoration and protection aspects, and functional coatings have become an enabling technology in a vast variety of different high-tech

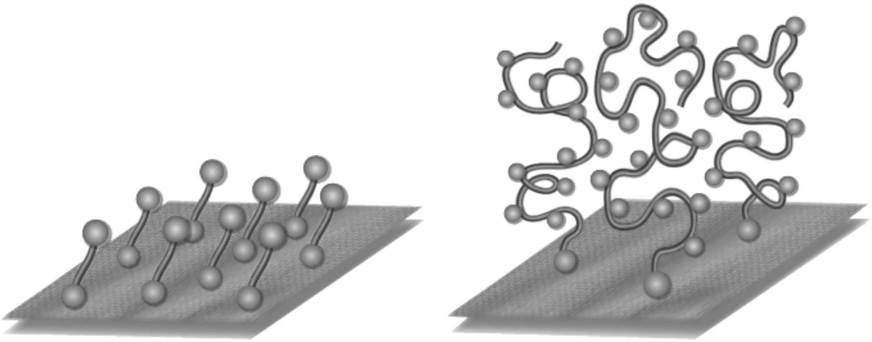

**Figure 1** Schematic depiction of the growth of polymer molecules at a surface of a solid substrate through surface-initiated polymerization.

areas. Fields in which such high-tech coatings are applied range from computer chips [1] and hard disk manufacturing [2] to the use of special coatings in biomedical and aviation applications [3,4]. Accordingly, many different techniques have been developed for the generation of protective coatings, and these will be discussed further below.

Surface-initiated polymerization reactions as a new pathway for the preparation of functional, high-tech coatings have recently received much attention [5,6]. This technique is based on the growth of polymer molecules at the surface of a substrate in situ from surface-bound initiators, which results in the attachment of polymer molecules through covalent bonds to this substrate (Figure 1). Polymer layers in which the polymer chains are irreversibly attached to the substrate are especially attractive for a variety of applications, as such layers can have a good long-term stability, even in rather adverse environments. For example, it poses no problem to expose surfaces with such surface-attached coatings to good solvents for the polymers without being concerned that the polymer will be either dissolved or displaced, and that the coating is more or less rapidly removed from the surface. In addition to the issue of stability, the number of functional groups present at a surface can also be greatly enhanced by connecting large polymer molecules with functional groups to the surface instead of binding the functional groups directly to that surface. Such a “skyscraper” approach allows high densities of functional groups to be obtained at the surface of the substrate through moving from the strictly two-dimensional arrangement of these groups present in typical surfaces to a more three-dimensional situation. An example, which illustrates such a behavior is the attachment of DNA probe molecules to surface-attached polymer chains, which can significantly enhance the sensitivity of a DNA-chip (Figure 2).

Systems in which the polymer chains are attached with one end to a solid substrate are very interesting, not only from a chemical but also from a physical point of view. If the grafting density of the polymer molecules is very high, the polymer chains adopt a rather unusual conformation wherein the individual coils overlap [7–9]. Under these conditions, the polymer molecules are strongly stretched away

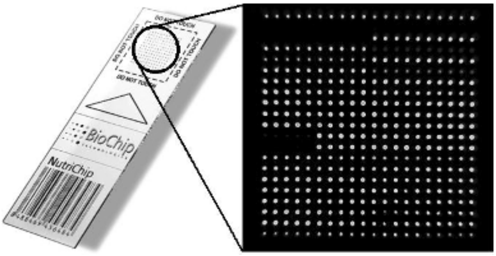

**Figure 2** Fluorescence image obtained from a DNA chip based on a oligonucleotide functionalized polymer brush. The pattern and the intensity of the spots allows for the determination of the sequence of the unknown analyte-DNA.

from the surface and achieve a molecular shape which is far from the typical random coil conformation that polymer molecules assume in solution. Such surface-attached films with strongly stretched chains are usually referred to as "polymer brushes" [10]. Polymer brushes are very interesting systems, as the strong stretching of the polymer chains leads to concurrent drastic changes in the physical properties of the systems. For unstretched polymer chains, a slight molecular deformation leads to a moderate increase of the energy stored in the system (entropy elasticity). However, when the molecules are already strongly stretched – as is in the case of a polymer brush – the energy penalty for the same small deformation is large. Accordingly, in all situations where the stretching of the polymer chains is of concern – for example, during the shearing of such surfaces or when the film is penetrated by other polymer chains from solution – very strong differences can be observed to the behavior of free coils [11–13].

Whilst systems in which polymer chains have one end tethered to a substrate appeared some years ago to be quite exotic, and significant doubts persisted that such brushes with high grafting densities could be obtained in practice, the development of methods where polymers are grown directly on the surface of a substrate by using surface-initiated polymerization has led to a large number of such systems becoming available.

However, before describing more detailed aspects of surface-initiated polymerization, more general aspects of coatings will be briefly discussed.

## 2
## Coatings: From First Principles to High-Tech Applications

For a large number of chemical and physical processes – both in daily life and in technical applications – the bulk properties of a material as well as the structure and composition of its surfaces determine the performance of the entire system. In order to control the interaction of a material with its environment, coatings consisting of thin organic films are frequently applied to the surfaces of these solids (Figure 3). In many cases, the coating serves simply as a barrier against a hostile envi-

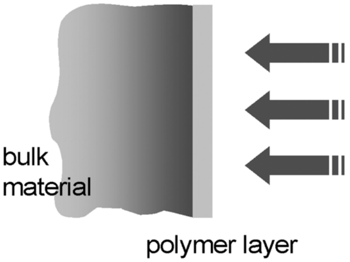

**Figure 3** Schematic depiction of use of thin polymer coatings to control the interaction of a material with the surrounding environment.

ronment and allows for protection against corrosion or other chemical or photochemical degradation. Although corrosion protection is certainly the most prominent aspect of surface coatings as far as market and materials volumes are concerned, thin organic coatings are also applied in a large number of high-tech applications, ranging form microelectronics [1] to biomedical devices [3,4].

When considering such applications, thin organic coatings are applied to control the interactions between the material and its environment. Examples of interface properties which can be controlled by deposition of a thin organic film onto a surface include friction [11,13–17], adhesion, adsorption of molecules from the surrounding environment, or wetting with water or other liquids. In medical applications, coatings allow control of the interaction of biological cells and biomolecules with artificial materials in order to enhance the biocompatibility of an implant, or to avoid the nonspecific adsorption of proteins onto the active surfaces of an analytical device [18].

It is well known that coatings, even when only a few Angstroms thick, can influence the surface properties of a material so strongly that the chemical nature of the underlying material becomes completely hidden and the interaction of the whole system with the surrounding environment is governed by these extremely thin coatings (“stealth effect”). This is an advantageous situation for materials engineering as it allows optimization of the bulk and surface properties of a material separately from each other. In addition, the application of functional coatings allows the coverage of a surface with groups which interact with other molecules in their environment through specific molecular recognition processes. Such a strategy is, for example, very important for the control of the adhesion of biological cells to artificial substrates. In such a case, thin layers containing cell recognition peptide sequences can induce strong adhesion of the cells to the substrate surfaces, to which they otherwise would show only a very unfavorable adhesion behavior [19].

One example of a system where the covering of a surface with an ultrathin coating is a prerequisite for that system to function is a computer hard disk [2] (Figure 4). If the uncoated surface of a thin film magnetic disk is subjected to strong shear, such as the sliding of a read/write head on the disk surface, then almost instantaneous damage can be observed. The disk shows, even upon the first contact with the head, a strong stick-slip behavior and a high friction coefficient, while the debris