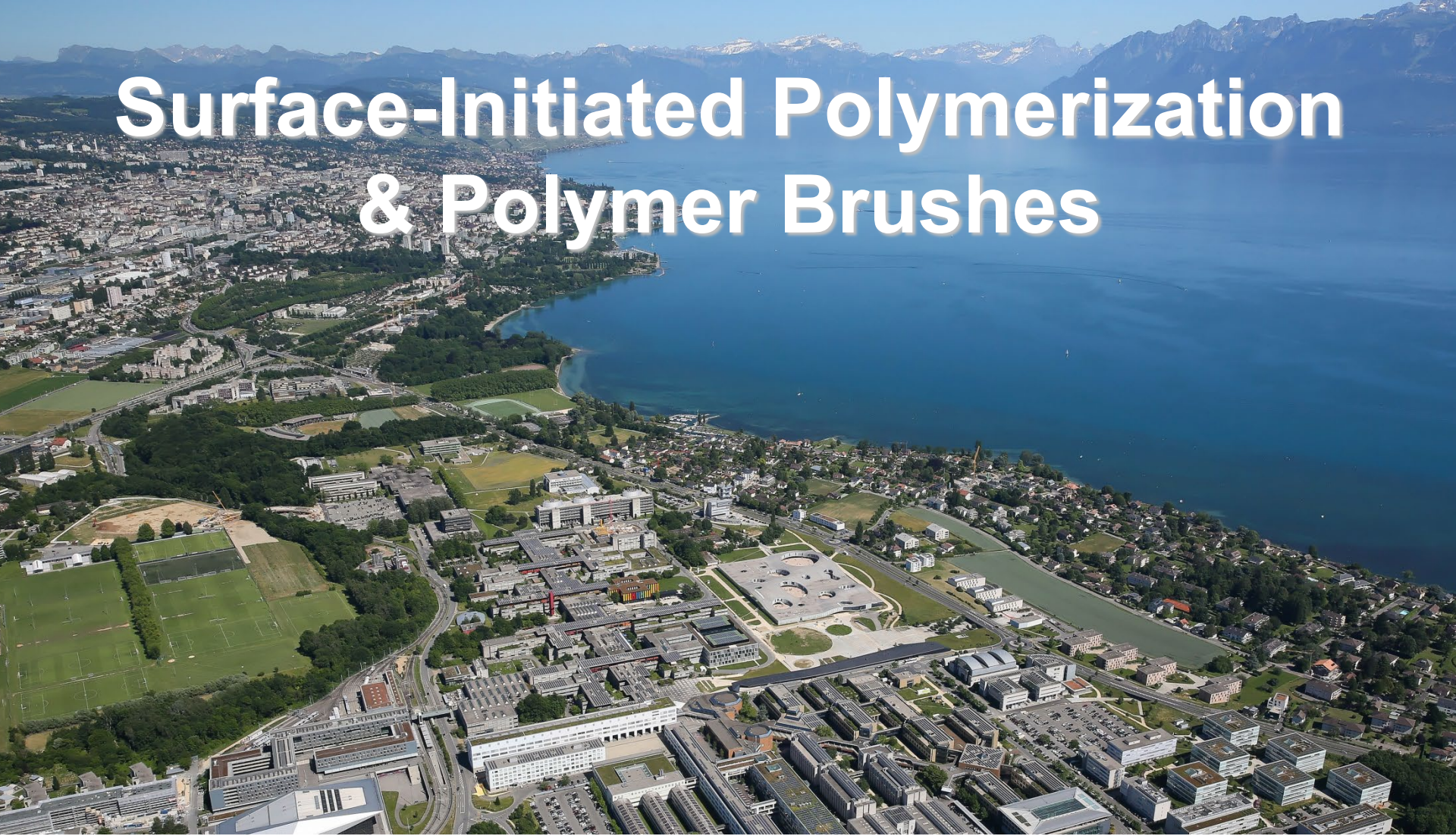


Surface-Initiated Polymerization & Polymer Brushes



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<https://lp.epfl.ch/>



EPFL

POLYMERS LABORATORY
LABORATOIRE DES POLYMÈRES

What is a polymer brush (and when is a brush a brush....)?

Making polymer brushes

Characterizing polymer brushes

What are polymer brushes good for ?

