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198

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Surface-Initiated Polymerization II

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V.2 **Surface-Initiated Polymerization II**

Volume Editor: Rainer Jordan

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198

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Preface

These two volumes on surface-initiated polymerization deal with recent developments in the synthesis, characterization and properties of structurally and chemically defined polymer coatings on surfaces. Nearly all polymerization techniques that have been developed in solution have now been adapted for the surface-initiated polymerization (SIP). The reader will find all relevant techniques discussed in these volumes, such as free, controlled and living radical polymerization, living anionic and cationic polymerization (Rigoberto Advincula), and ring-opening metathesis polymerization (Michael Buchmeiser). Most of them are used to prepare so-called polymer brushes, a term describing strictly linear polymers that are densely grafted via one end to an interface. Such coatings display unique physical properties useful for a variety of applications. In particular, the high structural control of polymer brushes that can be realized by controlled or living polymerization techniques draws much attention. The contribution by Takeshi Fukuda et al. on high-density polymer brushes outlines the synthetic possibilities as well as the unique properties of polymer brushes. Such coatings will surely play an important role in innovative surface science and nanotechnology. The present contributions also reflect an ongoing trend: the development of defined heterogeneities on nearly any length scale. This can be realized by structured polymer coatings, gradients and control of the topography via the SIP reaction conditions. Jan Genzer's contribution on the preparation of polymer brush gradients is a good example. As it relates to defined structural variation and control of the macromolecular design of grafting polymers via SIP, I would like to point the reader to the contributions by Takehisa Matsuda on surface graft microarchitectures or by David Bergbreiter discussing the synthesis and applications of hyperbranched polymers on surfaces.

Originally, the reviews were to be divided into, e.g., a *Synthesis*, *Properties* and *Application* section. Fortunately, this was not possible at all. Synthesizing a polymer coating by SIP is performing materials science from scratch. Introducing a slightly different monomer or changing the solvent will automatically alter the properties of the surface such as its wetting behavior, topography, elasticity, homogeneity, etc. It is exciting (and difficult!) to characterize the layers and find out why an altered reaction condition had such an impact upon the various layer properties. Thus, the researcher is immediately involved in various aspects of surface science and analytical challenges. This is reflected in all contributions. For example, Daniel Dyer discusses the fundamental and interesting aspect of the photoinitiated synthesis of polymer brushes. Of course,

the enormous advances in surface-sensitive characterization techniques developed for the investigation of self-assembled monolayers have provided the proper tools. However, as polymers are flexible, the investigation of the dynamic behavior of polymer coatings adds another dimension. The contribution by William Brittain on stimuli-responsive films gives an idea of the complex behavior of polymer brushes.

Besides the analytical techniques, the theoretical description of polymer brushes allows a deeper understanding of the complex dynamic behavior of polymers on surfaces and is useful for future developments. Here, Roland Netz gives – also for the non-expert – a very helpful theoretical background on the theoretical approaches for the description of neutral and charged polymer brushes.

The interest in polymer brushes and defined polymer coatings prepared via SIP is not at all restricted to the polymer community or the surface science community. The demand for tailored, functionalized and adaptive surfaces comes from a multitude of scientific branches and also from industry. Possible applications are already discussed in many of the contributions compiled here. Besides polymer science, surface chemistry and physics, they include catalysis, biomedical applications, microfluidics and nanotechnology. This creates a highly interdisciplinary, lively and fruitful environment.

Finally, I would like to thank all authors for their time and effort to make a state-of-the-art overview of surface-initiated polymerization possible. An edited book is only as good as its contributions and I had the privilege to compile contributions of the highest quality.

I am also grateful to Ms. Ulrike Kreusel and Dr. Marion Hertel from Springer for their professional help and patience.

Munich, January 2006

Rainer Jordan

Contents of Volume 197

Surface-Initiated Polymerization I

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Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization

Y. Tsujii · K. Ohno · S. Yamamoto · A. Goto · T. Fukuda

Photoinitiated Synthesis of Grafted Polymers

D. J. Dyer

Photoiniferter-Driven Precision Surface Graft Microarchitectures for Biomedical Applications

T. Matsuda

Polymer Brushes by Anionic and Cationic Surface-Initiated Polymerization (SIP)

R. Advincula

Metathesis Polymerization to and from Surfaces

M. R. Buchmeiser

Contents

Hyperbranched Surface Graft Polymerizations

D. E. Bergbreiter · A. M. Kippenberger 1

Surface-Grafted Polymer Gradients:

Formation, Characterization, and Applications

R. R. Bhat · M. R. Tomlinson · T. Wu · J. Genzer 51

Surface Rearrangement of Diblock Copolymer Brushes

– Stimuli Responsive Films

W. J. Brittain · S. G. Boyes · A. M. Granville · M. Baum · B. K. Mirous ·
B. Akgun · B. Zhao · C. Blicke · M. D. Foster 125

Theoretical Approaches to Neutral and Charged Polymer Brushes

A. Naji · C. Seidel · R. R. Netz 149

Author Index Volumes 101–198 185

Subject Index 211

Hyperbranched Surface Graft Polymerizations

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1	Introduction	2
2	Hyperbranched Poly(acrylic Acid) Grafts	4
2.1	Hyperbranched Poly(acrylic Acid) Graft Synthesis on Gold Surfaces	5
2.1.1	Derivatives of Hyperbranched Poly(acrylic Acid) Grafts	8
2.1.2	Aqueous Solvation of Hyperbranched Poly(acrylic Acid) Films	15
2.1.3	Patterning of Hyperbranched Poly(acrylic Acid)-Derived Grafts	17
2.2	Hyperbranched Grafts on Polymer Surfaces	18
2.2.1	Synthesis of Hyperbranched Poly(acrylic Acid) Grafts on Polyethylene Films	19
2.2.2	Hyperbranched Grafts on Polypropylene Wafers	26
2.2.3	Hyperbranched Grafts on Polyethylene Powders	27
3	Hyperbranched Nanocomposites	30
4	Hyperbranched Grafting by Surface Initiated Ring Opening Polymerization	35
4.1	Grafting Hyperbranched Polyglycidol	36
4.2	Grafting of Hyperbranched Poly(ethyleneimine)	37
5	Hyperbranched Grafts of Organic/Inorganic Hybrid Polymers	39
5.1	Polysiloxane Hyperbranched Grafts	39
5.2	Dendritic Hyperbranched Grafts of Pd(II) Coordination Polymers	41
6	Dendrimer Analogs as Hyperbranched Grafts	43
7	Conclusions	46
	References	46

Abstract This review summarizes the synthesis of irregular hyperbranched polymer grafts on various inorganic and organic substrates. The synthesis of these hyperbranched grafts are generally based on “graft on a graft” polymerizations and include diverse sorts of graft polymers. The “graft-on-a-graft” strategies discussed here include chemistry leading to the synthesis of hyperbranched poly(acrylic acid) grafts, polysiloxane grafts, dendrimer/polyanhydride graft nanocomposites, ring-opening polymerization grafts, and polyamidoamine grafts. Other relevant chemistry of these grafts including chemistry leading to derivatives of hyperbranched poly(acrylic acid) grafts, further modification by polyionic interactions, polyvalent hydrogen bonding, and functional group manipulation is discussed. Examples of reactions of monomers with polyvalent surfaces that lead to hyperbranched grafts are also briefly discussed.

Keywords Dendrimer · Hyperbranched grafts · Nanocomposite · Polyvalency · Surface modification

Abbreviations

PAA	poly(acrylic acid)
PTBA	poly(<i>tert</i> -butyl acrylate)
MUA	mercaptoundecanoic acid
FTIR-ERS	Fourier Transform Infrared external reflection spectroscopy
XPS	X-ray photoelectron spectroscopy
PE	polyethylene
PP	polypropylene
ATR-IR	attenuated total reflectance infrared
PNIPAM	poly(<i>N</i> -isopropylacrylamide)
TEA	2-thiopheneethyleneamine
ROP	ring opening polymerization
APES	3-aminopropyltriethoxysilane

1

Introduction

There is great interest in designing functional interfaces. Hyperbranched grafts are alternatives to existing “linear” grafts for formation of such interfaces. They are of interest because they can provide interfaces with different sorts of properties. Hyperbranched grafting is also conceptually more attractive than other approaches because the multiple grafting of oligomeric grafting reagents can compensate for inefficiencies in reactions at surfaces (Fig. 1). If, for example, an initial surface graft has coverage defects or if defects are introduced during the graft-on-a-graft synthesis due to incomplete reactions, subsequent hyperbranched grafting stages can “heal” these defects more efficiently than the traditional monomer grafting strategies that produce linear graft chains (Fig. 1b versus 1a). This same effect was noted previously by Ferguson in layer-by-layer grafting of mica particles and polycationic polymers on hydrophobic surfaces like octadecyltrichlorosilane treated Si/SiO₂ wafers and hexadecanethiol-modified silver films and is a general feature common to other layer-by-layer grafting chemistry [1, 2]. As shown in Fig. 1, the advantages of hyperbranching are considerable. In the particular schematic drawing of three graft stages shown in Fig. 1b, hyperbranched grafting is far more effective than linear grafting through three stages in Fig. 1a even when there is a relatively low (50%) efficiency in the first step of grafting.

