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Polymer Brushes

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INDEX

PLENARY LECTURES

ORAL CONTRIBUTIONS

POSTER CONTRIBUTIONS

ABSTRACTS

INVITED LECTURES

PL 1

POLYMER BRUSHES PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATIONS

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Abstract

Atom transfer radical polymerizations (ATRP) has been successfully used for the preparation of polymer brushes attached to flat inorganic surfaces and also to nanoparticles using grafting anto and grafting-from procedures. Also, ATRP was employed for synthesis of bioconjugates by covalently linking synthetic polymers to proteins and nucleic acids. Recent advances in synthesis, characterization and applications of polymeric brushes prepared by ATRP will be discussed.

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PL 2

THE LIGHT WAY TO POLYMER BRUSHES

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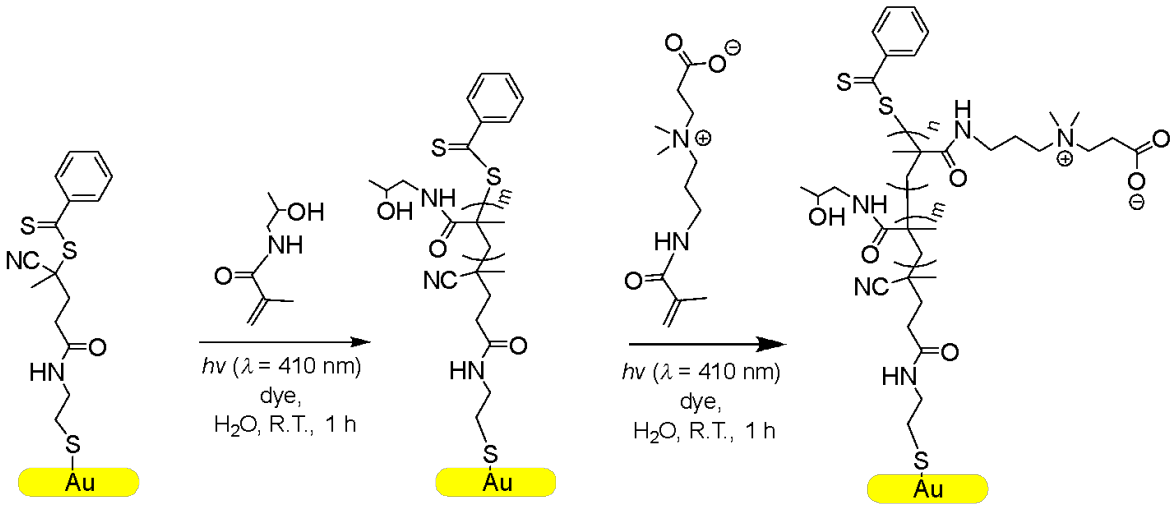
Abstract

The construction of polymer brushes with increasing complex architectures and the inclusion of specific functionalities has driven many aspects of surface science. Especially the development of a range of controlled radical polymerizations allowed the formation, study and application of a wide range of such densely packed surface-modified surfaces. The lecture will start by providing novel entries that these methods have provided into self-healing polymer brushes, and the quest for ever-smaller fluorine contents in them.
However, these often came at the price of complicated procedures and the need for a rigorously inert and dry atmosphere. This strongly limited the field, and there was evidently a need for easier and more robust procedures.

Over the last 5 years we have developed a range of visible light-induced methods to obtain high-quality polymer brushes that provide control over a range of properties. Such approaches were shown to work well even in water under ambient atmosphere (see *e.g.* the Figure below). The second part of the presentation will display this development, and will present a perspective on which ways to go from here.



Mild & visible light-induced formation of diblock polymer brushes

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PL 3

TAILORING POLYMER BRUSHES FOR BIOMEDICAL APPLICATIONS THROUGH EFFECTIVE FUNCTIONALIZATIONS

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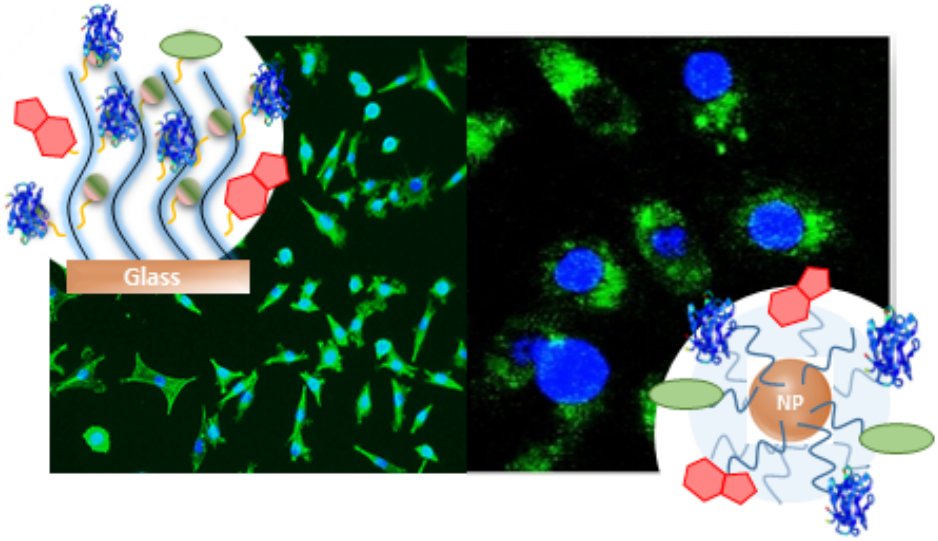
Abstract

In the past decade, polymeric coatings have transformed from basic protective barriers to dynamic interfaces. These interfaces enhance material functionality by engaging in specific interactions and communication with the surrounding environment. Notably, polymeric coatings featuring bioactive ligands, spanning from small molecules to biomacromolecules, are pivotal in the development of diverse diagnostic and biosensing platforms. For applications requiring stability in an aqueous environment, inherent anti-biofouling properties, and easy conjugation with biological probes, a 'clickable' hydrophilic polymeric coating is often preferred. Polymer brushes, resulting from the "graft-from" method involving the growth of polymer chains directly from surfaces with immobilized initiators or chain transfer agents, have gained prominence as a versatile coating platform. Importantly, implementing contemporary controlled/living radical polymerization techniques provides precise control over thickness and architecture. These techniques also yield coatings with diverse chemical compositions, exhibiting high tolerance toward a wide range of functional groups. This talk will focus on approaches taken by our group toward fabricating various functional polymer brush interfaces for modulation of protein immobilization and sensing, as well as controlling cell-surface interactions.



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PL 4

HARNESSING NATURE'S BLUEPRINTS TO DESIGN ANTIFOULING INTERACTIVE BIOINTERFACES BASED ON POLYMER BRUSHES

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Abstract

Nature's ability to engineer functionality in materials arises from the hierarchical self-assembly of seemingly simple (macro)molecular building blocks. Deciphering these intricate blueprints forms a robust foundation for the bio-inspired synthesis of materials that can seamlessly interact with living systems and execute of novel functions. This lecture showcases a curated selection of research endeavors conducted in our laboratory, all centered around the overarching objective of crafting bio-inspired antifouling interactive materials for biomedical applications. Resistance to fouling of molecules and cells is a cornerstone for developing selective interactions. In the first part of my talk, I will introduce adaptive hemocompatible nanocoatings that mimic simple functions of natural endothelium and are capable of modulating hemostasis as well as detecting and digest of blood clots.[1] The basis of this technology are advanced polymer brushes that prevent the activation of coagulation and that are further functionalized to modulate hemostasis locally. This technology is translated to oxygenator membranes. Second, I will delve into our innovations concerning 'Kill&Repel' and adaptive antimicrobial nanocoatings tailored for medical devices.[2] Here we design molecules in which a fragment is affine to the surface while the other carries a macromolecule, i.e. a specific enzyme or a polymer to generate a brush. The physisorption of these hybrid macromolecules gives rise to coatings that are antifouling and bear endolysins to target bacteria specifically. In this way, if a bacterium is able to reach the surface is killed by the endolysin, and the debris is repelled by the brushes, preventing the fouling and subsequent secondary colonization. This coating strategy has proven effective against *S. agalactiae* and *S. aureus* when applied to wound dressings.

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PL 5

POLYMER BRUSHES AND NANOPOROUS SCAFFOLDS HELPING EACH OTHER TO MODULATE IONIC TRANSPORT IN CONFINED ENVIRONMENTS

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Abstract

The rational design of robust platforms enabling the selective transport of ionic species has received considerable attention during the last decade. This interest stems from the wide variety of technological applications relying on "gated" transport processes, such as ultrafiltration or controlled delivery. The generation of interfaces discriminating the transport of cationic and anionic species, i.e.: permselectivity, is an intrinsic mechanism of nature, as can be seen in cornea or human skin which exploit fixed charges in the membrane to generate differential permeabilities. When dealing with synthetic materials, manipulating chemistry and topology down to the nanoscale is essential to achieve this goal and, as such, represents one of the ongoing challenges in materials science.

In this presentation we will discuss different routes to manipulate and control the transport of different chemical species by using polymer brushes, with agile response to minute environmental changes, into nanoconfined environments. Within this proposed framework we will describe the use of photoelectrochemically etched substrates, solid-state nanopores and mesoporous films as scaffolds for creating robust and shape-persistent nanoscopic channels. We will show that the incorporation of responsive polymer brushes into the robust nanoscopic channels provides new opportunities to molecularly design hybrid architectures with controllable transport properties.

PL 6

FUNDAMENTALS AND APPLICATIONS OF POLYMER BRUSHES IN AIR

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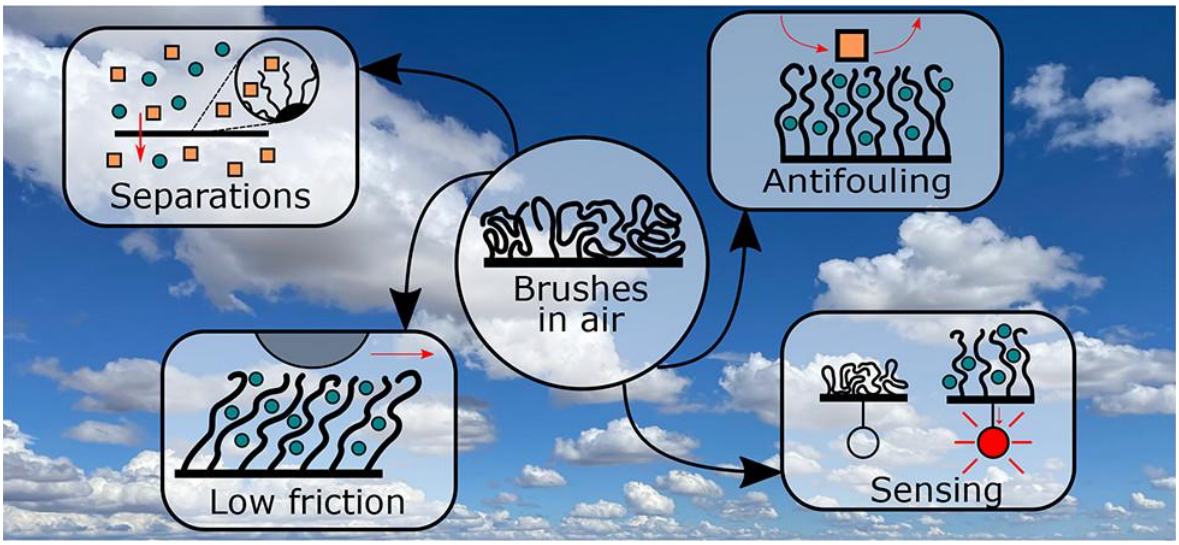
Abstract

Polymer brush research focused traditionally on their properties in liquid. Yet, for many applications, it is relevant to study their properties in air. Recent work has shown that brush in air behave qualitatively different from brushes in liquid [1]. In this presentation, I will discuss recent progress in unraveling the fundamental concepts of brushes in air, such as their vapor-solvation and the partitioning of solvents in the brushes. Moreover, I will provide an overview of the broad range of applications of these brushes in air (e.g., in separations or vapor sensing).



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PL 7

SELF-LIMITED GRAFTING OF PHOSPHORUS END-TERMINATED POLYMERS: TRACKING THE KINETICS AND THERMODYNAMICS OF THE "GRAFTING TO" PROCESS

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Abstract

Recently, an effective bottom-up technology for the doping of silicon substrates was proposed, taking advantage of the self limiting nature of the *"grafting to"* process from melt.[1,2] In particular, polymers end-terminated with a P-containing moiety were end-grafted onto deglazed and non-deglazed silicon substrates generating P δ-layers to be used as dopant sources. Measuring the P concentration in the δ-layers, the effective grafting density at equilibrium was shown to correlate with the polymer molar mass, consistentely with the self-limiting model of the "grafting to" reaction from melt.[3] However, recent investigations revealed that the "*grafting to*" reaction is much more complex than usually believed. [4] Monitoring P concentration during the differnt stages of the gafting process allowed to demonstrate that partitioning by molecular weight takes place at interfaces in which the low molecular weight species are preferably incorporated into the polymeric brush. Depending on the specific chemistry of the "*grafting to*" reaction, this preferential incorporation operates also in the case of polymers with polydispersity $Đ < 1.1$, featuring relatively narrow molecular weight distributions.[5] These effects limit the capability to effectively control the number of polymer chains in the brush layer, reducing at the end the control on the dose of P atoms in the dopant source. As a counterproof, monodisperse polypeptoids were proposed to overcome this problem, obtaining P δ-layers with precisely predetermined amounts of dopant atoms by simply changing the monomer units in the polypeptoid chains.[6] These results suggest a viable solution to deterministically control the composition of a brush layer paving the way to functionalization of surfaces with precisely tuned characteristics.