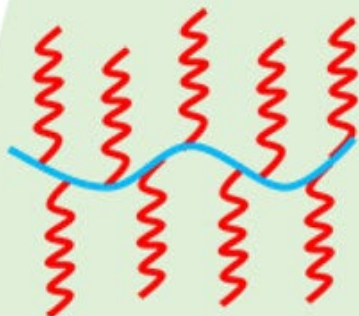
Brushes



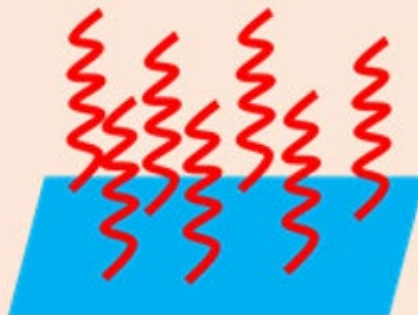
Molecular Brushes

Polymer Brushes

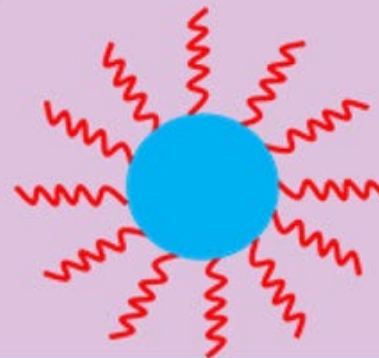
1-D



2-D



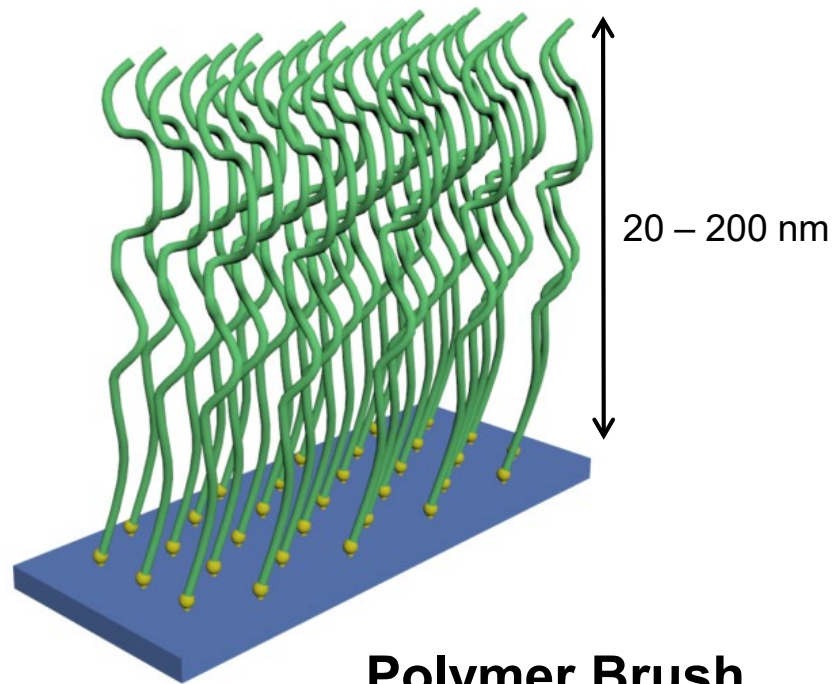
3-D



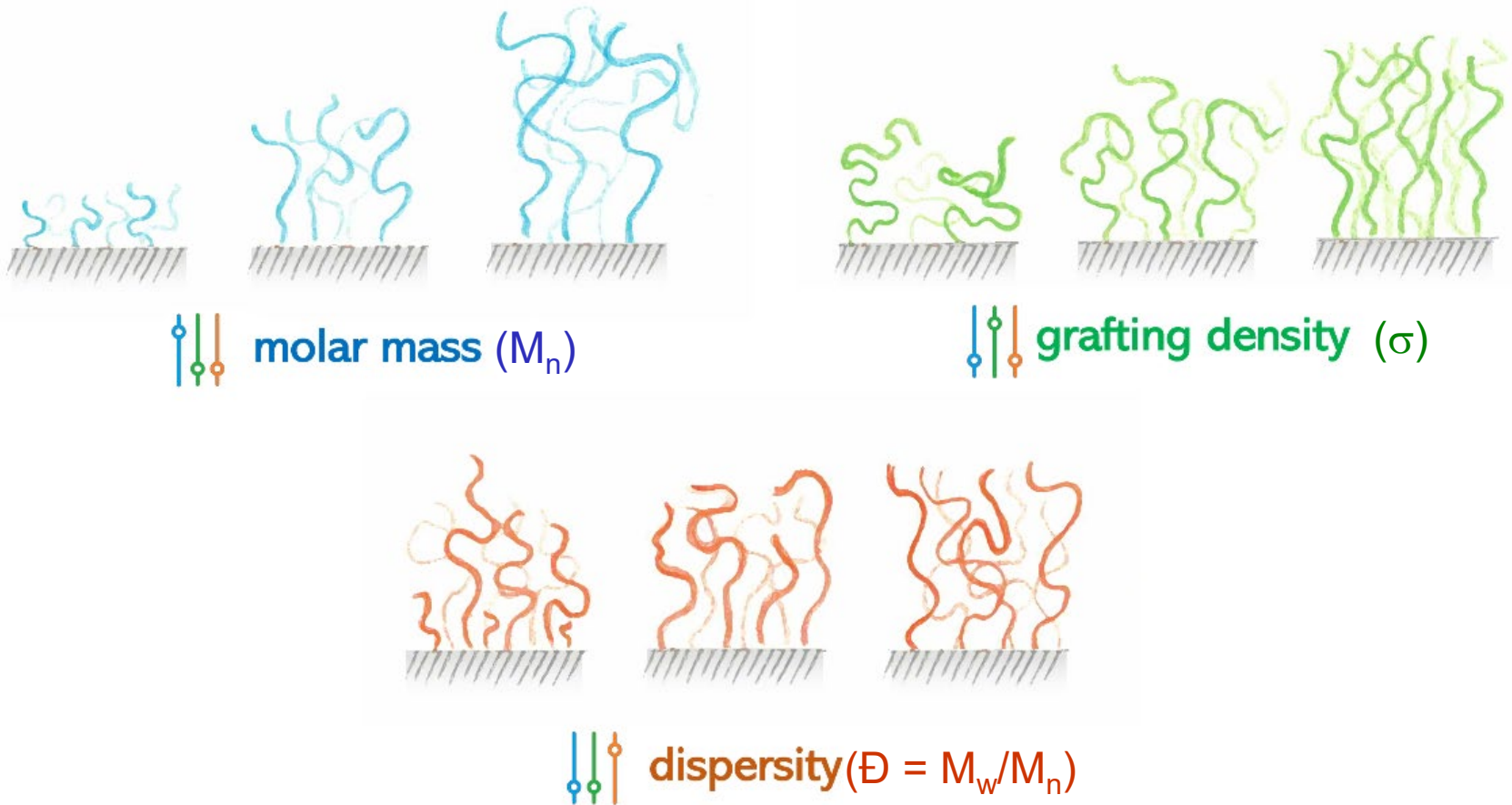
Efficient Synthesis and Application

What are Polymer Brushes ?

For this lecture and today, polymer brushes are assemblies of polymers that are tethered via one chain end to a solid (planar or spherical) substrate



Main Structural Parameters of Polymer Brushes



Note: molar mass and grafting density are directly related to the dry film thickness of a polymer brush:

- At a given grafting density, changing polymer molecular weight will result in a change in dry film thickness
- For a given polymer molecular weight, changing the grafting density will lead to a change in film thickness

When is a Brush a Brush ?

Grafting density
(nm^{-2}):

$$\sigma = \frac{h \rho N_A}{M_n}$$

h : dry film thickness of the brush
 ρ : polymer density
 N_A : Avogadro's constant
 M_n : number-average molecular weight of the polymer grafts