The synthetic strategies that lead to irregularly hyperbranched grafts based on surface confined “graft-on-a-graft” polymerization reactions are the focus of this review. Limited examples of monomers reacting with polyvalent surface-bound reagents leading to hyperbranched polymers are also discussed. In general, the chemistry described here is confined to reactions

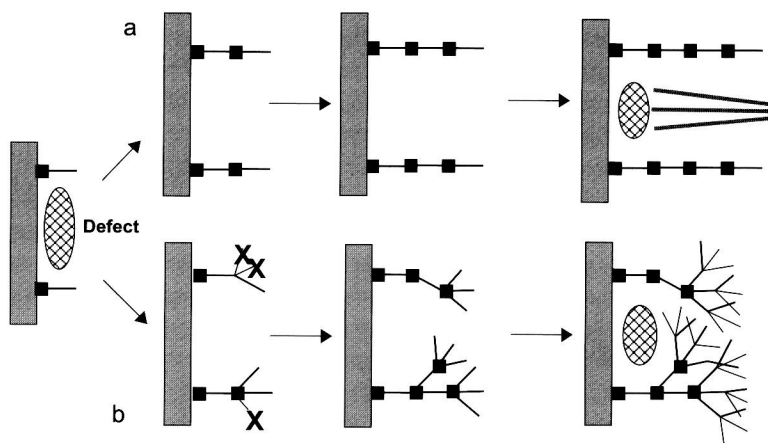


Fig. 1 A schematic drawing comparing linear grafting **a** with hyperbranched grafting **b** in coverage or “healing” of surface defects. An efficiency of 100% is assumed in all three steps in linear grafting (**a**). In the hyperbranched graft example (**b**), a 50% efficiency is assumed in the first step but 100% efficiency and three branches per graft stage are assumed in steps two and three

that involve condensation polymerization reactions or reactions that involve the reaction of an electrophile with a nucleophile. This review begins with hyperbranched grafting of poly(acrylic acid) on hard inorganic or metal surfaces and soft polymer surfaces. Methods for derivatizing these films either by covalent modification or with polyvalent noncovalent interactions are discussed. Limited examples of applications of these materials are described. For example, Crooks’ group has used some of these synthetic methods to prepare patterned surfaces. In cases like this where this subject has been reviewed, it is only briefly discussed here. Other hyperbranched grafting strategies including multilayer grafting of polyvalent nucleophiles and electrophiles, grafting via ring opening polymerizations, and the synthesis of dendritic grafts using polyvalent surface-bound reagents and monomers are discussed subsequently. There are other very successful synthetic strategies for preparing hyperbranched films based on free radical polymerizations that will not be a topic of discussion in this review. For example, Müller has developed a novel method of hyperbranched graft polymerization of imers (initiator-monomers) by self-condensed vinyl polymerization (SCVP) via atom transfer polymerization (ATRP) [3, 4]. Another example would be Matsuda’s preparation of hyperbranched grafts by iniferter (initiator-transfer agent-terminator) polymerization [5, 6]. A detailed description of these iniferter polymerizations can be found in Matsuda’s contribution in this volume. A similar approach by Tsubokawa is described as a post-graft polymerization of vinyl monomers and is useful as a route to hyperbranched grafts [7–9]. Surfaces with hyperbranched grafts can also be prepared by

grafting commercially available hyperbranched polymers to surfaces. For example, Tsukruk has studied grafted hyperbranched polyesters with terminal epoxides that are attached to Si – OH surfaces [10, 11]. There are many examples where dendrimers are attached to surfaces by covalent or non-covalent interactions [12–17]. This chemistry too is not discussed here unless the dendrimers are used as reagents with linear polymers or oligomers to prepare hyperbranched grafts.

2

Hyperbranched Poly(acrylic Acid) Grafts

The synthesis of hyperbranched grafts of poly(acrylic acid) (PAA) using a “graft-on-a-graft” strategy is a general method for modifying a variety of surfaces. It requires as a starting material a surface that contains some functional groups though the amplification of functionality inherent in the chemistry means that a surface with only a modest level of functional groups can produce an interface with a macroscopically detectable concentration of functional groups. Examples of surfaces that have been modified include silicon (using the hydroxyl groups of the $\text{Si}(\text{OH})_x$ layer), gold with functional self-assembled monolayers, glass, and surface-oxidized polyolefin films and powders. In each case, robust ultrathin supported-films are the products. This covalent multistep strategy is based on functional group protection/deprotection and affords modest control over the product film thickness. In PAA grafting, this control is based on the number grafting stages that are used. The product hyperbranched grafts range in thickness from ca. 30 Å to greater than 1000 Å. The film thickness initially increases rapidly in a non-linear fashion since each additional layer is added in a branching fashion multiplying the number of grafting sites (Fig. 2). After several grafting stages the thickness increases in a linear fashion. This variable extent of progress of this grafting chemistry as measured by either ellipsometry on reflective metal surfaces or as measured by titration of the $-\text{CO}_2\text{H}$ groups being introduced on higher surface area materials is very similar substrate to substrate (Fig. 2) [18, 19].