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PL 8

WRITING POLYMER IMAGES INTO MESOPOROUS SILICA FILMS USING VISIBLE LIGHT INDUCED POLYMERIZATIONS

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Abstract

Biological pores and channels demonstrate a transport performance which is unreached by technical materials. One key factor for this performance is their nanoscale structure and their arrangement of functional components. Fascinated by this performance and nanoscale precision we aim to advance control and precision of polymer functionalization of technological porous materials. Thereby, automated polymer writing as well as precise local placement of multiple polymers into porous materials is an important aspect.
This talk will highlight our recent advances related to automated polymer writing and local polymer functionalization in nanopores. This includes polymerization control and re-initiatiation of polymerization to graft block co-oligomers in silica mesopores mainly focusing on iniferter-initiated RAFT polymerizations.[1] The effect of this chain architecture control on ionic mesopore accessibility will be discussed. Furthermore, visible-light- and surface plasmon induced nanopore polymer functionalization[2, 3] as well as automated polymer writing of polymers, including block-copolymers, using a high-resolution fluorescence microscope will be presented.[4-6] Interestingly, we were able to demonstrate polymer writing using iniferter initiation even at visible light wavelengths outside the absorption wavelength of the respective initiator. Using this approach of polymer writing, we achieved writing of block copolymer images with polymerization times of 1 second per pixel, polymer spot sizes on the micrometer scale resulting in images sizes on the millimeter length scale. We expect this approach of automated local polymer writing to be of general interest for miniaturized design of polymer functionalized surfaces and porous materials.

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PL 9

EXPANDING THE SCOPE OF SURFACE-INITIATED POLYMERIZATION

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Abstract

Surface-grafted polymer thin films, which are commonly referred to as polymer brushes, have emerged as a unique class of surface coatings. Chain-end tethering polymers in close proximity using surface-initiated polymerization methodologies enforces a stretched conformation of the polymer grafts, which leads to several unique materials properties. Polymer brush films, for example, can be designed that are exceptionally effective in preventing biofouling, or which possess extraordinarily low friction coefficients.

This presentation will highlight three recent discoveries from our laboratory that take advantage of surface-initiated polymerization reactions to generate polymer surface coatings with unique properties. In a first example, it will be shown how surface-grafted polymer films can be designed and prepared that display piezo- and pyroelectric properties, which is of great interest e.g. for energy harvesting applications. In a second example, it will be shown how, for a polymer film of a given thickness and composition, solvent uptake and swelling can be controlled, essentially by molecular engineering at the polymer brush – substrate interface. Since solvent swelling is essential to non-fouling and lubrication applications, this provides a new approach to engineer such properties. Finally, it will be shown how concepts from supramolecular chemistry can be harnessed to generate surface-grafted polymer films that potentially could be grown and removed in a repetitive, reversible manner.

PL 10

MACROMOLECULAR DESIGN STRATEGIES WITH POLY(2-OXAZOLINE)S

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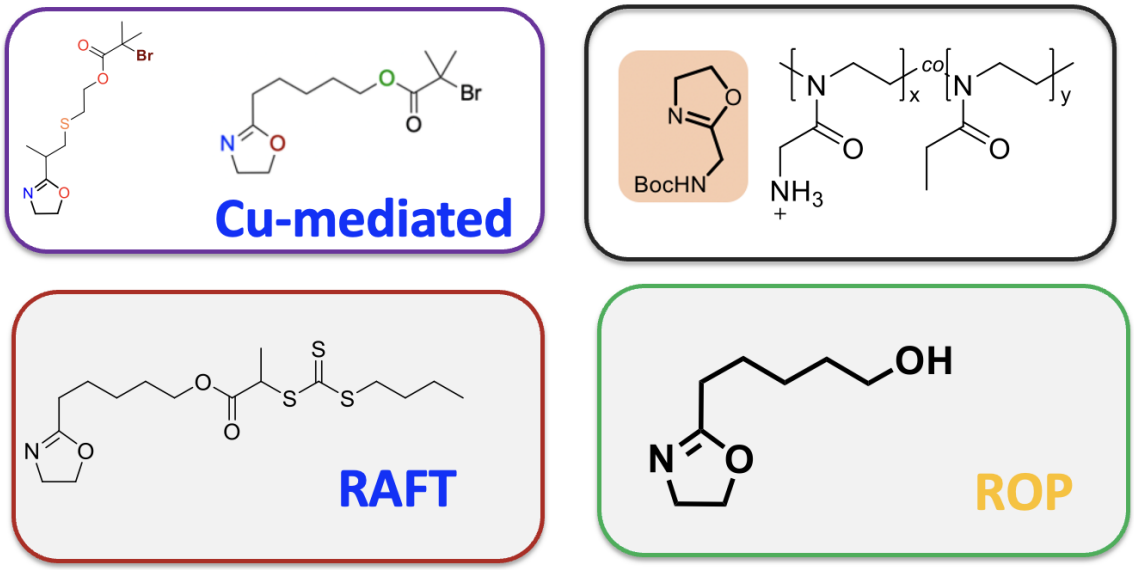
Abstract

Poly(2-oxazoline)s are promising class of polymers that allows several design possibilities. Functional 2-oxazoline monomers with initiator or chain transfer agents allow creating macroinitiators for brush copolymers. In this talk, we will highlight various combinations of 2-oxazolines that are polymerized by cationic ring opening polymerization and acrylates/acrylamides that are polymerized by controlled radical polymerization techniques.



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PL 11

MULTISCALE MOLECULAR SIMULATIONS OF GRAFTED MATERIALS

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Abstract

The addition of polymer chains onto a surface is a very useful tool to improve materials properties or to achieve new ones. The key point of this type of technologies lies in the ability to create new interfaces. Computer simulations can be a useful tool aimed at exploring the molecular mechanisms underlying the effects of the grafted chains on the materials behaviour.
To implement realistic models of such polymeric materials several specific coarse-grained (CG) models have been proposed.[1] A further speed up of CG simulations is obtained by combining the traditional Molecular Dynamics (MD) approaches with a field representation of the non-bonded interactions called hybrid particle-field molecular dynamics (hPF-MD).[2].
Several applications of hPF-MD technique to grafted materials will be presented. In the first part of my talk I will present simulation results related to grafted nanoparticles in polymer composites.[3,4] The second part will be devoted to molecular and lattice-based models aimed to rationalize by a microscopic interpretation the grafting to processes of polymer melts onto silicon surfaces.[5,6]

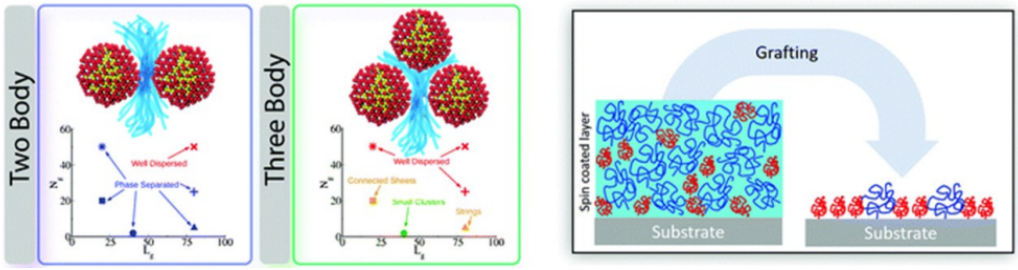

Figure 1. Left) schematization of two body and three body interactions between silica nanoparticles embedded in polystyrene melts. Right) schematization of the grafting to process of a bidisperse polymer melt onto a solid surface.

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PL 12

GRAFTED POLYEHTYLENE BRUSHES ON SILICA: FROM GRAFTED BRUSHES MODELS TO ADHESION WITH POLYETHYLENE

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Abstract

In order to study the interfacial phenomena developed between a polyethylene grafted brush and polyethylene, *i.e*. interpenetration of chains, potential co-crystallization, resulting adhesion, and fracture mechanisms, α-chlorosilane terminated polyethylenes having different molar masses were prepared 1/ using an homogeneous catalyst, the cyclopentadienyl zirconium dichloride and the methyl aluminoxane (MAO) as co-catalyst (M_n=1,134 g.mol^{-1}; I_p=4.4); 2/ using a heterogeneous metallocene supported on silica and MAO as catalyst (M_n=3,710 g.mol^{-1}; I_p=4.3) ; 3/ using a metallocene homogeneous catalyst, the ethenyl-bis-indenyl zirconiumdichloride and MAO as co-cotalyst to synthesize an ethylene-hexene copolymer (M_n=325,000 g.mol^{-1}; I_p=2). These functional PEs were grafted onto activated silicon surfaces (hydroxyl groups density : 4.5 OH.nm^{-2}) to design grafted brushes used as connecting molecules between a silica surface and a neat metallocene polyethylene matrix (HDPE). The grafting of alkylchlorosilanes (alkyl chain length varying from C_4H_9 to $C_{30}H_{61}$) was also considered in comparison to the polymer chains. The grafting efficiency was demonstrated by means of ^{29}Si NMR and wetting measurements according to the hydrophobic nature of the grafted brushes in comparison with the hydrophilic character of silica. The resulting thickness and refractive index of the dry grafted brushes were characterized using spectroscopic ellipsometry. The grafting ratios are given from microanalysis measurements and surface topography is observed using AFM. All of these techniques are in a good agreement and the organization of the tethered layers at the surface is proposed.
These previous chlorosilane-terminated polyethylene (PE) were semi-crystalline polymers able or not to crystallize with the free chains of a covering polyethylene film processed by melting and cooling.. The adhesion developed at the polyethylene/silica interface was studied as a function of the molar mass of functionalized-polyethylene grafted chains. For that purpose, the asymmetric double cantilever beam test was used to determine the fracture energy, G_i, of the interface. For both high-density and low-density polyethylene/silica assemblies, the fracture energy of the interface, G_i, was found to increase with the length of the interfacial connecting chains. The locus of the failure was studied by means of wettability measurements and atomic force microscopy analysis of the surfaces after separation. The higher values of the fracture energy of the interface with HDPE can be explained by a better compatibility of the tethered-PE chains with the free chains of the PE matrix which are more linear than LDPE. It was demonstrated that for the brushes prepared with the shortest chains (alkylchlorosilanes), the connectors were extracted from the bulk PE (LDPE or HDPE) whereas for the polymeric chains, a cohesive failure occurred for the silica/HDPE interfaces. Such a study can be used to design the connecting polymer chains for improving the adhesion between silica and semi-crystalline polymers in nanocomposites and fiber-based composite materials.

PL 13

STRUCTURAL DISPERSITY DETERMINES THE PROPERTIES OF POLYMER BRUSHES

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Abstract

The application of polymer adsorbates featuring different molar mass, molecular architecture or topology has represented a versatile strategy to generate polymer "brush" interfaces with variable physicochemical properties.
Although the relationship between polymer structure and surface properties of the generated assemblies has been widely elucidated, little is known regarding the effect of adsorbate's dispersity on interfacial characteristics.
This is especially relevant when polymer adsorbates forming brushes on solid surfaces are constituted by comb-like polymers including oligomeric side chains. In this particular case, reversible deactivation radical polymerization (RDRP) methods can be exploited to tune the dispersity of the main chain, while the dispersity of side chains can be precisely modulated through the controlled synthesis and purification of macromonomers.
Tuning the dispersity of polymer adsorbates thus not only reveals fundamental parameters in the designing of polymer interfaces, but also emerges as an additional tool to precisely adjust technologically relevant interfacial properties of polymer brushes, such as biopassivity and lubrication.

ORAL CONTRIBUTIONS

OC 1

POLYMER BRUSHES BY SI-PET-RAFT FOR SENSING APPLICATIONS

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Abstract

Coatings based on polymer brushes offer distinctive surface properties such as sensing, antibiofouling,[1] antiviral,[2] and lubrication features.[3] Different controlled radical polymerization methods have been applied to create these coatings. However, these methods frequently involve complex handling procedures and the need for an inert atmosphere, which has prompted the search for more resilient, more straightforward, and gentler techniques to achieve similar polymer coatings. In pursuit of this goal, we have modified the photoinduced electron transfer reversible addition−fragmentation (PET-RAFT) technique specifically for surface-initiated synthesis of polymer brushes (SI-PET-RAFT).
The SI-PET-RAFT polymerization occurs under mild conditions free of metals and tolerant to oxygen, activated by visible light. Moreover, employing light as the catalyst for this polymerization enables the formation of intricate hierarchical and patterned structures. We have explored different polymerization conditions and their effect on the control and livingness of the SI-PET-RAFT process.[4] We further created polymer brush layers based on N-(2-Hydroxypropyl) methacrylamide, butyl methacrylate, carboxybetaine methacrylate and oligo(ethylene glycol) methyl ether methacrylate. Moreover, we applied SI-PET-RAFT to create affinity layers to sense volatile organic compounds such as ethanol, limonene, carvone, $\alpha\alpha$-pinene.

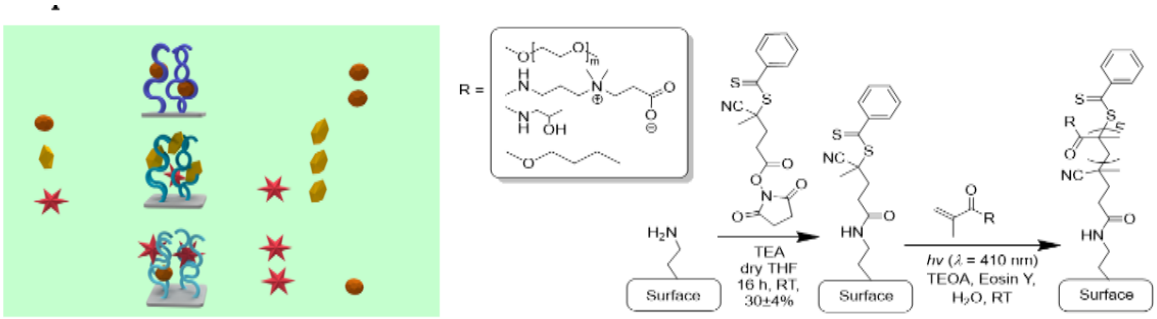

Figure 1. General Scheme of SI-PET-RAFT.