Reduced tethering density:

$$\Sigma = \sigma \pi R_g^2$$

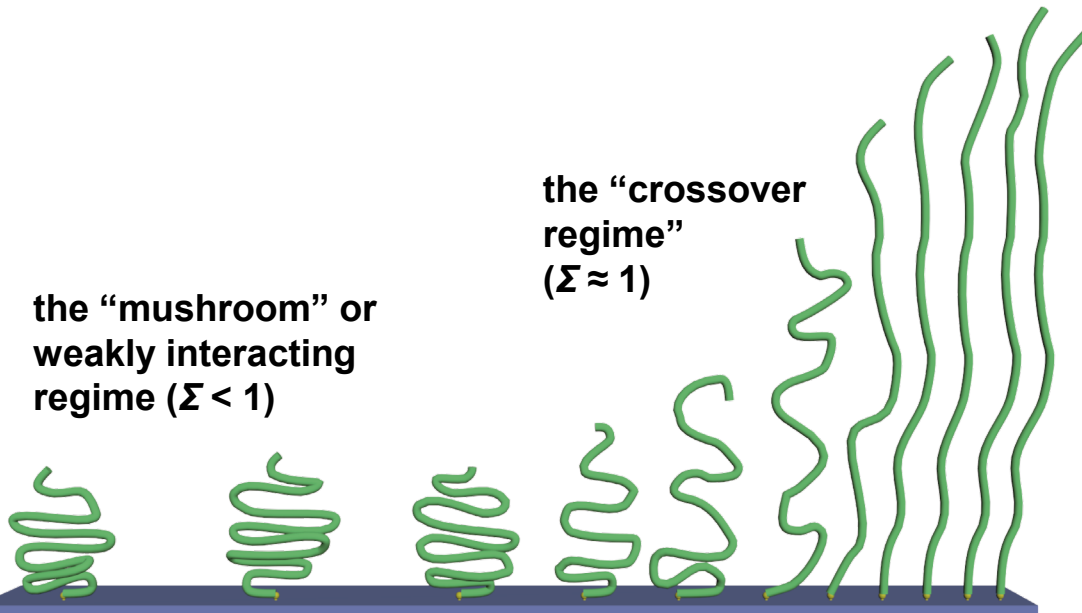
R_g : radius of gyration of a tethered chain at specific experimental conditions of solvent and temperature

Σ represents the number of chains that occupy the surface area covered by a single chain under ideal conditions

the highly stretched “brush regime” ($\Sigma \gg 1$)

the “crossover regime”
($\Sigma \approx 1$)

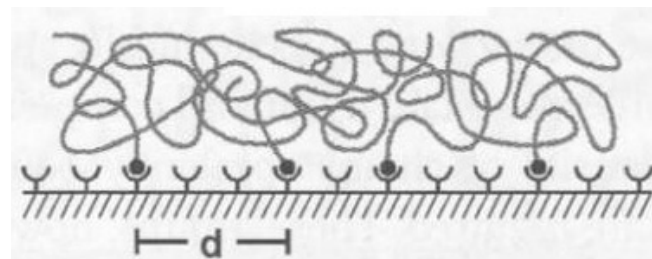
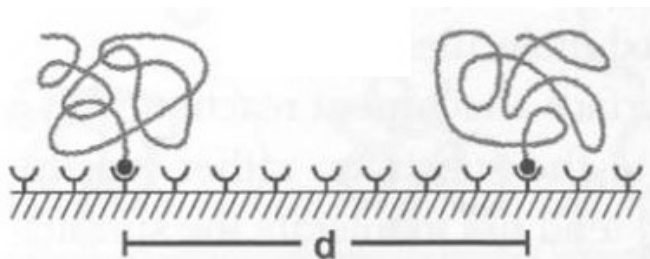
the “mushroom” or weakly interacting regime ($\Sigma < 1$)



Conformations of Chain-end Tethered Polymers

The conformation of surface-anchored polymer chains is determined by

- (i) The grafting density
- (ii) Polymer - substrate, polymer - polymer, and polymer - solvent interactions
- (iii) pH, temperature, ionic strength

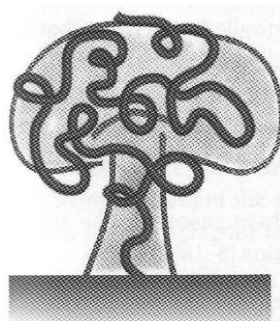


If the distance between two anchoring points is larger than the radius of gyration of the polymer chains, they act as single chains (no specific steric hindrance).



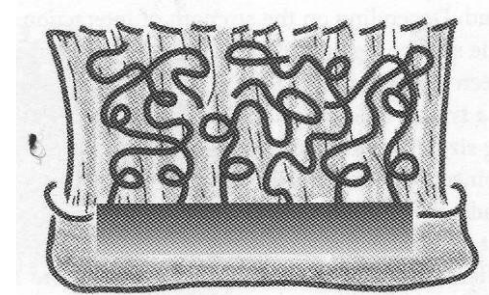
Pancake conformation

(strong interaction between the chains and the surface)



Mushroom conformation

(weak interaction between the chains and the surface)



Rühe, J. in: *Polymer Brushes* (Advincula, R. C., Brittain, W. J., Caster, K. C., Ruhe, J., Eds.) WILEY-VCH, Weinheim, 2004.

What is a polymer brush (and when is a brush a brush....)?

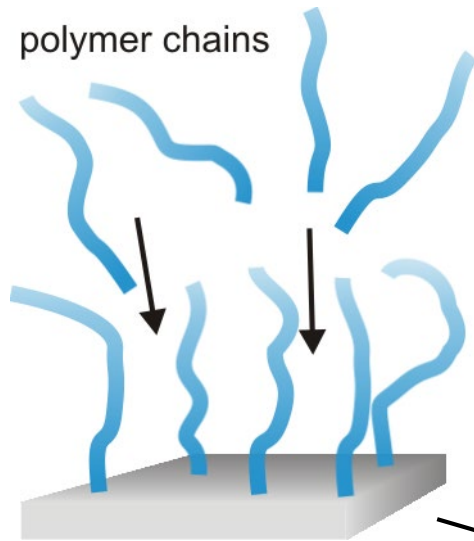
Making polymer brushes

Characterizing polymer brushes

What are polymer brushes good for ?

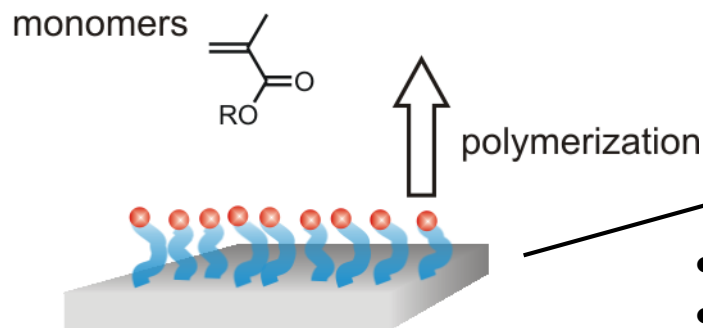
Polymer Brushes

Grafting onto:



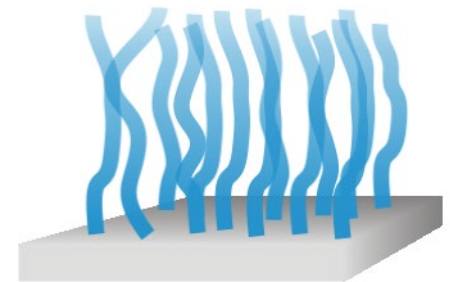
- Experimentally simple
- Limited grafting densities
- Limited film thicknesses

Grafting from:



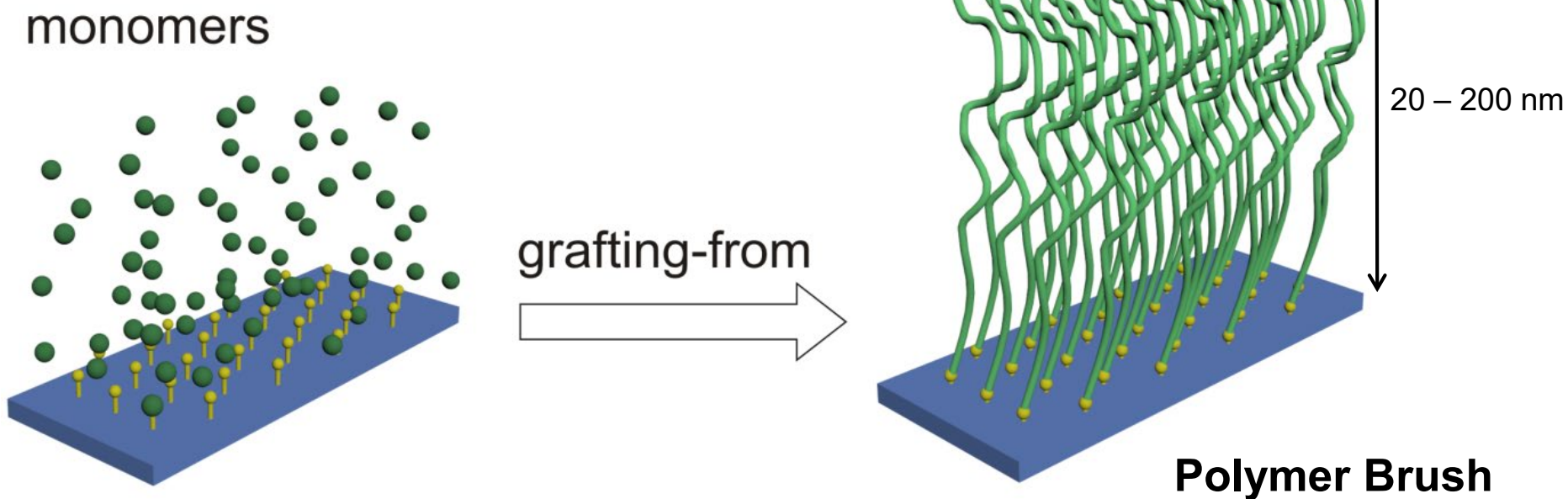
- Multistep protocol
- High grafting densities
- Control over film thickness and composition

polymer brush

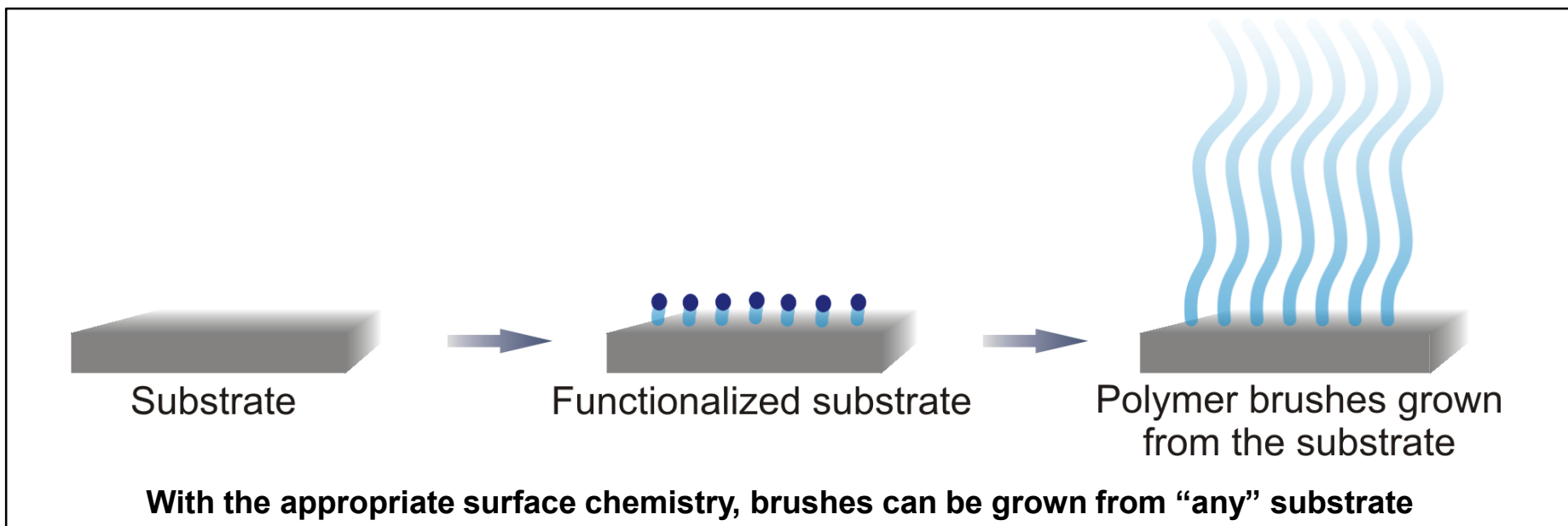


- High surface concentration of functional groups
- 3D substrates

Surface-Initiated Polymerization (SIP)



Surface-Initiated Polymerization (SIP)



Surface-initiated controlled / “living” polymerizations allow:

- High grafting densities (fast and quantitative initiation)
- Control over film thickness via polymerization time
- Access to a broad range of polymer brush architectures

Controlled / “living” radical polymerizations are the predominant technique:

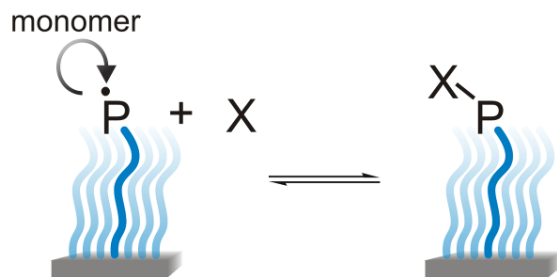
- Compatible with aqueous reaction media
- Broad monomer and functional group scope and tolerance

Surface-Initiated «Living» Polymerizations

Modern living free radical polymerization techniques are based on the use of special polymerization mediators, which **temporarily and reversibly** transform propagating radicals into dormant species.