The graft-on-a-graft strategy was conceived of as a synthetically “forgiving” alternative to an attempted but ineffective borane-based radical graft polymerization onto vinyl terminated self-assembled monolayers [20] on gold and was based on earlier observations that a poly(acrylic acid) graft modified with new graft sites could be used to prepare a more dense and presumably thicker graft with subsequent polymerization or grafting steps [21]. It was also conceptually more attractive than other approaches that used monomers as grafting agents because the multiple grafting of oligomeric grafting reagents could compensate for inefficiencies in reactions at surfaces as discussed above (Fig. 1).

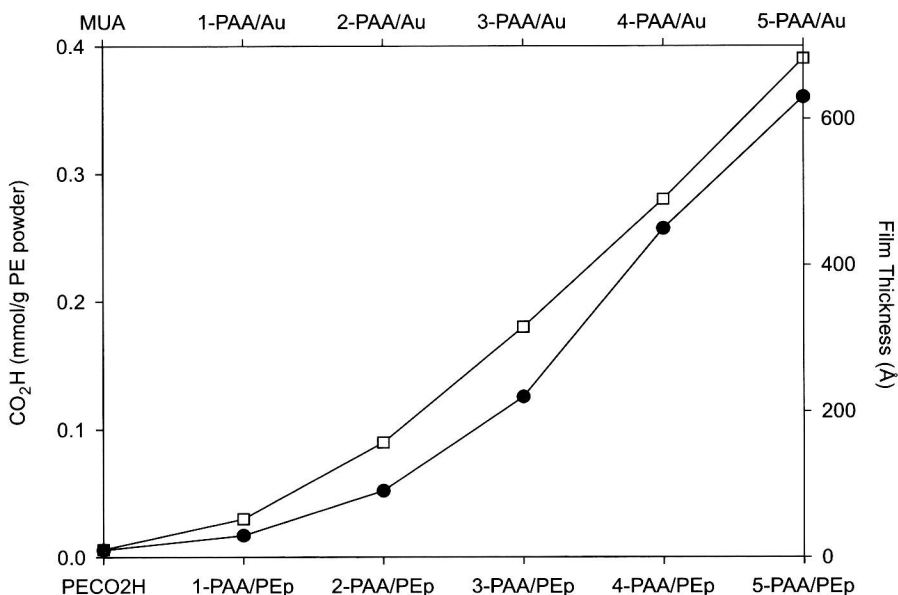


Fig. 2 Progress of hyperbranched poly(acrylic acid) graft formation on smooth gold films as measured by ellipsometry (●) or on polyethylene powders as measured by titration (□) of the supported CO_2H groups

2.1

Hyperbranched Poly(acrylic Acid) Graft Synthesis on Gold Surfaces

The synthesis of surface grafted hyperbranched films of poly(acrylic acid) was first described on gold substrates [18]. This synthesis of hyperbranched grafts of poly(acrylic acid) (PAA) on gold, shown in Scheme 1, began with a self-assembled monolayer of mercaptoundecanoic acid (MUA). Activation of the carboxylic acid groups of this monolayer was accomplished by formation of mixed anhydrides with ethyl chloroformate. While other activating agents (e.g. carbonyl diimidazole or DCC worked), the best yields were obtained with alkyl chloroformates. Subsequent amidation of this electrophilic surface by an oligomeric reagent, α,ω -diamino-poly(*tert*-butyl acrylate) (PTBA), yielded a 1-PTBA graft on MUA functionalized gold (1-PTBA/Au). This 1-PTBA/Au graft was initially converted to a 1-PAA/Au graft by acidolysis with *p*-toluene sulfonic acid/ H_2O . Subsequent work showed that this acidolysis proceeded equally well using methanesulfonic acid (15 min, room temperature). Activation of the carboxylic acid groups of this first 1-PAA/Au graft with more ethyl chloroformate followed by treatment of the new polyanhydride surface with more α,ω -diamino-poly(*tert*-butyl acrylate) oligomer produced a 2-PTBA/Au graft. Acidolysis of this second graft layer of PTBA produces a 2-PAA/Au graft. Repeating