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OC 2

SYNTHESIS OF N-(2-FLUOROETHYL) ACRYLAMIDE BRUSHES VIA SURFACE-INITIATED ATOM TRANSFER RADICAL POLYMERIZATION: A PROMISING ANTIFOULING MATERIAL

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Abstract

Fluorinated polymer brushes constitute a category of surface-tethered macromolecular architectures with potential applications in the development of advanced antifouling functional materials and 19F MRI contrast agents [1]. To achieve the kinetic control for tuning the thickness, surface-initiated atom transfer radical polymerization (SI-ATRP) is frequently used as a "living-like" approach. However, the polymerization of fluorinated monomers via ATRP poses challenges, as the monomer may act as an initiation point during the reaction due to the presence of the C—F site [2].
This study is focused on the synthesis of a novel polymer brush based on N-(2-fluoroethyl) acrylamide (FEAm), aiming to compare its antifouling properties with those of its 2-hydroxyethyl-based counterparts: N-(2-hydroxyethyl) acrylamide (HEAm) and 2-hydroxyethyl acrylate (HEA). The polymer layers were grown from surfaces coated with self-assembled monolayers bearing 2-bromoisobutyryl or 2-chloropropionyl-initiating groups. The polymerizations of polyFEAm, polyHEAm, and polyHEA brushes proceeded in water at near ambient temperature and yielded well-controlled kinetics as seen by the near-linear growth of layer thickness with time. The chemical composition of the polymers was verified spectroscopically. Analysis of both surface-initiated and solution polymerizations revealed the absence of any initiation from the fluorinated monomer, ensuring the preservation of the integrity of the C—F bond. Surface plasmon resonance (SPR) measurements demonstrated that the brush-coated surfaces exhibited remarkable antifouling properties. Notably, the polyFEAm brushes reduced fouling from blood plasma by more than 95%, thus matching the antifouling properties of the polyHEAm and polyHEA counterparts. These findings establish the synthesized polyFEAm polymer brushes as promising candidates for advanced antifouling materials.

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OC 3

POLYMER BRUSH-SUPPORTED RECYCLABLE PHOTOCATALYSTS

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Abstract

Visible light organo-photoredox catalysis has demonstrated its enormous potential for enabling challenging chemical reactions while being a cheaper and greener alternative to transition metal-based catalysts. Specifically, in recent years, organic compounds that show thermally activated delayed fluorescence (TADF) have found increasing use as photocatalysts[1]. Nevertheless, contamination of the final product and disposal of the photocatalyst represent weaknesses in such homogeneous catalytic systems.

In order to circumvent these limitations, we developed photocatalytic systems supported by polymer brush-functionalized silica microparticles, thus enabling their efficient recovery and recycling through simple centrifugation/separation methods.

The photocatalyst design relies on the modification of a cyanoarene-based core, using 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) and an acrylate function, to yield a catalytically active co-monomer that can be incorporated within a polymer chain through radical polymerization. Surface-initiated activators regenerated by electron transfer atom transfer radical polymerization (SI-ARGET-ATRP) provided core-shell particles with the photocatalyst integrated in the brush shell.

The obtained particle brush-supported photocatalytic materials were applied in an array of benchmark reactions both in organic and aqueous media. High photocatalytic efficiency was obtained in decarboxylative addition reactions and the core-shell particles could be reused in several catalytic cycles by virtue of their easy separation from the reaction environment.

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OC 4

OXYGEN TOLERANCE DURING SURFACE-INITIATED PHOTO-ATRP: TIPS AND TRICKS FOR MAKING BRUSHES UNDER ENVIROMENTAL CONDITIONS

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Abstract

Surface-initiated reversible deactivation radical polymerization (SI-RDRP) enables the fabrication of polymer-brush coatings with fully tunable and technologically relevant properties. However, the presence of oxygen can hamper RDRP processes, and thus the development of SI-RDRP techniques tolerant to environmental conditions is critical for the scalability of these surface modification methods[1].

In this work, we focus on surface-initiated photoinduced atom transfer radical polymerization (SI-photoATRP) and demonstrate how a fine adjustment of both composition of reaction mixtures and polymerization setup enable to grow thick polymer brushes over large areas without the need for deoxygenation of reaction mixtures. Efficient oxygen consumption can be achieved by judiciously adjusting the concentrations of the Cu-based catalyst and the "free" alkyl halide initiator in solution, finally enabling to perform SI-photoATRP within scalable and more practical settings[2].

A strategy for the detachment of POEGMA brushes was also developed in order to analyze the obtained polymer chains. Treatment of brush-modified silicon substrates with organic hydrofluoric acid mixtures (MIX·nHF) enables the release of polymer chains into solution under mild conditions and without the use of hard-to-separate fluoride salts.

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OC 5

LIGHT-MEDIATED ATOM TRANSFER RADICAL POLYMERIZATION (ATRP) AS A TOOL TO GRAFT POLYMER BRUSHES FROM FLUOROPOLYMERS

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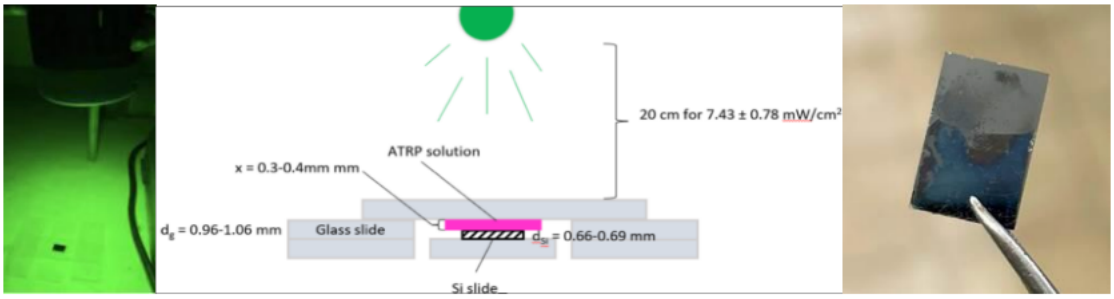
Abstract

Poly(vinylidene fluoride) (PVDF) has excellent resistance to solvents, acids and hydrocarbons and can withstand temperature of up to 400oC before decomposing. The material features high dielectric strength and unique piezoelectric properties. It is used in number of applications, including filtration membranes, cable insulators, cathode binders as well as sensors and power generators. However, its low polarity, low reactivity and lack of functional groups limits its applications, e.g., in water-filtration membranes and adhesive binders.
PVDF may be surprisingly well modified by ATRP, albeit usually under rather harsh conditions, i.e. conventional ATRP with large amounts of Cu/L catalyst (> 2000 ppm), high temperatures and long reaction times [1]. We show that light-mediated ATRP is a convenient (oxygen tolerant), fast (>100 nm/5 min) and mild (room temperature) approach. The procedure is demonstrated to work in bulk (dissolved polymer), on flat surfaces (heterogenous system) as well as with different classes of PVDF. We also try to shed light on the modification mechanism. The bond dissociation energy (BDE) of C-F (> 400 kJ/mol) may be greatly reduced when conjugated with double bonds [2], situation likely to occur given readiness of PVDF to dehydrofluorinate [3]. The double bonds alone may also participate in grafting through process [4]. The double bonds were detected by means of nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS). Finally, the altered materials and substrates are tested for their mechanical properties as well as interfacial applications.



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OC 6

POLYETHYLENE GLYCOL BASED BRUSHES FOR MEDICAL APPLICATIONS

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Abstract

Polyethylene glycol-based brushes have been at the forefront of biological applications and nanomedicine due to their anti-fouling properties, low toxicity, wide availability, and use history in medicine and drug delivery materials [1]. The tailoring of chemical composition, thickness, adaptive physicochemical properties and surface density provide a versatile toolbox to obtain polymer brushes with the desired characteristics.

The present study is part of the KIDNEW European project [2], which aims at designing an artificial implantable kidney based on nanofabricated silicon membranes for filtration. This requires in particular to functionalize such membranes with long-lasting efficient coatings preventing non-specific adsorption of blood plasma proteins. In this work, a surface-initiated activator regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) was used to synthesize "bottle brushes" of polyethylene glycol methyl ether methacrylate monomers (PEGMA) varying the number of ethylene oxide repeating units. The optimization of synthesis conditions was conducted by evaluating the influence of the macro-initiator, silanization and a coupling of both synthetic strategies [3] on the stability of brushes upon long term immersion in aqueous medium. The brushes' characterization was performed by ellipsometry and atomic force microscope (AFM). Anchors were found to play an important role in the brushes' long-term stability. PEGMA brushes anti-fouling properties were assessed by quartz crystal microbalance with dissipation (QCM-D), demonstrating the effectiveness of both freshly grafted and aged brushes in preventing bovine serum albumin adsorption in physiological conditions. This research delivers a synthetic approach highlighting the importance of anchoring functionalities in designing PEG-based brushes with potential application in biomedical devices.

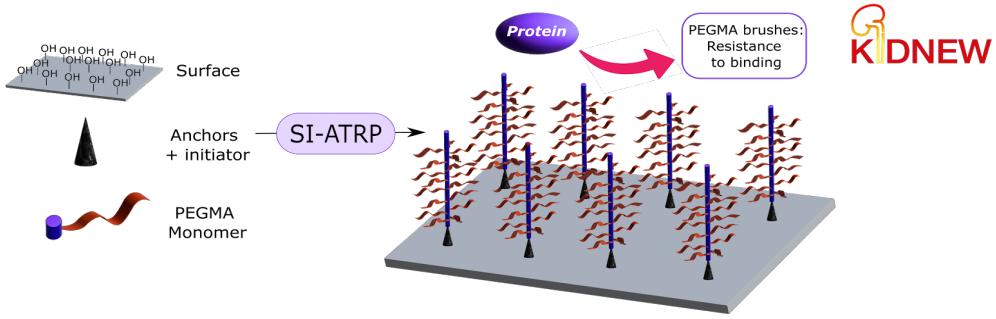

Figure 1: Representation of PEGMA bottlebrushes synthesized by SI-ATRP from silicon oxide substrates.

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OC 7

SULFONIUM-BASED POLYMERS FOR ANTIMICROBIAL USE: INFLUENCE OF STRUCTURE AND COMPOSITION

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Abstract

We are facing a shortage of new antibiotics to fight increasingly resistant bacteria. As alternative to conventional antibiotics, antimicrobial polymers (AMPs) disrupt the bacterial cell membrane through a combination of cationic and hydrophobic moieties. While quaternary ammonium salts (QAS) are the most examined structures, sulfonium-cations are currently examined to broaden the scope of these polymeric therapeutics. Especially, main chain sulfonium cation-containing polymers show good antimicrobial activity. In contrast, the potential of side chain sulfonium polymers remains less explored with structure-activity relationships (SAR) still being limited.
Thus, in this study, we thoroughly investigate key factors influencing antimicrobial activity in side-chain sulfonium-based AMPs. For this, we combine sulfonium cations with different hydrophilic (PEG) and hydrophobic (aliphatic or aromatic) groups to create a small polymer library. For all compositions, we additionally examine the position of cationic and hydrophobic groups on the polymer backbone, i.e., examining same center and different center structures. Ultimately, we compare the bactericidal activity of these sulfonium-based AMPs to their quaternary ammonium cationic (QAC) analogues.
The bactericidal activity of polymers was quantified via broth dilution assays against Bacillus subtilis, E. coli, Pseudomonas aeruginosa, and S. aureus. MIC values indicated the following trends: (1) increasing the hydrophobicity of functional groups increases inhibition of bacterial growth but reduces selectivity over human cells, (2) same center polymers were more effective but less selective than different center polymers, (3) sulfonium polymers show superior bactericidal activity and selectivity when compared with QAC analogues.
In summary, these trends are suggested to support the structural optimization of new sulfonium-based AMPs.

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OC 8

SURFACE-ATTACHED FILMS OF UCST HYDROGELS FOR BIOLOGICAL APPLICATIONS

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Thermo-sensitive polymers are of growing interest in many biomedical applications such as drug delivery, microfluidic biotechnologies [1] or single cell culture. In this vein, there is a need to fabricate devices based on thermo-sensitive polymers that exhibit their transition close to the physiological temperature. The LCST (Lower Critical Solution Temperature) polymers are extensively investigated but their transition can present limitations for some biological applications. Consequently, it is necessary to develop systems that present the opposite transition such as UCST (Upper Critical Solution Temperature) polymers, far less represented in the literature. The general idea of this project is to design surface-attached hydrogel films and surface-attached hydrogel micro-patterns with UCST properties.
Like polymer brushes, hydrogels are here grafted onto the substrate by covalent bonds. They are also covalently cross-linked together to ensure the chemical and mechanical stability to environment change (solvent, temperature…). Contrary to polymer brushes, surface-attached hydrogels have no limitation in term of thickness, the thickness widely ranging from a few nanometers to several micrometers. The swelling/collapse amplitude of responsive hydrogels is also much higher than that of polymer brushes with four times change or more.
As for biological applications the responsive polymers selected must be insensitive to saline solutions, the affinity of the polymer with water has to be governed by hydrogen bond interactions which can be finely tuned with temperature (T > UCST: swelling, T < UCST: collapse). We focus on acrylamide-based polymers which can keep their UCST behavior in salt conditions such as poly(N-acryloylglycinamide)- or poly(N-methacryloylglycinamide) [2]. The surface-attached hydrogels are fabricated by using a novel, simple and versatile approach called CLAG [3] which consists in simultaneous Cross-Linking And Grafting functionalized polymer chains by (thiol-ene) click chemistry. (Figure 1).