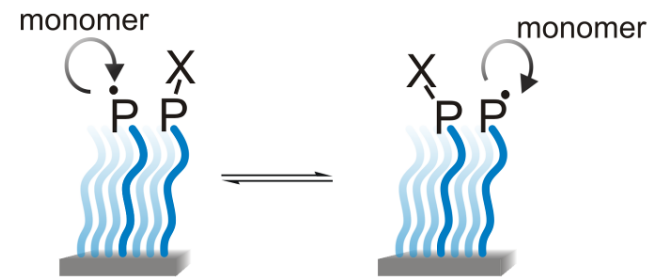
This reversible transformation is either accomplished by reversible deactivation or by reversible chain transfer.

Reversible deactivation



e.g. for SI-NMP or SI-ATRP

Reversible chain transfer



e.g. for SI-RAFT

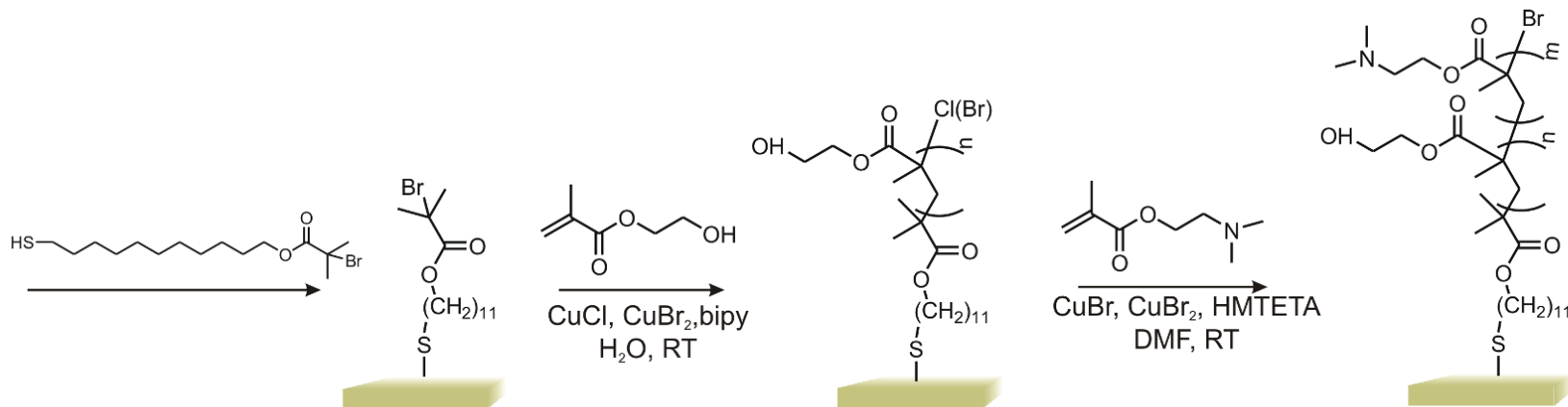
A fast transformation between dormant and propagating radical species ensures the **homogeneous growth** of the overall ensemble of polymer chains.

As a result living polymerizations are characterized by:

- a linear evolution of molecular weight with time (for low conversions).
- polydispersity values of typically 1.1.

Surface-Initiated ATRP

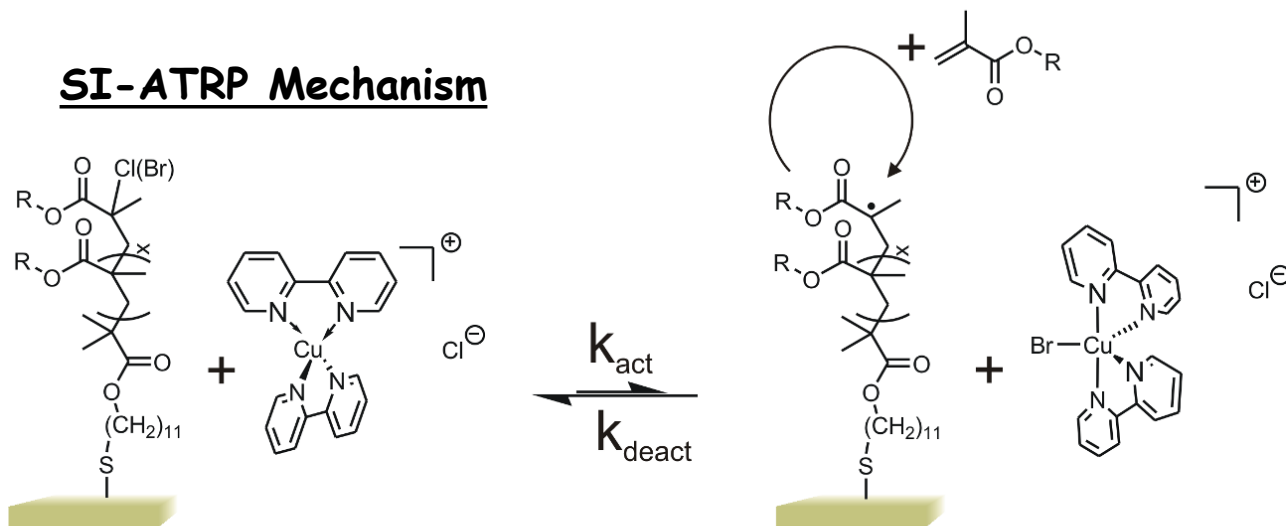
Atom transfer radical polymerization (ATRP)



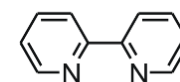
Au

Huang, W.; Kim, J.-B.; Bruening, M. L.; Baker, G. L. *Macromolecules* 2002, 35, 1175