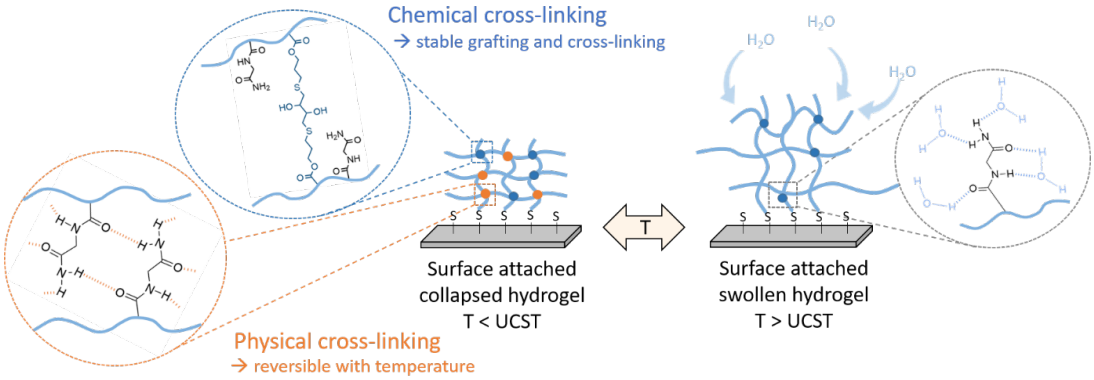

Figure 1. *Thermo-sensitive hydrogel. Chains-chains interactions (left, orange dots) in the collapsed state or water-chains interactions (right) in the swollen state of a cross-linked hydrogel (blue dots).*

Acrylamide-based monomers and functionalized polymers are first synthesized as elementary bricks to be cross-linked and grafted. We measure the thickness of surface-attached hydrogels in water as function of temperature to show their UCST properties in aqueous and physiological solutions which is very promising for biomedical applications

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OC 9

GROWING POLYMER BRUSHES FROM TWO AND THREE DIMENSIONAL SUBSTRATES FOR TAILORING THEIR PHYSICOCHEMICAL PROPERTIES

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The fabrication of polymer brushes is an attractive and versatile strategy to tailor the physicochemical properties of a broad variety of (bio)materials. Recent developments in surface initiated reversible deactivation radical polymerization (SI-RDRP) techniques enable to grow polymer brushes from diverse surfaces through simple procedures and under environmental conditions.[1] These traits are essential to promote the fabrication of polymer brushes in industrial settings. This presentation highlights the versatility of SI-RDRP approaches for the growth of polymer brushes, particularly in terms of monomer and substrate scope. Not only 2D materials, such as SiO_2 wafers, but also 3D polymeric materials could be functionalized with polymer brushes exhibiting different hydrophilicity, charge, and response to external stimuli. The functionalization of 3D polymeric materials encompasses porous nano/microparticles, aerogels and elastomeric scaffolds prepared by high internal phase emulsion (HIPE)[2] polymerization processes. The introduction of an "inimer" (i.e., initiator-monomer) during the synthesis of these materials allows for incorporating functional groups that can be later exploited for grafting polymer brushes and modulate the material properties.

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OC 10

UNDERSTANDING AND TAILORING MULTIRESPONSIVE TRANSITIONS OF POLYELECTROLYTE BRUSHES AT THE NANOSCALE

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Abstract

Thermoresponsive polymer films offer a great potential for the development of smart surfaces. The capability to respond to environmental changes of temperature with a significant change of physicochemical surface properties evoked much interest in the field of biomedical sensors, novel drug delivery systems and tissue engineering[1]. According to their phase separation behavior the class of thermoresponsive polymers is divided into polymers with a lower critical solution temperature (LCST) as well as with an upper critical solution temperature (UCST). Although both types of thermoresponsivity show similar potential in the development of smart materials the phenomenon of UCST behavior is significantly underrepresented in the literature. In contrast to comprehensively studied LCST polymers like poly(*N*-isopropyl acrylamide) (PNiPAAm) only a few polymers, like poly(*N*-acryloyl glycinamide) (PNAGA), are currently known to exhibit UCST behavior [2]. Moreover the UCST mechanism of free chains in solution and especially the temperature-dependent swelling/deswelling process of polymer films has not been fully understood until now. Hence, the objective of this presentation is to present a method to prepare nanoscopic Poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) polymer brushes exhibiting LCST and induced UCST type behavior and a comprehensive in-situ study using spectroscopic ellipsometry and infrared spectroscopy[3, 4].

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OC 11

SYNTHESIS OF SALT-RESPONSIVE, ULTRA-STABLE, RASPBERRY-LIKE NANOPARTICLES VIA SURFACE-GRAFTING OF POLYCATIONIC POLY(GLYCIDYL-METHACRYLATE) BRUSHES WITH IN-SITU SURFACE PROBING

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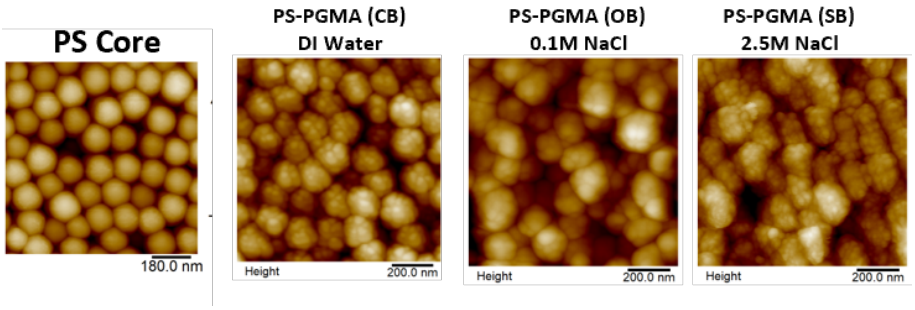
A method to synthesize stable, raspberry-like nanoparticles, NPs, using surface grafting of poly(glycidyl methacrylate) (PGMA) brushes on a polystyrene (PS) core with varying grafting densities is reported. A two-step functionalization reaction of PGMA epoxide groups generates permanently, positively charged, salt-responsive polyelectrolyte brushes, which result in both steric and electro-static stabilization enhancing colloidal stability by ~95% in salt solutions at ambient and elevated temperatures. Additionally, the grafted chains undergo a reversible swelling in the presence of different ionic strength (IS) salts, which modulates the surface properties including roughness, stiffness, and adhesion. Atomic force microscopy (AFM) both under dry and wet conditions was used to image conformational changes during the swelling and deswelling transitions as well as to probe the nanomechanical properties. The polyelectrolyte brushes undergo a conformational transition from a collapsed state (CB) to a swelled state in the osmotic brush (OB) regime between 0.01-0.1M IS,[1,2] triggered by the osmotic gradient. At IS~1M, the brushes contract and the globules reform (salted brush state, SB) as evidenced by an increase in the surface roughness and a reduction in the adhesion of the brushes. Beyond IS~1M, Crystal Micro-balance with Dissipation monitoring (QCM-D) measurements show that salt uptake continues to take place predominantly on the exterior surface of the brush since salt adsorption is not accompanied by a size increase as measured by Dynamic Light Scattering (DLS). The study adds new insights to our understanding of the behavior of NPs bearing salt-responsive polyelectrolyte brushes with enhanced colloidal stability and adaptive swelling thresholds that can ultimately modulate surface properties.



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OC 12

POLYMER BRUSHES AS STRUCTURAL MOTIF FOR BIOMIMETIC NANOMATERIALS

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Polymer and polyelectrolyte brushes resemble supramolecular structures that are widespread in living nature, such as pericellular layers of charged biopolyelectrolytes (glycosaminoglycans), proteoglycans, which in complex with hyaluronic acid are constituent elements of the cartilage tissue, neurofilaments in neural axons, nucleopore complexes, etc.
Comprehensive theoretical and experimental studies of well-defined model systems can provide important information underlying bio-lubrication, molecular recognition and cell adhesion, selective transport of molecules across biological membranes etc. Here we focus on the results of theoretical and computational modelling for a number of biomimetic brush-like systems: (i) Structural and tribological properties of surfaces modified with tethered molecular brushes ("brushes of brushes") were studied by self-consistent field methods and it was proven that substantial improvement of the lubrication properties (i.e., reduction of the friction coefficient) can be achieved due to branching of the brush-forming macromolecules; (ii) Swelling and mechanical properties of "hairy" gels formed by crosslinked bottlebrushes were studied by scaling theory in combination with coarse-grained Monte Carlo simulations and it was demonstrated that controlling of the gel properties can be achieved through variation of polymerization degree and grafting density of the brush-forming chains, the swelling ratio and the osmotic modulus of the gel exhibit, respectively, a maximum and a minimum as a function of the bottlebrush strand thickness; (iii) Interaction of polyelectrolyte brushes with amphiphilic protein-like nanocolloids and oppositely charged macromolecules was studied using analytical Poisson-Boltzmann approach; analysis of the position-dependent insertion free energy of the particle enabled predicting condition (pH, ionic strength, the brush architecture) for the particle uptake/exclusion in/from the brush and to evaluate respective kinetic barriers; (iv) Selective transport of nanocolloidal particles through mesopores with polymer brush grafted to the inner wall was modelled using 2-gradient numerical self-consistent field method. Ultimately, these theoretical insights may have important implication for development of high-performance biomimetic functional polymer materials.

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OC 13

POLY(AMINOETHYL METHACRYLATE) DERIVATES FOR CO_2 CAPTURE AND RELEASE

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Abstract

Poly(aminoethyl methacrylate) (PAEMA), poly(ethylene oxide)-block-(aminoethyl methacrylate) (PEO-PAEMA) and their guanidinylated derivates, poly(guanidine ethyl methacrylate) (PGEMA) and poly(ethylene oxide)-block-(guanidine ethyl methacrylate) (PEO-PGEMA) were prepared by RAFT polymerization and subsequent guanidinylation. The polymers were studied with respect to their interaction with carbon dioxide by NMR and calorimetric measurements and the extent and kinetics of adsorption and desorption of CO_2 were investigated by thermogravimetry under controlled gas atmospheres. The polymers were found to reversibly adsorb CO_2 at room temperature and release it at moderate temperatures.
The study also revealed relations between the polymer chemical composition and CO_2 adsorption and release characteristics that are useful in future formulations for CO_2 adsorbent polymer materials.[1]

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OC 14

NON-COVALENT GRAPHENIC BRUSH-LIKE POLYCATION COMPOSITES FOR ADVANCED GAS SIEVING

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Abstract

The peculiar shape of graphenic sheets, characterized by an atomic thickness, prompted its application as a building block for the fabrication of 2D molecular architectures.[1]
Indeed, several layered nanostructures have been fabricated in the last years[2] and membrane separation emerged as the most promising playground for different separations, including gases.[3] Due to its functional groups and its water processability, oxidized graphene (Graphene Oxide, GO) was widely used in membranes fabrication.[4]
Interestingly, superior stability and resistance to deterioration of the sieving systems prepared were achieved using polymer-brush modified GO.[5] Staring from these observations, we decided to investigate preparation of a non-covalent GO brush-like polycation composite for gas sieving applications. Inspired by a layer-by-layer method, we self-assembled polycationic chains and GO sheets to prepare a multilaminate composites. The alternated and layered architecture was proved by surface ζ-potential and XRD analyses, respectively. Moreover, XPS spectra confirmed instauration of an ionic interaction between graphenic sheets and polycations chains. Indeed, no traces of polycation original counter anion was detected in the fabricated multilaminate, testifying accomplishment of a complete ion exchange process.
Our approach consented to control fabricated architectures in terms of number of deposited layers and allowed to achieve interlayer spacings of different entity with respect to the usual distances presented by neat GO laminates. Also, post-fabrication treatments permitted structural modification of prepared layered structure.
Gas permeation experiments confirms dependence of the transport rates (permeances) upon the fabricated architecture. The permeances of a series of differently dimensioned gaseous penetrants (He, H2, CO2, Ar, N2, CH4) were experimentally determined and corresponding ideal selectivities calculated. Interestingly, determined selectivities strongly depended on the fabrication condition of the various multilaminate and, in some cases, values overtook performances of currently available sieving systems.
Drove by such understandings, an on-demand fabrication of a properly tuned gas sieving system could be envisioned.

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OC 15

FILLER DISPERSION IN ELASTOMEIC COMPOUNDS

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Abstract

Silica used as a filler in elastomeric compounds tends to form agglomerates that worsen the final properties of the compound. A solution to reduce the formation of agglomerates is the addition of functionalized polymers that contain a group able to bond with silica.
The goal of this work is the analysis of the effect on filler dispersion due to the dimension of the functionalized grafted polymer molecules and the free molecules of the polymer matrix.
Firstly, we analyze the flocculation of the filler considering the interaction of two filler aggregates by means of suitable potentials. Under a few simplifying hypotheses we exploit scaling laws for the thickness of the brush [1] to estimate the molar mass of the grafted polymer that is required to preserve the dispersion of the filler.
Then we present the results of a computer simulation of the behavior of the filled compound that includes a simplified mixing process and we compare the simulated filler structures with those observed in real systems.