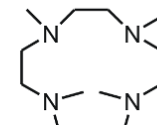
SI-ATRP Mechanism



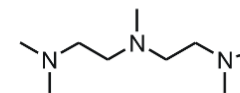
ATRP Ligands



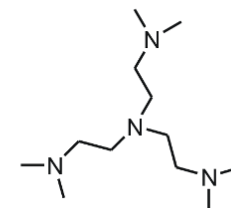
bpy



HMTETA



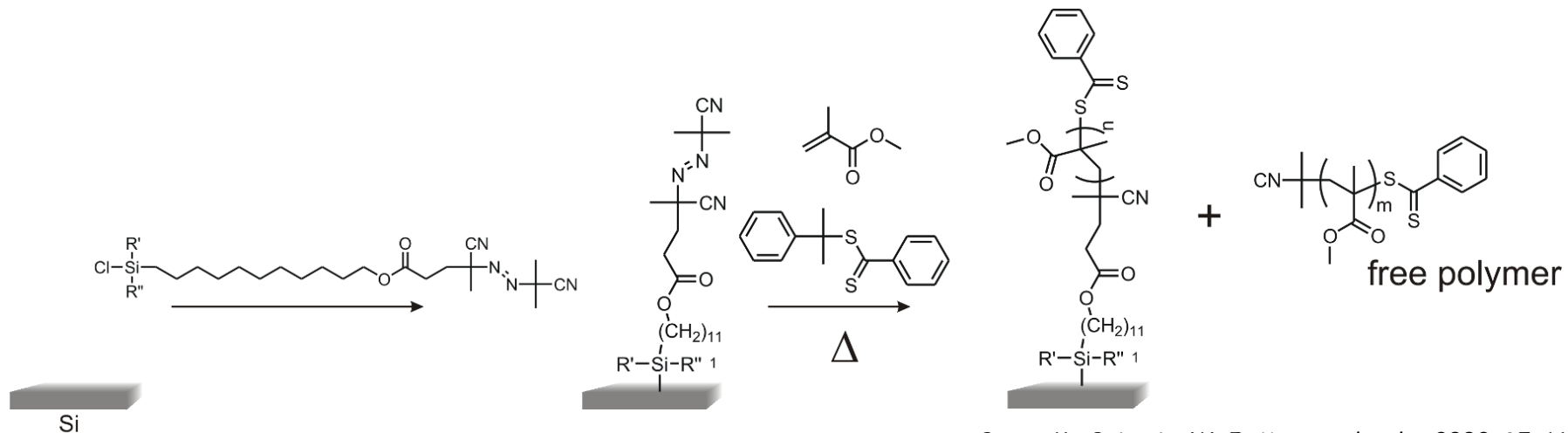
PMDETA



Me₆TREN

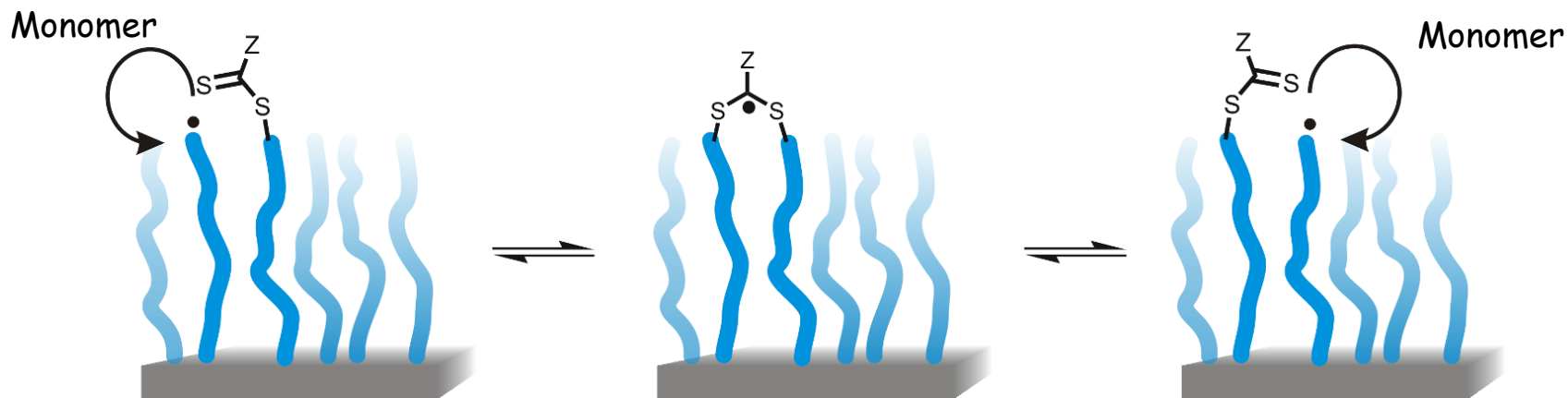
Surface-RAFT Polymerizations

Reversible addition-fragmentation chain transfer polymerization (RAFT)



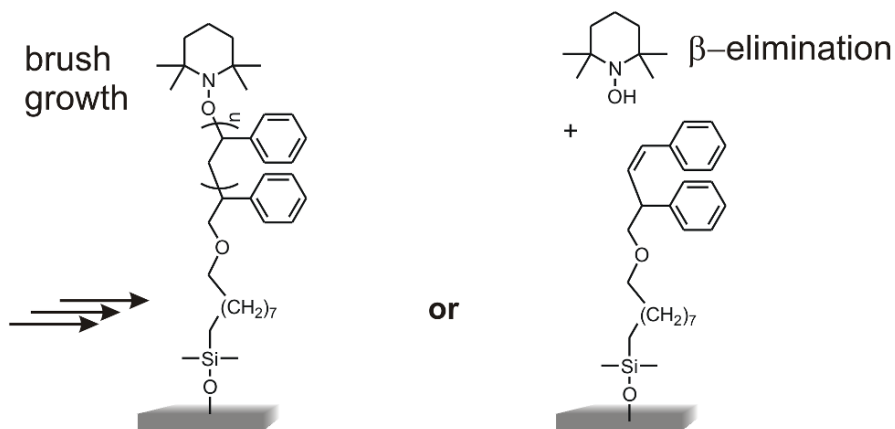
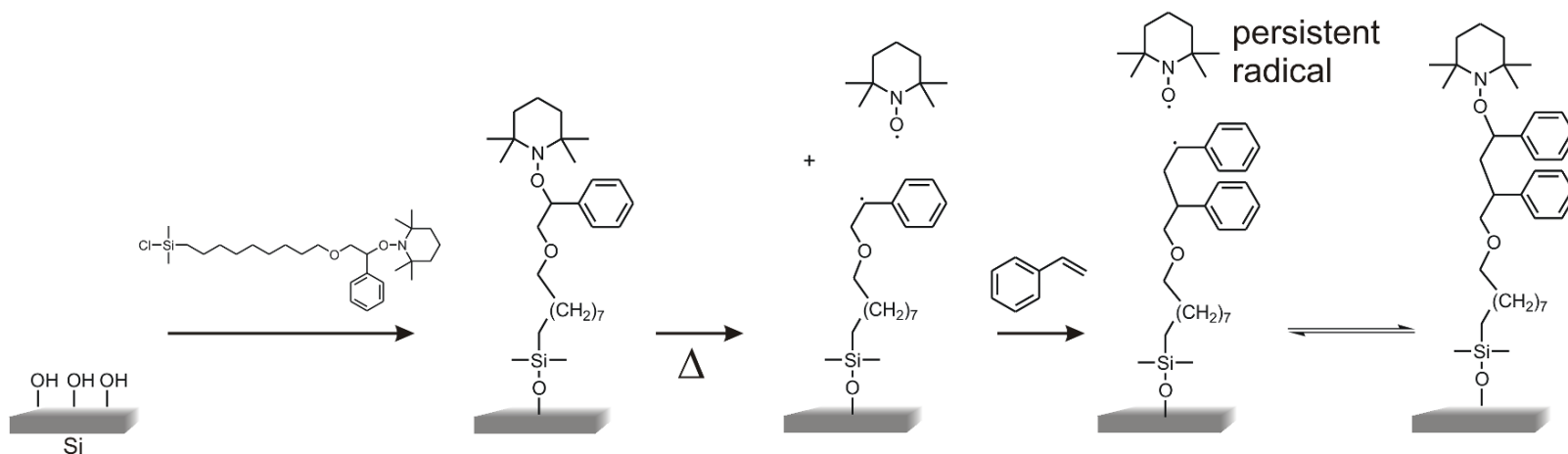
Baum, M.; Brittain, W. J. *Macromolecules* **2002**, *35*, 610

SI-RAFT Mechanism

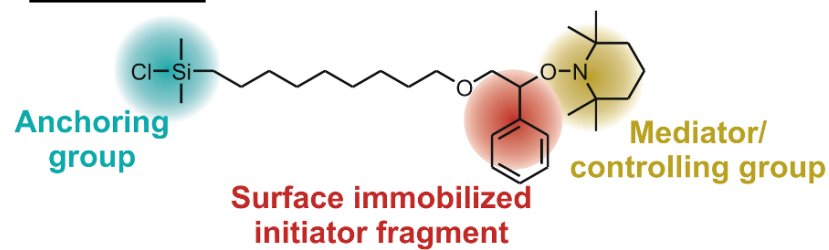


Surface-Initiated NMP

Nitroxide-mediated polymerization (NMP)

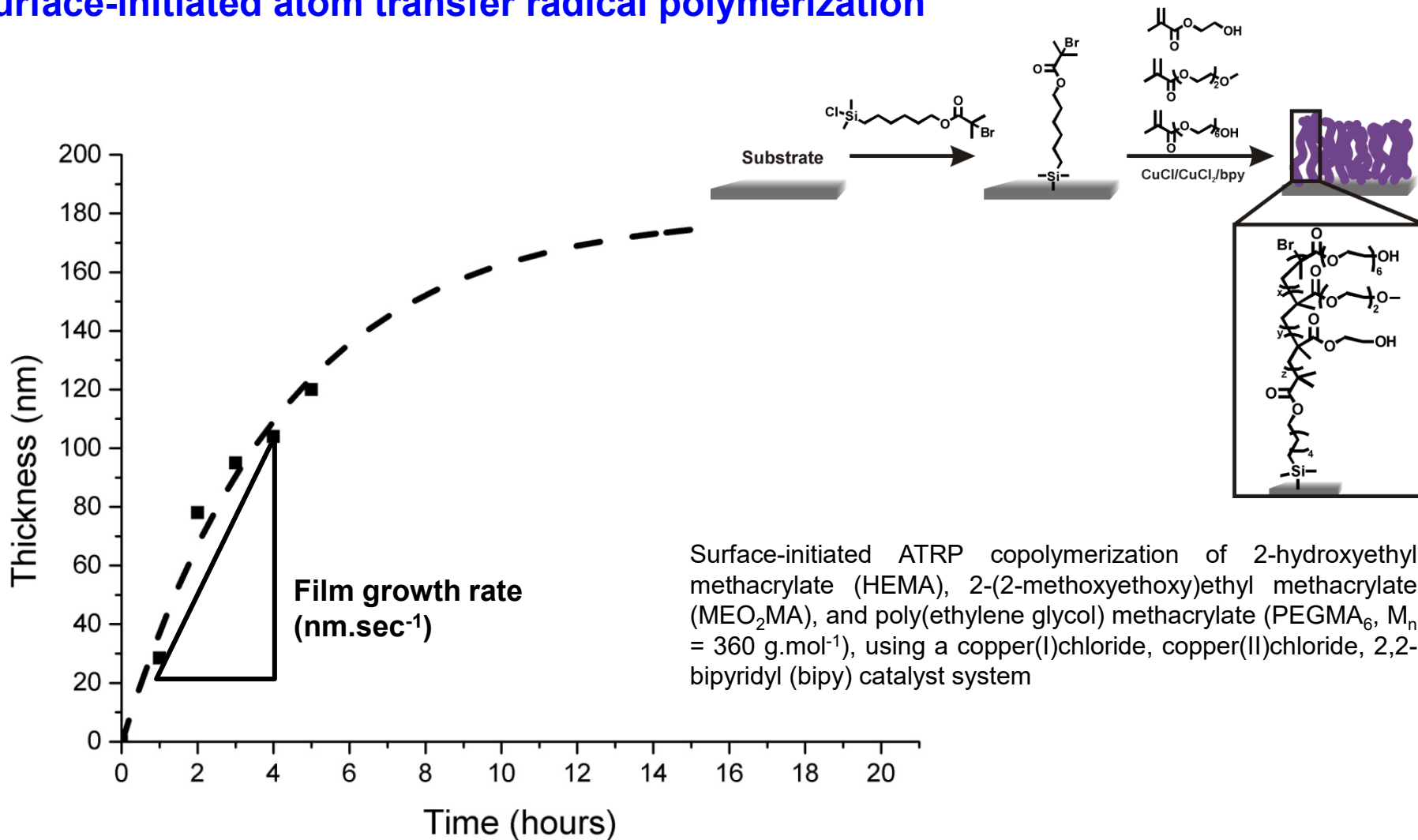


Initiator

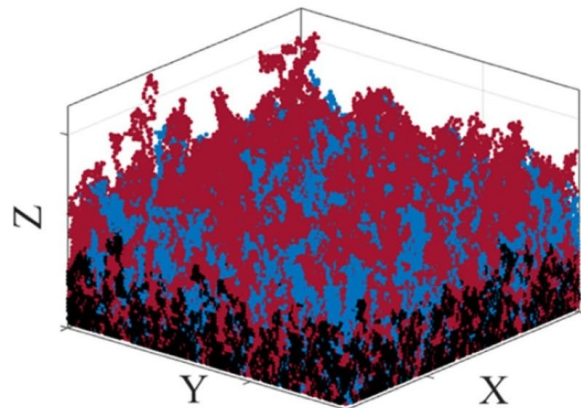


Control of Polymer Brush Film Thickness

Control of dry film polymer brush thickness via surface-initiated atom transfer radical polymerization