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OC 16

OSMOLYTE EFFECTS ON THE INTERNAL STRUCTURE OF A THERMORESPONSIVE POLYMER BRUSH

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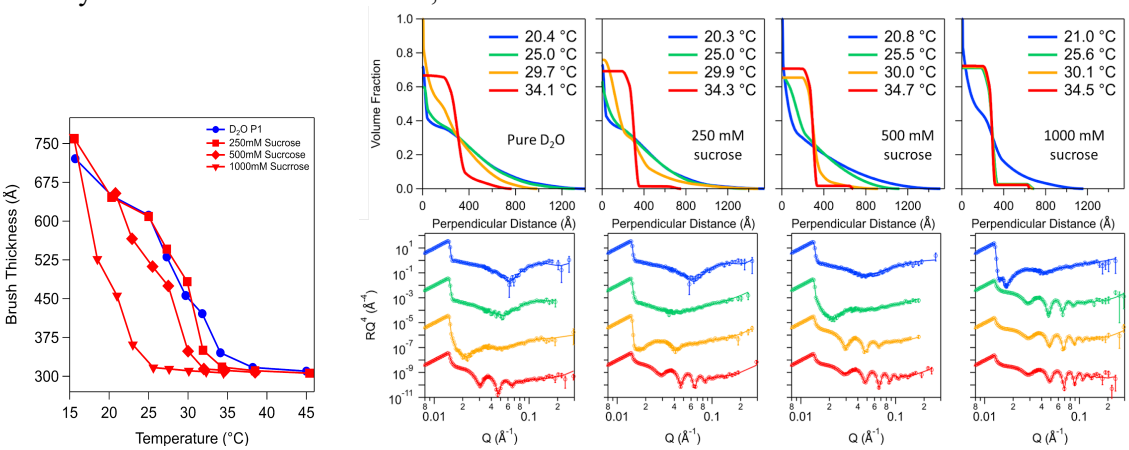
While it is well known that sugars play an important role in biological systems, they also act as osmolytes. For example, sucrose, a common disaccharide comprised of a glucose and fructose sub-unit, can destabilise bio- and synthetic macromolecules through osmolyte-type behaviour at elevated concentrations.[1] Despite the ubiquity of these molecules, there is a lack in mechanistic and structural studies of these systems. Exploring these mechanisms is crucial for understanding complex biological systems and may lead to an exploitation of the osmolyte effect for therapeutic purposes.[2] To understand the osmolyte properties of sugars, synthetic polymers can be employed to understand the driving forces that give rise to their effects in comparatively simpler systems. One such polymer is Poly(*N*-isopropylacrylamide) (PNIPAM), a well-know thermoresponsive polymer that undergoes a temperature induced phase transition at its lower critical solution temperature. PNIPAM brushes are excellent model systems due to their well-defined swollen-to-collapsed transition allowing the internal structure and conformation of the brush to be examined in both good and poor solvent conditions.[3, 4]
We examined the influence of mono- and disaccharides on the temperature induced transition of a PNIPAM brush using neutron reflectometry. The use of neutrons to interrogate these systems enabled subtle variation in the brushes internal structure to be elucidated, therefore, highlighting variations directly related to molecular volume, conformation and concentration.



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OC 17

HOW DO TOPOLOGY VARIATIONS AFFECT HYDRATION OF GRAFTED POLYMER BRUSHES?

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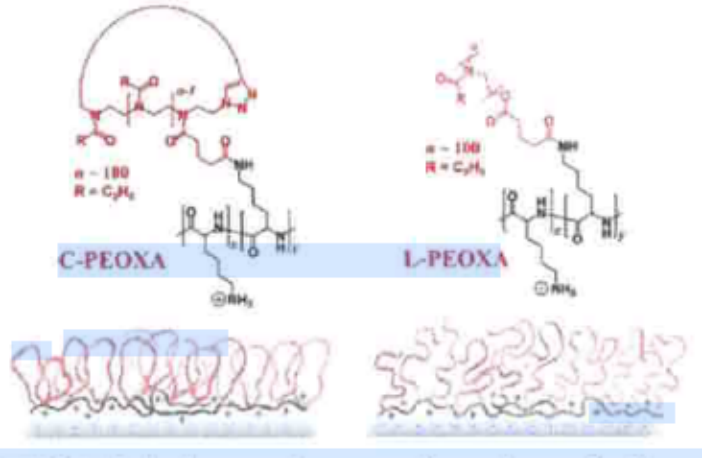
Abstract

Polyrner brushes have demoristrated growing interest during last years, in particular in combination with exposure to aqueous environment. By utilizing tirne-of-flight neutron reflectornetry (ToF-NR), we correlate the swelling properties of hydrophilic cyclic grafted polymer brushes to their therrnodynarnics. Cyclic poly(2-ethyl-2-oxazoline) (C-P EOXA) brushes exhibit more compact conformations with lower roughness compared to their linear analogues (L-PEOXA, Scheme 1 [1]), due to the absence of dangling chain ends. In addition, due to increased interchain steric repulsions, cyclic brushes feature larger swelling ratios at the same composition and comparable molar mass. Moreover. the two topologies exhibit differences in ageing, upon repetitive swelling/drying cycles. We present a case where current Flory-like expressions breakdown in the explanation ofthe experimental observations.



Scheme 1. C-PEOXA and L-PEOXA brushes obtained from the assembly of the corresponding rafi copolymers on Ti02 substrates, adapted fron3 [1].

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OC 18

POLYMER BRUSH COLLAPSE UNDER SHEAR FLOW

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Abstract

Shear is observed in many natural and technological systems, affecting their structure, dynamics, function and performance. Entangled polymers exhibit unique flow behaviours, as relaxation processes occur on time scales relevant to our daily lives, from milliseconds to hours or even days. Investigating the relation between out-of-equilibrium microscopic structure and dynamics of fluids and their macroscopic rheological response can enhance our understanding of viscoelastic flow, leading to improved material properties and applications.
This study combines neutron reflectometry (NR), rheology, and computer simulations to characterize the behaviour of polystyrene (PS) brushes under shear by an entangled PS semi-dilute solution. Two brushes with different chain lengths and grafting densities were used. NR reveals similar shear effects on both brushes restricted to the overlap region, causing a decrease in brush thickness and a sharper brush-bulk interface. In addition, the brush thickness returns to equilibrium upon cessation of shear, and the effect can be cycled many times over. The collapse of the brush occurs regardless of the type of brush used, indicating that the dynamics governing the structural change are determined by the free chains in solution rather than the brush itself. Coarse-grained computer simulations of the interfaces were in agreement with the experimental data. This research shows the feasibility of engineering shear-responsive polymer brushes in entangled polymer solutions, with potential applications in nanosensors and dynamic surface friction and adhesion control.
We are currently developing a new cell to measure rheology, NR, and polarized IR spectroscopy simultaneously. This will allow us to access the structure of the brush both perpendicular (NR) and parallel (IR) to the interface. We will present the current state and the initial results obtained with this new set-up.

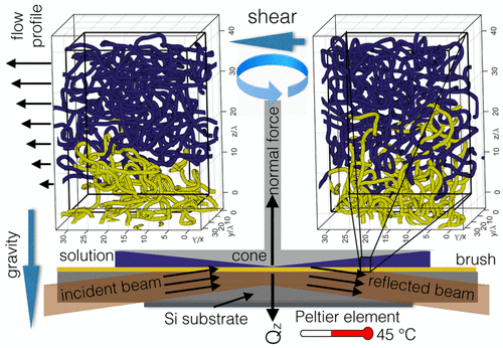

Figure 1. Experimental setup of the rheo-NR experiments and simulated polymer conformations at rest (right) and under shear (left). The application of shear pull out the free chains from the brush decreasing its thickness.

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OC 19

FUNTIONAL POLYMER BRUSHES SYNTHESIZED VIA DIRECT POLYMERIZATION OR POST-POLYMERIZATION MODIFICATION

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Abstract

Surface coatings derived from polymer brushes have unique properties allowing control over the interaction between material and environment. Till now, various synthetic routes are introduced for incorporating target functionalities into polymer brush thin films, including direct polymerization of functionalized monomers, or post-polymerization modification of reactive polymer brushes in cases when the direct polymerization is impossible due to incompatibility of the polymerization system with the desired functional groups.

In this contribution, we focus on three types of functional surface coatings: i) highly antifouling polymer brushes based on fluorine containing acryl- and methacrylamides, ii) polymer brushes containing reactive terminal triple bond in the polymer side chains, and iii) polymer brushes bearing fluorescent side groups [1]. For the fluorine and triple bond containing brushes two synthetic strategies were applied: i) direct surface initiated controlled radical polymerization (SI-ATRP and SI-RAFT) of monomers containing the appropriate functionalities, or ii) post-polymerization modification of synthesized via SI-ATRP polymer brushes containing active ester side groups. The fluorescent polymer brushes were obtained via different post-polymerization strategies, i.e. amidation of active ester containing parent polymer brushes and Huisgen type "click" modification of polymer brushes bearing azide reactive groups in the side chains. All polymerizations were performed on Si and glass flat surfaces, modified with a self-assembled monolayer of the corresponding ATRP initiator or RAFT chain-transfer agent. Two different brush types were gained in order to demonstrate the potential of the strategies for designing complex polymer architectures – homopolymer brushes bearing functional groups along the whole length of the polymer chain, and hierarchical polymer brushes with the functional groups concentrated on the shorter second block. The physico-chemical properties of all surfaces were detailly studied by spectroscopic ellipsometry (SE), infrared reflection-absorption (IRRAS) and X-ray photoelectron (XPS) spectroscopies. Fluorescent microscopy performed over the polymer brushes bearing fluorescent groups confirmed the homogenous character of the modified films.

Aknowledgment
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OC 20

COMBINED REACTIVE GRAND CANONICAL MONTE CARLO AND SELF-CONSISTENT MEAN-FIELD INVESTIGATION OF MONODISPERSE AND BIDISPERSE POLYMER BRUSHES

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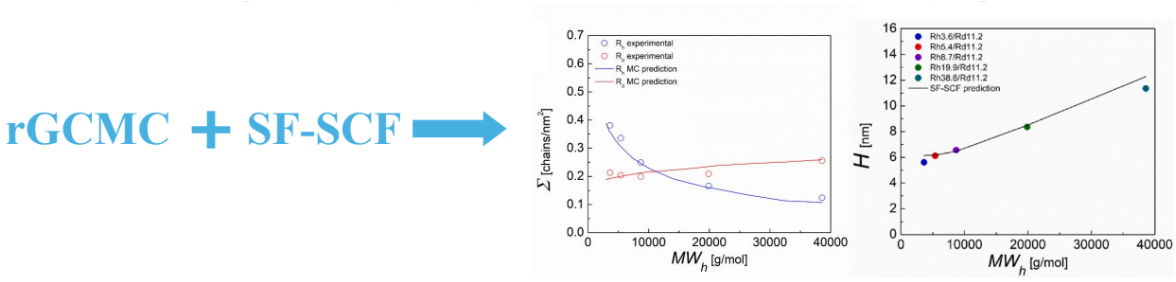
Abstract

Reactive Grand Canonical Monte Carlo (rGCMC) and Scheutjens–Fleer Self-Consistent Field (SF-SCF) techniques [1] has been used to draw topological maps of the grafted interface layer between a solid flat substrate and the polymer melt phase in contact with it. Model parameters are preliminary obtained from non-linear regression of experimental data of grafting density and brush height of monodisperse brushes. Afterwards, these parameters are able to fully predict morphological features of bidisperse brushes such as grafting density, brush thickness and surface roughness. Model predictions are satisfactorily compared with experimental data (retrieved from [2, 3]) of partly deuterated hydroxyl terminated poly(styrene d8-st-methyl methacrylate) and a hydroxy terminated poly(styrene-st-methyl methacrylate) copolymers blends thermally grafted to a silicon wafer. In this way, it was possible to better elucidate the mechanisms of the preferential grafting of "short" chains during the grafting to process.



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OC 21

POLYELECTROLYTE BRUSHES OF GRADIENT COPOLYMERS OF CHARGED AND NEUTRAL MONOMERS: INSIGHTS FROM COARSE-GRAINED MOLECULAR DYNAMICS SIMULATIONS

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Abstract

Polyelectrolyte brushes are intrinsically responsive to a variety of external stimuli ranging from salt concentration, counterion type, or pH, which provides these coatings with a unique responsiveness that can be applied in various applications. We studied polyelectrolyte brushes that have a gradual change in composition along the polymer backbone with coarse-grained molecular dynamics simulations. These charged chains consist of neutral monomers at the immobilized end and charged monomers at the free end. We exposed these brushes to an external electric field with different field strengths and observed their response to this stimulus. [1] These brushes stretch or collapse under influence of such external fields by increasingly deforming more and more chains from their equilibrium configuration. Such deformations provide control over the height and local composition of the brush. To reach a complete transition, the predominant variable of interest is the number of charged moieties that are present in the coating. Additionally, we find that the absorption of small, neutral particles in these gradient brushes can be modulated through this deformation if such particles absorb under unperturbed conditions. [2] We envision that this field-induced response will enable new electrically-driven separation technologies.

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OC 22

STRUCTURE FORMATION OF NANOPARTICLES ON A POLYMER BRUSH: EFFECT OF POLYMER-NANOPARTICLE INTERACTION

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Abstract

The prospect of composite materials based on a polymer brush and nanoparticles (NPs) depends on the precise spatial arrangement of NPs within the brush. Therefore, understanding the insertion mechanism and controlling the distribution of NPs in the brush is crucial for optimal applications of nanocomposite materials. We approach this problem by performing extensive molecular dynamics simulations of the brush-NP system. The brush is described by a weakly semiflexible bead-spring model and NPs are considered as hard spheres of diameter 7σ, where σ is the bead size. As the attraction between polymers and NPs is weak, NPs tend to spread and form a monolayer on the brush surface. The thickness of such a layer is about the size of a NP. As the interaction strength is increased beyond a threshold value, NPs start to penetrate into the brush. Our findings indicate that the assembly of NPs in or on a brush can be precisely controlled by tuning the strength of attraction between polymers and NPs.

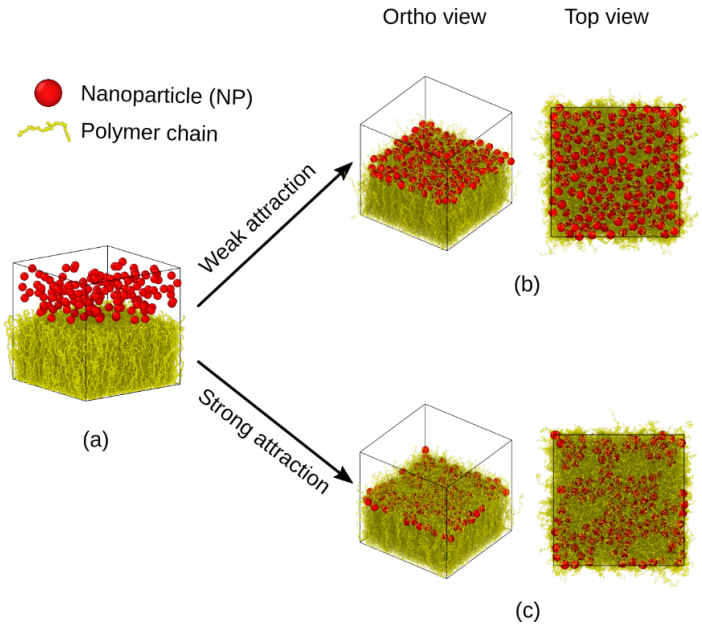

Figure: (a) Initial configuration of brush/NP composite, where the brush consists of polymer chains (yellow beads) end tethered to an impermeable surface, while the NPs are represented by red spheres with a diameter 7σ. Initially, the NPs are randomly distributed above the brush surface. As the attraction between the polymer and NPs is turned on, the equilibrium structure varies. With weak attraction (b), the NPs localize on top of the brush, forming a nearly ordered layer with a width approximately equal to the diameter of a NP. In contrast, with strong attraction (c), the NPs penetrate the brush and form aggregates. The grafting density of the polymer brush is $0.245\sigma^{-2}$, and polymer chains contain 80 beads with a bead size of σ.

OC 23

DYNAMICS OF DROPLET MOTILITY ON HYDROPHOBIC POLYMER BRUSH SURFACES FACILITATED BY VAPOR INTERACTION

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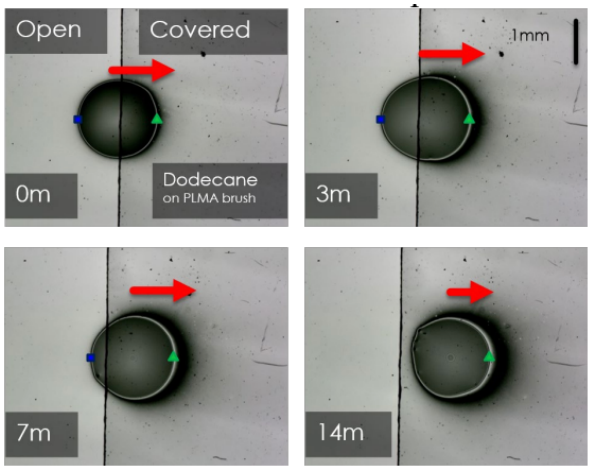
Abstract

Polymeric foams play indispensable roles in industrial applications because of their superior Polymer brushes swell fully in good solvents, and partially when subjected to a good vapor. The spreading of volatile liquids on brush layers is governed by subtle combination of hydrodynamic flow, vapor transport and swelling kinetics. We studied the wetting dynamics of alkanes on oleophilic polymer brush layers of poly- lauryl-methacrylate (PLMA), synthesised via surface initiated activators regenerated by electron transfer atom transfer radical polymerization (SI-ARGET-ATRP). A rich phenomenology is observed including the formation of a wide halo, characterized by a gradient in degree of swelling of the brush layer ahead of the slowly advancing contact line[1]. Local evaporation and condensation conspire to stabilize the inhomogeneous nonequilibrium stationary swelling profiles.

Significantly, when a gradient in vapor concentration above an alkane droplet is imposed, macroscopic movement may be induced without exerting external forces. We acquire both spatial and time-dependent swelling profiles in the halo region as well as droplet contact angles from interferometry measurements. We find the advancing contact angle to be lower than the receding contact angle, contrary to typical moving droplets. We believe the vapor concentration imposes in a gradient in local swelling close to the contact line, corresponding with a gradient in equilibrium contact angle gradient. As a result, the droplet experiences a pulling force in the direction of the lower contact angle, causing movement. Additionally, the contact angle seems to exhibit notable viscous drag along the contact line. Utilizing the acquired contact angles, we calculate the total horizontal component force and relate this to the droplet movement.



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OC 24

IMPACT OF SUBSTRATE NATURE ON THE *GRAFTING TO* PROCESS

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Abstract

Interfacial reactions between end-functionalized polymers and suitable substrates are generally defined as *grafting to* reactions and are commonly employed to cover inorganic surfaces with chemically anchored uniform polymer brushes with high thickness control and reproducibility. Since the *grafting to* process is a self-limiting reaction and the grafting density (Σ) is proportional to $M_n^{-0.5}$, with M_n being the average molecular weight of the polymer, the *grafting to* reactions can be exploited to deliver controlled amounts of dopant atoms into silicon substrates. Recent research has focused on elucidating the reaction mechanism on SiO_2 substrates[1] and gaining insight into the polymeric brush composition in terms of molecular weight partitioning[2]. Despite evidence demonstrating the significant role of surface nature in determining brush formation[3], a thorough investigation into its impact on the *grating to* process is still needed. Depending on the treatment employed to activate the silicon wafer surface for the *grafting to* reaction, different functional groups are exposed – specifically, silanols (Si-OH) groups of a native silicon oxide surface or silicon hydride (Si-H) groups of a deglazed silicon surface. Both types of functional groups can be exploited for reaction with the hydroxy group of the grafting polymer, resulting in distinct grafting reaction mechanisms.
In this context, three hydroxy-terminated homopolymers – $PS_{3.9}OH$, $PS_{13.9}OH$, and a partially deuterated $PSd8_{4.8}OH$, – as well as a binary blend consisting of $PS_{13.9}OH$ and $PSd8_{4.8}OH$, were grafted onto deglazed and non-deglazed silicon wafer from a melt at different temperatures. Initial insights into the influence of substrate nature on the *grafting to* process were derived from the characterization of the brush thickness and its composition through ellipsometry and TGA-GC-MS analysis.

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OC 25

WELL-DEFINED POLY(2-ISOPROPENYL-2-OXAZOLINE) BRUSHES PROVIDE ENHANCED BIOCOMPATIBILITY AND VERSATILITY IN SURFACE FUNCTIONALIZATION

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Abstract

Poly(2-isopropenyl-2-oxazoline) (PIPOx), a bio-compatible polymer[1] amenable to clean and orthogonal post-polymerization modifications, has recently emerged as a suitable candidate for the preparation of functional polymer brushes via surface-initiated reversible-deactivation rad-ical polymerization (SI RDRP). However, the field currently lacks a universal SI RDRP method that would provide a straightforward control over the PIPOx brush thickness and be applicable to non-planar surfaces. Herein, we designed an aqueous, metallic copper-mediated RDRP (Cu(0)-RDRP) protocol for SI grafting of IPOx that manifests an excellent degree of temporal control over the PIPOx brush thick-ness up to more than 100 nm. The superior kinetic control was achieved through the use of an all-chlorine initiation/catalytic Cu(0)-RDRP system and careful ligand selection, demon-strating a clear advantage over previous ap-proaches based on brominated initiators.[2] Additionally, we found that using neat water as a reaction medium for the Cu(0) catalyst gen-eration in the standard disproportionation step significantly accelerates the brush growth. Im-portantly, a surface plasmon resonance analysis demonstrated for the first time the high re-sistance of PIPOx brushes against non-specific protein fouling, as documented by a significant (96 %) decrease in protein deposition from un-diluted blood plasma and negligible adsorption from fetal bovine serum and other protein solu-tions. Finally, we showcased in model scenarios the versatility of the prepared well-defined PIPOx brushes by modifying them with suita-ble functional carboxylic acids under mild con-ditions in order to subsequently synthesize graft copolymer brushes or trigger a CuAAC click reaction. Our results highlight PIPOx brushes as an attractive platform for the fabri-cation of low-fouling, multifunctional surfaces.

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OC 26

SMART LEACHING OF ESSENTIAL OILS FROM MESOPOROUS SILICA PARTICLES

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Abstract

Microbial colonisation of surfaces forms a dangerous reservoir for pathogens contributing to the spread of infections which can cause significant cost to human life and the economy at large. There is a tangible need for innovative antimicrobial coatings that are highly effective, safe, self-disinfecting and removing bacteria, fungi and viruses more cost-effectively than current non-biodegradable, toxic, and fossil fuel-based coatings in use. RELIANCE project aims to design and develop smart response self-disinfectant antimicrobial nanocoatings based on a new range of smart antimicrobial nanoparticles [1].
These particles consist of mesoporous silica particles (MSP) modified with biobased bioactive compounds as carvacrol or eugenol, which are essential oils (EOs) coming from non-edible plants. To achieve better control of the EOs release, the MSP surface is modified with stimuli- responsive polymer brushes, which are organic molecules that exhibit different polymer chain conformation upon external stimulation as temperature (T) and pH [2]. Poly(2-(ethyl amino)ethyl methacrylate) polymer (PDEAME) is selected for the functionalization as it responses to both pH and T. These brushes are grown from MSP via surface-initiated atom transfer radical polymerization (SI-ATRP), which is one of the most effective methods to synthetise polymer brushes on particles surfaces [3]. The PDEAME brushed onto MSPs are characterized by Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), which give information about the polymerization performed. In addition, elemental analysis is also carried out to confirm not only the presence, but also quantify the amount of nitrogen (N) in the product since the selected monomer (DEAME) has N element in its structure.
Regarding the release of the EOs, pH and T responsive behaviour of PDEAME brushes grafted on MSP is investigated to ensure the control leaching of the EOs into the environment to fulfil the main objective of the RELIANCE project.

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Acknowledgment

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OC 27

Molecular weight distribution effect in silicon doping by *grafting to* reaction of phosphate end-capped polymers

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Abstract

The precise control of the position and amount of dopant atoms placed in silicon substrates, generally defined as precision doping, is one of the cornerstones of the downscaling of microelectronic devices so well described by the famous Moore's law. Recently, an innovative approach based on the *grafting to* reaction of phosphate end-capped polymers was exploited in a precision doping perspective[1]. In fact, due to the self-limiting nature of *grafting to* reactions from melt, the maximum number of polymer chains included in the obtained brush (i.e. the grafting density, Σ) and consequently the number of deposited dopant-phosphorus atoms are forced by the law $\Sigma \sim M_n^{-0.5}$, with M_n being the average molecular weight of the polymer[2].
Unfortunately, the assumption that the M_n in the brush is equal to the M_n of the polymer before grafting was recently challenged for hydroxy end-capped polymers by the intrinsically disperse nature of synthetic polymers[3] even prepared by controlled ARGET ATRP reaction. In details, shortest chains result preferentially grafted on to the substrate thus lowering the M_n of the polymer in the brush. This effect, when transferred onto the doping process, clearly reduces the control efficiency.
To shed light on this issue, in this contribution the effect of the molecular weight distribution was evaluated for binary blends of phosphate end-capped polystyrene and polystyrene-d_8 samples with different molecular weight grafted on silicon oxide at different temperatures for different time periods. The brush composition was then evaluated by TGA-GC-MS analyses. Preferential grafting of short chains was confirmed as for hydroxy end-capped polymers but some relevant differences were also observed especially corresponding to the lowest temperatures and shortest grafting times.

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OC 28

CORRELATING HEXADECANE'S TEMPERATURE-DEPENDENT WETTING TRANSITION ON PODMA BRUSHES WITH AFM-DERIVED MICROSCOPIC INSIGHTS

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Abstract

Stimulus-responsive polymer brushes exhibit a remarkable ability to adapt and transform their properties, structure, and morphology in response to specific external triggers (Temperature, pH, mechanical stress. In this work, we study the wetting behaviour of oil on hydrophobic temperature-responsive poly(octadecyl methacrylate) (PODMA) brushes below and above the bulk melting temperature (29ºC). Upon depositing a hexadecane droplet on top of PODMA brushes at ambient temperature, a distinctive high contact angle (31º) prevents the droplet from spreading on the surface. However, above the melting temperature, a first temperature range characterized by brush swelling without spreading is observed, followed by a second temperature range characterized by a transition from partial to complete wetting, leading to the need for further investigation. Our aim is to explain these phenomena from both a microscopic (Atomic Force Microscopy (AFM) Force Volume) and macroscopic (Video imaging) interpretation. The AFM Force-Volume technique was employed to assess the nanoscale mechanical properties of PODMA brushes below and above its melting temperature. At room temperature, standard force-distance curves representative of a stiff surface were captured. Above the bulk melting temperature, a two-stage transition through gradual alterations in the shapes of the force-distance curves and a progressive increase in energy dissipation was observed. The hard-sample behaviour observed at room temperature aligns with the emergence of crystalline domains in the structure, correlated with poly(alkyl-methacrylates) featuring side chains extending beyond 12 carbons [1]. The two-stage melting transition was correlated to the bulk melting (Tb) and the surface melting (Ts). Above the bulk melting temperature, it is known that linear hydrocarbon chains ($16 < n < 50$) exhibit surface freezing: an ordered crystalline layer is formed on top of a liquid bulk with a higher melting temperature (Ts) than the bulk (Tb) [2]. The bulk melting (Tb) was identified at 34°C, marked by distinctive tails in force-distance curves indicative of heightened energy dissipation sporadically observed across the surface. The melting of the surface was identified at 37°C, as an extended tail and a huge increase in energy dissipation uniformly manifested across the entire surface, indicating the melting of the surface (Ts). Our measurements suggest that the macroscopic wetting transitions can be explained by the microscopically measured melting transitions. In the first transition (swelling without spreading), the polymer bulk melts, while a crystalline top layer allows for surface pinning. During the second transition (partial to complete wetting), surface melting occurs. The interface becomes more flexible, allowing the contact line to overcome pinning points. The discrepancy between micro- and macroscopically measured transition temperatures may be explained by the effect of solvent-induced melting depression. To quantify this effect, we will reproduce AFM force volume measurements on hexadecane-infused brushes.

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POSTER CONTRIBUTIONS

P1

SYNTHESIS OF PDEGMA BRUSHES WITH TEMPERATURE-SENSITIVE FUNCTIONAL END GROUPS ON IMPLANT SURFACES USING THE INTERFACE-MEDIATED PET-RAFT POLYMERIZATION TECHNIQUE

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Abstract

The development process of controlled/living radical polymerization techniques that enable successful surface applications continues [1]. In general, with the development of Atom Transfer Radical Polymerization (ATRP) , techniques such as ARGET-ATRP, SARA-ATRP, e-ATRP have been developed using different components. Like the ATRP technique, the development of Reversible Addition Fragmentation Chain Transfer Radical Polymerization (RAFT) and the use of appropriate components according to the application area continues today. Especially with the development of RAFT polymerization, interface-mediated Photoinduced Electron/Energy Transfer-Reversible Addition-Fragmentation Transfer (PET-RAFT) polymerization, which is tolerant to oxygen, creates less chemical pollution in bio-application studies, and allows synthesis at room temperature, offers many advantages [2]. .
Poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) brushes have been synthesized in the literature by surface-initiated ATRP, ARGET-ATRP, interface mediated -RAFT and PET-RAFT polymerization [3-5]. However, the synthesis and detailed kinetic analysis of temperature-sensitive PDEGMA brushes with functional end groups on implant surfaces have been little studied. In this study, PDEGMA brushes were synthesized on model implant surfaces by PET-RAFT polymerization. In the characterization of PDEGMA brushes; ATR-FTIR and XPS techniques were used for chemical analysis. The chemical composition of the surface was determined by water contact angle measurements, the morphological analysis of polymer brushes growing on the surface was determined by AFM technique, and the change in the thickness of polymer brushes over time was determined by ellipsometer.

Acknowledgments
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P2

SOLVENT EFFECTS ON THE SI-RAFT POLYMERIZATION *N*-(2-HYDROXYPROPYL) METHACRYLAMIDE

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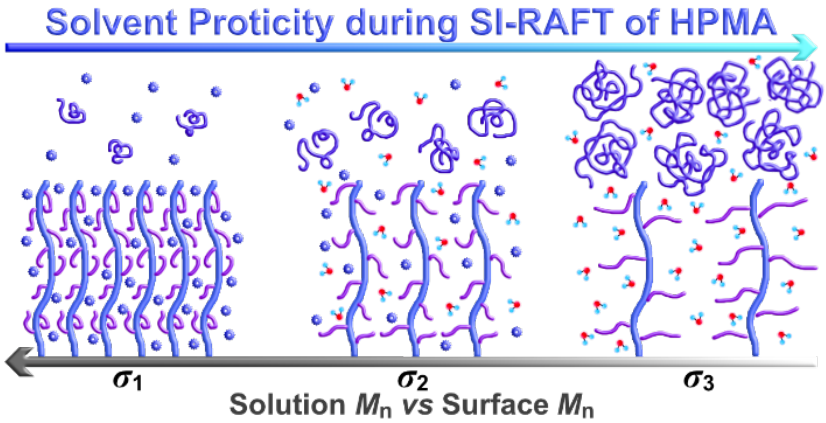
Abstract

Brushes of poly[*N*-(2-hydroxypropyl) methacrylamide] (poly(HPMA)) are of great interest for biomedical applications owing to their outstanding antifouling properties.[1] During their preparation via surface-initiated reversible addition–fragmentation chain-transfer (SI-RAFT) polymerization, the polymer growth proceeds concurrently from the surface and in the solution, but the polymerization kinetics of both processes may differ. To understand this discrepancy and its effect on the properties of the obtained polymer brushes, we study the solvent effects during the polymerization of HPMA, investigating the macromolecular parameters of polymers formed on the surface and in the solution. Changing the solvent proticity and polarity influences the solution propagation rate, leading to mass transfer limitations in the surface polymerization and a concomitant discrepancy in the molar masses of the polymer formed in solution and grafted from the surface. Importantly, the solvent effects directly determine the grafting density of surface-grafted poly(HPMA) by altering the conformation of the growing chains. These results highlight how decisive solvent effects are on the SI-RAFT polymerization of HPMA and that they may be key to regulate the physical and macromolecular parameters of the obtained surface-grafted poly(HPMA) brushes

Acknowledgement: This work was supported by the Czech Science Foundation (project no. 22-27329S)



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P3

STRUCTURE FORMATION IN POLYMER BRUSH/GOLD NANOPARTICLE COMPOSITE MATERIALS

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Abstract

Metal/polymer nanocomposites are versatile hybrid materials and find use in many fields such as photonics, biomedical engineering and catalysis. A promising realization of this type of hybrid material is the controlled self-assembly of gold nanoparticles inside the polymer brush, which induces color changes upon exposure to environmental changes enabling sensor applications. Therefore, we aim for gaining insights and control over the structure formation process leading to more elaborate nanocomposite fabrication.
The polymer brushes in our model system serve as a matrix for the immobilization of gold nanoparticles (AuNPs). Uptake of AuNPs into the brush matrix is affected by the brush thickness and the grafting density. The system makes use of various salts as a stimulus for the self-assembly of citrate-capped gold nanoparticles in a polymer brush[1].
Aggregation behavior of the AuNPs under salt influence is monitored by UV/Vis spectroscopy. Results indicate a dependence on the type of ion, according to the Hofmeister series (Fig. 1). The utilized polymer brushes are synthesized by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP). To determine the grafting density of the polymer brush, film thicknesses are measured and cleavage of the polymer brush at the initiator molecule is used to investigate the molecular weight distribution of the polymer brush.

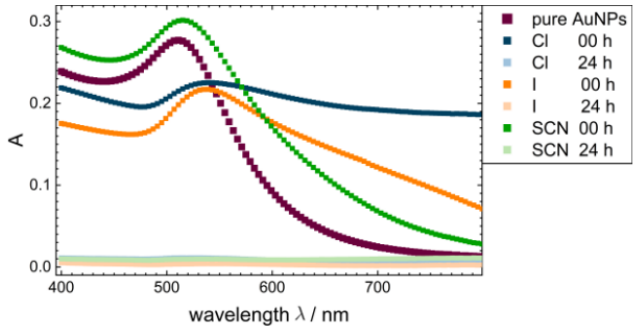

Figure 1. Absorption spectra of 5 nm AuNP suspensions, pure and mixed with 100 mM sodium salt solutions along the Hofmeister series (NaCl, NaI, NaSCN). The spectra were taken immediately after mixing and 24 h later.

Acknowledgements
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P4

SYNTHESIS AND ELECTROMECHANICAL PROPERTIES OF POLYSILOXANES MODIFIED WITH DIFFERENT CONTENTS OF SULFONYL SIDE GROUPS FOR DIELECTRIC ELASTOMER ACTUATORS

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Abstract

In the current scientific landscape, considerable endeavors are dedicated to enabling robots to mimic human behavior. Conventional robots have heavily relied on rigid and challenging-to-process materials. However, recognizing the inherent softness of mammals, researchers are shifting their focus toward using soft materials. Among the promising choices for this application are dielectric elastomer actuators (DEAs), known for their soft, stimuli-responsive nature and compliance, enabling substantial deformations. These actuators are manufactured by sandwiching an elastomer between compliant electrodes. The main factors deter-mining their properties are dielectric permittivity, elastic moduli, and dielectric film thickness [1]. So far, polysiloxanes are one of the most applied dielectrics in DEAs. They have a backbone of altering oxygen and silicon atoms with two side groups. Polysiloxanes exhibit elasticity over a broad temperature range due to the low glass transition temperature (Tg) down to -120 °C [2].
As a side group on silicon, the vinyl group enables the addition of polar groups, enhancing dielectric permittivity. In this study, poly(methylvinyl)siloxane was synthesized and modified with different contents of sulfonyl and butyl groups through a thiolene-addition re-action. The polymers were characterized by NMR, DSC, TGA, and GPC. Additionally, they were cross-linked to free-standing films using pentaerythritol tetrakis(3-mercapto propionate) cross-linker. All films are characterized by DSC, TGA, DMA, UTM, and Impedance Spectroscopy and exhibit a Tg below room temperature. The materials demonstrating the most favorable elastic properties were employed in constructing DEAs.

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P5

MODIFICATION OF SUBSTRATES WITH FUNCTIONAL POLYMERS VIA PHOTO INDUCED ATRP

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Abstract

Development in sustainable chemistry, including the field of polymer synthesis, involves also light induced chemical reactions and/or the decrease of the amounts of inorganic catalyst employed[1,2]. Recent ecological and economical advances include atom transfer radical polymerizations (ATRP) that can be light-induced, involving enhanced oxygen tolerance and employing ppm amounts of the catalyst [2,3]. Regarding surface modifications, it is possible to minimize the reaction medium volumes in the microliter scale leading to grafted polymer brushes with thickness more than 100 nm [3].
In the present work, the benefits of the previous advances are focused on poly(2-oxazolines), a class of biocompatible polymers with tunable properties ranging from hydrophilic to hydrophobic. For biomedical applications, they are considered an alternative to poly(ethylene glycol), which however undergoes oxidation[4]. Specifically, poly(2-isopropenyl-2-oxazoline) (PIPOx), which can be obtained by radical polymerizations[4], is grafted from silicon wafers via photo induced surface-initiated ATRP. It was possible to obtain polymer brush layer with controlled thickness up to ~90 nm. The conditions were needed to be optimized due to slowing the polymerization, as the pedant groups trap the copper salt. It was found that a more active ligand, namely tris[2-(dimethyl amino)ethyl]amine (Me_6TREN) is sufficiently effective. From the various organic solvents that were employed, dimethyl sulfoxide (DMSO) was proved to be the most convenient one. Moreover, the substrates exhibited antifouling properties even for thin brush layers of around 14 nm, while PIPOx modified n-type silicon wafers showed also enhanced heavy metal trapping properties.

Acknowledgments
The authors thank grant agencies for financial support through projects VEGA 2/0137/23 and APVV-19-0338.

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P6

PROOF OF POLYMERIC CONCEPT BASED ON *IN VIVO* EVALUATION OF MALEIC ACID MODIFIED CHITOSAN

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Abstract

The aim was to develop a polymer conjugate named chitosan-maleic acid (CS-MA) with enhanced mucoadhesiveness and activityagainst *Escherichia coli*. Therefore, chitosan (CS) and maleic acid (MA) were conjugated via formation of amide bond. Characterization via proton nuclear magnetic resonance and infrared spectroscopy was carried out and attached maleic acid groups were quantified by free amino groups assay [1]. Biocompatibility of the conjugate was assessed following resazurin assay on fibroblasts, membrane damage on human erythrocytes and Hen's Egg-Chorioallantoic membrane tests. Polymers were characterized in terms of swelling behavior, pH, hardness, *in vitro* drug release and disintegration. To test mucoadhesive properties of CS-MA polymer, rheometer, rotating cylinder, inclined plane, and texture analyzer were the instruments utilized. Furthermore, antibacterial efficacy of the conjugate was established by direct agar diffusion method and *in vivo* test was carried out to determine tolerability of the modified polymer. Results exhibited successful synthesis of the biomaterial, maintaining the great biocompatibility of native chitosan even though a 68.81% of modification was achieved. Additionally, mucoadhesive studies showed improved properties of CS-MA compared to native polymer, with 2.42-fold, 4-fold, 3.42-fold and 4.05-fold increase in dynamic viscosity, retention time, overall attachment work and peak force of detachment, respectively. Finally, antibacterial activity was enhanced in 1.77-fold and *in vivo* experiments showed no irritation and good tolerability of CS-MA polymeric conjugate. In conclusion, CS-MA effectively developed exhibiting promising features capable of revolutionizing the polymeric field.

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P7

SYNTHESIS OF HYDROPHILIC-*b*-HYDROPHOBIC DIBLOCK COPOLYMER BRUSHES FOR SWITCHING THE WETTING BEHAVIOUR

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Abstract

We present synthesis of hydrophilic-b-hydrophobic diblock copolymer brushes by surface initiated atomic transfer radical polymerization [1]. Novel is that the hydrophobic copolymer is synthesized from the hydrophilic copolymer block. The aim is to obtain a low energy surfaces being water-repellent with contact angles >90° [2]. Correspondingly, the hydrophilic block attracts water. For such a diblock copolymer brush architecture, we expect molecular rearrangements and stimuli responsive wetting effects upon being brought in contact with water.
We prepared poly(2-hydroxyethyl methacrylate) (PHEMA) as a hydrophilic block from the silanized silicon substrate and we graft polystyrene (PS) or Poly(1-hexyl methacrylate) (PEHMA) as hydrophobic block on top of the PHEMA block. The synthesis of the hydrophobic copolymers are performed in toluene as well as in a mixture of toluene and dimethyl sulfoxide. The layered structure of the hydrophilic-b-hydrophobic deblock copolymer brushes is confirmed by XPS-depth profiling measurements. We tune the wetting properties by variation of the molecular weights of the associated copolymer blocks. In particular, the surface switch from hydrophobic to hydrophilic upon contact with a water droplet. The latter switching depends on the temperature and the contact time with the water droplet. We investigate details of the change of the copolymer architecture on macroscopic and molecular level by dynamic water contact angle measurements and nano-infrared scanning force microscopy. The synthesized hydrophilic-b-hydrophobic diblock copolymer brushes is a toolbox for exploring and controlling dynamic wetting phenomena, which are present for sliding drops [3].

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P8

POLYMER BRUSH-SUPPORTED PHOTOCATALYSTS IN CONTINOUS FLOW REACTOR

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Abstract

Large-scale photochemical synthesis under mild conditions represents an optimal approach for green chemical production. However, scalable photocatalytic processes have been scarcely reported mainly due to the loss of irradiation efficiency caused by the solvent media and the complexities associated with the recovery and recyclability of the photocatalyst.
Here we present the integration of polymer brush-supported photoredox catalysis in a continuous flow reactor using visible light at room temperature. The co-polymerization of the photocatalyst with a water-soluble monomer offers the potential for conducting photoredox reactions in an aqueous environment. The system involves a thermally activated delayed fluorescence (TADF)-type photocatalyst incorporated as monomer within polymer brushes synthesized via surface-initiated atom transfer radical polymerization (SI-ATRP) from the inner walls of glass capillaries employed as a flow reactor. The primary objective is to ensure the reusability of the anchored photocatalyst and to compare the efficiency of the photochemical reaction in both batch and flow systems. To test the applicability of our system, two benchmark reactions were investigated: Giese decarboxylative addition was performed with dimethyl maleate and maleic acid to showcase the feasibility of photoredox reactions in organic and aqueous solvents, respectively.

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P9

SYNTHESIS AND CHARACTERIZATION OF POLYMER BRUSH BASED ON SiO_2-g-PEMA

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Abstract

Surface-confined macromolecules known as polymer brushes are being increasing applied to a variety of areas. As more information is gained on the molecular structure of polymer brushes and how they respond to environmental stimuli, these applications are becoming wider ranging and better defined.
One of the simple routes previously developed by Zongyu Wang et al.[1] to synthesize brushes with high molecular weight particles by surface-initiated atom transfer radical polymerization (SI-ATRP) from silica nanoparticles was applied.
The obtained SiO_2-g-PEMA (Sillicon dioxyd-grafted-polyethylmethacrylate) polymer brush was characterized by different techniques such as Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), Dynamic light scattering (DLS), Grafting density and Number-average molecular weights (Mn) and MWDs were determined and all obtained results are discussed in this communication.

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P10

Dispersity Within Brushes: A Key Parameter to Modulate Interfacial Properties

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Abstract

Dispersity has become a crucial tool for tuning the properties of polymers brushes, alongside molar mass, topology, and grafting density.1,2 Despite numerous reports on controlling dispersity of polymer backbones, the role of dispersity of side chains within graft polymers is still underexplored.3,4 Herein, we investigated the influence of side-chain dispersity of graft polymers constituted by a polymethacrylate backbone and oligomeric ethylene glycol (OEG) side chains (i.e., POEGMAs). These were generated from commercial OEGMA macromonomer mixtures (Mn ~500 Da) exhibiting a broad distribution of OEG lengths (2–15 OEG units), and from a discrete macromonomer (8 OEG units), isolated by flash chromatography. The brushes were prepared via atom transfer radical polymerization (ATRP) and their properties were thoroughly studied by variable angle spectroscopic ellipsometry (VASE), quartz crystal microbalance and dissipation (QCM-D), contact angle (CA), and atomic force microscopy (AFM) on flat macroscopic substrates and by dynamic light scattering (DLS) on gold nanoparticles. Uniform side-chain brushes exhibited higher hydration and lubricity, reduced adhesion, and provided better colloidal stability across temperature ramps. These findings present new possibilities for the development of technologically relevant biomaterials.

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P11

ELECTRIC FIELD-REGULATED PROTEIN ADSORPTION ON ANTIFOULING POLYMER BRUSHES

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Hunger has increased globally since the pandemic, affecting 735 million people in 2022. Furthermore, the challenge of meeting nutritional needs is growing formidable due to the adverse impact of extreme climate conditions on agricultural productivity. Meanwhile, affluent Western nations continue to squander approximately 30% of their food supply, with roughly 20% of these losses occurring during the industrial food processing stage. The efficient recovery of valuable nutrients, such as proteins and flavor molecules, from these industrial waste streams is hindered by the limitations of current separation technologies.

Presently, these technologies often rely on the extensive heating of feed streams or the use of copious solvents for capturing and subsequently releasing these nutrients on/from solid supports. Our objective is to establish a more sustainable adsorption and desorption process for proteins, utilizing precise regulation of protein uptake through the application of an electric field. However, the regulation of protein uptake faces challenges due to the irreversible binding of amino acids, leading to fouling of the electrodes.

To address this issue, we developed antifouling polymer brushes composed of zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (poly MPC) with thicknesses of up to 40nm. These brushes were synthesized using an innovative and optimized SI-ATRP procedure, with strong anchors to ensure the stability of the brush over time.

Subsequently, we investigated the adsorption and desorption behavior of Lysozyme (a positively charged protein) and Bovine serum albumin (a negatively charged protein) on these antifouling layers while applying an electric potential ranging from -0.3 to 0.4V on these surfaces, employing an electro quartz crystal microbalance (E-QCM). Our findings demonstrated that these electric fields have the capacity to effectively regulate the quantities of adsorbed proteins. As a result, this innovative approach shows great potential for improving the recovery of valuable nutrients from industrial waste streams, thereby contributing to the reduction of food waste.

P12

INFLUENCES OF DELAMINATIONS ON THE COMPRESSION STRENGTH OF COMPOSITE LAMINATIONS

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Introduction

Carbon fiber composites (CFC) have a wide rang of applications[1]. However,the laminated CFCs are sensitive to the external impacts, which always lead to the delaminations,resulting in sharp reduction of residual strength of the composite. At this work, the influences of delamination defects on the compressive strength of laminated CFCs are exhibited.

Material and Methods

Prepreg(MT700/802) was used for preparing the laminated CFCs, a 4mm×10mm sized delamination defects with different depths and locations are pre-embedded in the CFCs. Ultrasonic non-destructive test and compression test were in the accordance with GJB1038.1A-2004 and QJ1403-2004, respectively.

Results and Discussion

When the delamination defects were in the middle of the specimen, the ones possessed higher compression strength with the deeper delamination defects than those with shallower delamination counterparts. Likewise, there was the same trend with defects at the edge of the specimen. Quasi-isotropic laminates with defects pre-embedded in the 1/5,2/5,1/2 of the thickness are fabricated. Ultrasonic non-destructive tests in Fig 1,Fig 2,and Fig3 show that the pre-embedded defects have been got as expected.Table 1 shows the compression test results.

CFC laminaitions are sensitive to the defects, the edge effect had an important influence on the performance of composite[2]. When defects are on the surface or edges, the defects propagate easily, reducing the residual compressive strength of composites. This means that when the defects are at the same depth, the specimen with defect at the edge possess lower residual strength, at the same time, the defects at the same location , the shallower depth ones possess lower residual compression strength.

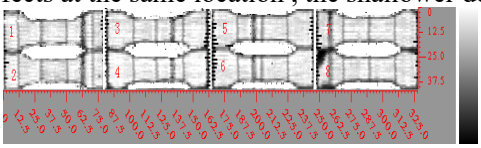

Fig 1 Specimen without defects

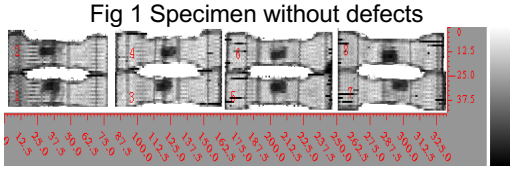

Fig2 Defect in the middle of Specimen

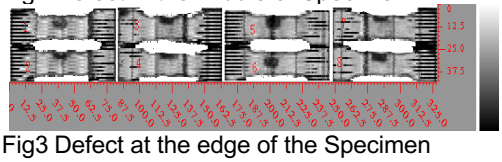

Fig3 Defect at the edge of the Specimen

Table1 The compression strength(unint:MPa) of specimen with different delamination defects

Delamination defect Depth	Location of the defect in the specimen		Specimen without defects
	Middle	Edge	
1/5 of the thickness	697	611	805
2/5 of the thickness	737	631	804
1/2 of the thickness	776	683	804

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P13

MOLECULAR DETERMINATION STUDIES OF FUNCTIONALIZED PFMA BRUSH PLATFORMS FOR MOLECULE DETERMINATION

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Studies on the unique architectures and functional properties of polymer brushes synthesized by controlled/living radical polymerization techniques (Atom Transfer Radical Polymerization Technique, Reversible Addition Fragmentation Chain Transfer Radical Polymerization, etc.) have been the focus of attention of researchers in recent years [1,2]. The use of functionalized polymeric brushes for molecular determination offers new and alternative possibilities. The RAFT agent, especially used in RAFT polymerization, enables the easy conjugation of new molecular structures by easily reducing the remaining part of the component in the tip region of the brushes to the thiol group [3,4]. It offers significant advantages when combined with the unique properties of polymeric brushes through the conjugation of new molecules and their use in molecule determination. In this study for GSH determination, PFMA brushes were synthesized using interface-mediated RAFT polymerization on silicon disc surfaces. After the synthesis of PFMA brushes, the 1,4-maleimidobutane molecule was covalently attached to the thiol-terminated PFMA brushes using hexylamine. Fluorescence-labeled glutathione was determined on PFMA brushes functionalized with maleimide. [5]. It is thought that the prepared polymer brush platforms will be a new and alternative detection method for many molecules.

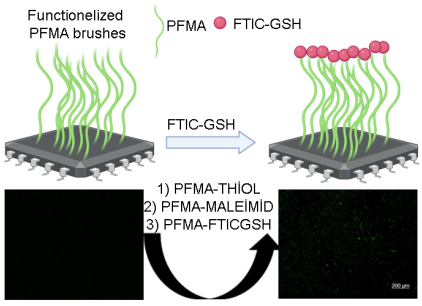

Figure 1. Use of functionalized PFMA brushes in model molecule determination [5]

Acknowledgments
Notes: This work is dedicated to the memory of Prof. Tuncer Caykara, who passed away on December 19, 2021.

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P14

HEMOGLOBIN-CATALYZED ATOM TRANSFER RADICAL POLYMERIZATION FOR SURFACE MODIFICATION OF WOUND DRESSING MATERIALS

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Abstract

Skin wound repair is a complex physiological process, which generally includes four phases: hemostasis, inflammation, proliferation, and remodeling[1]. Traditional wound dressings are prone to adhering to the wound which can promote the proliferation of microorganisms leading to a potential risk of secondary injury[2]. Cryogels, a class of hydrogels, represent a promising wound dressing material due to their interconnected porous structure, facilitating gas exchange and wound exudate absorption[3]. Herein, a cytocompatible hemoglobin- catalyzed surface-initiated atom transfer radical polymerization (SI-ATRP) was exploited for precisely tailor the antibacterial activity and hydrophilicity of wound dressings' surface. This method was initially tested on silicon substrates to define the monomer scope. Then, chitosan-based cryogels were constructed and functionalized with an ATRP initiator. These materials can serve as a scaffold to grow a variety of polymer brushes via SI-ATRP, to modulate the interfacial properties of the cryogels. Thus, zwitterionic or charged polymer brushes were grown from one side of the cryogel to achieve antimicrobial properties, while hydrophobic brushes were introduced on the opposite side, which could facilitate the removal of the dressing. In conclusion, a robust and cytocompatible method was developed to tailor the properties of wound dressing materials.

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P15

SUPERLUBRICITY BETWEEN POLYZWITTERIONIC BRUSHES-COVERED DISSIMILAR SURFACES IN AQUEOUS MEDIA

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Abstract

Polymer brushes, when swollen in good solvents, are known to have good lubricating properties. This is due to the long-range entropically originated repulsion between brushes, which acts to keep the surfaces apart and maintaining a relatively fluid layers at the interface between them [1]. In aqueous media, the low friction is enhanced by "hydration lubrication" of polyzwitterionic brushes, as the energy is dissipated through shearing hydration water of highly-hydrated monomers, which in fluid phase [2]. However, the two substrates to which polymer brushes are tethered, are similar in most studies to date. In the present study, poly[2- (methacryloyloxy)ethyl phosphorylcholine] (pMPC) brushes are "grafted from" two dissimilar substrates, mica and gold, using surface-initiated atom transfer radical polymerization. This allows the manipulation of gold surface potential using a three-electrode-modified surface force balance, enabling the reversible application of a transverse electric field (E-field) across the brushes. The pMPC-brush interactions showed a typical Alexander-de Gennes behavior in normal direction, whose range however varied with the E-field. When sliding under compression, very low sliding friction, down to $\mu \approx 0.003$, is seen when the two substrates bear similar surface potentials, where μ (=force to slide/load) is the coefficient of friction, but μ may be modulated reversibly by varying the gold potential. The origins of this potential-dependent behaviour are considered.

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AUTHOR INDEX

AUTHOR INDEX