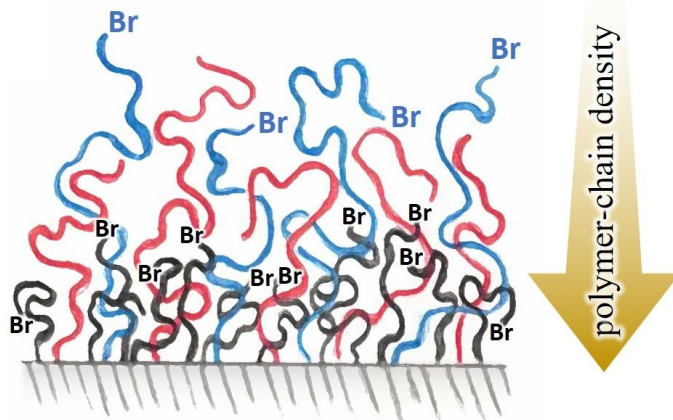
Grafting Density, Chain Conformation & Dispersity



— Dead chain on surface

— Dormant chain on surface

— Hindered dormant chain on surface



Grafting density:

- Number of chains anchored to a surface per unit surface area.

Conformation:

- The conformation of a single, surface-anchored polymer chain can be different in proximity of the substrate as compared to the polymer brush - air or polymer brush - solvent interface.
- This is related to the loss of polymerization active chain ends as the brush grows.
- As a consequence, a polymer brush also has a non-uniform density (higher at the interface, and lower at the top).

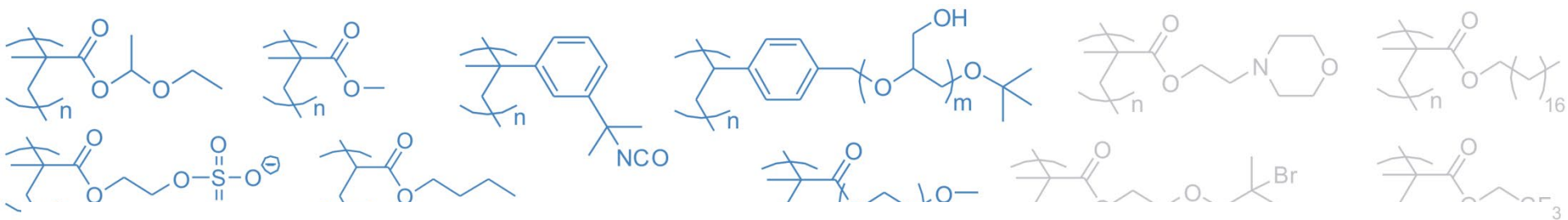
Dispersity:

- Is related to the «livingness» of the polymerization, and thus influences chain conformation and the polymer brush density profile.

Top: F. J. Arraez, P. H. M. Van Steenberghe, J. Sobieski, K. Matyjaszewski, D. R. D'hooge, *Macromolecules* **2021**, *54*, 8270-8288.

Bottom: Image credit: Prof. E. Benetti (Padua)

Synthesis of Polymer Brushes



Chem. Rev. **2009**, *109*, 5437–5527

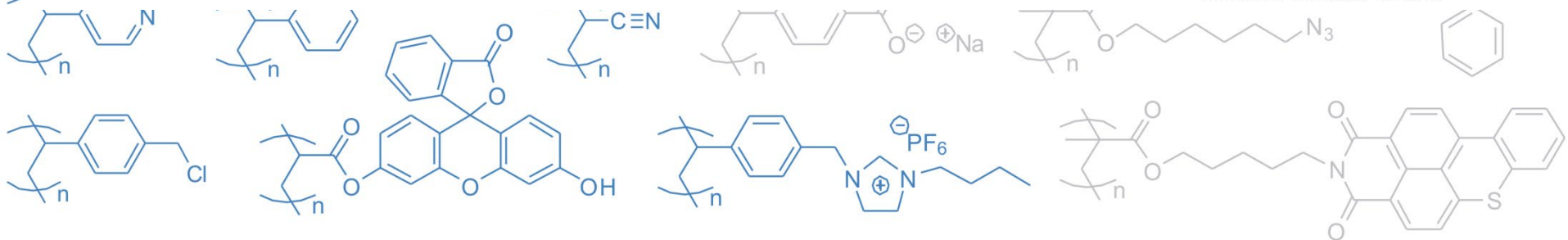
5437

Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications

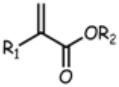
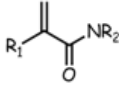
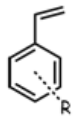
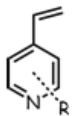
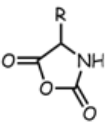
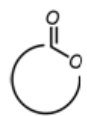
Raphaël Barbey, Laurent Lavanant, Dusko Paripovic, Nicolas Schüwer, Caroline Sugnaux, Stefano Tugulu, and Harm-Anton Klok*

École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux, Laboratoire des Polymères, Bâtiment MXD, Station 12, CH-1015 Lausanne, Switzerland

Received February 5, 2009

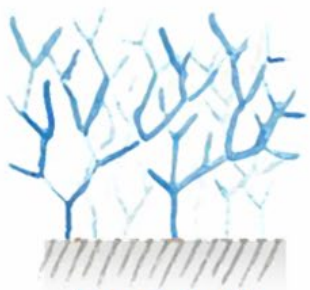


Monomers Polymerized via SIP

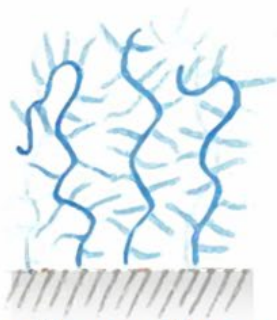
			SI-FRP	SI-NMP	SI-ATRP	SI-RAFT	SI-PIMP	SI-AP	SI-CP	SI-ROP	SI-ROMP
	(Meth)acrylates	Neutral	PHEMA, PHEA, PBMA, PDMAEMA, PGMA	PMMA, PBA, PtBA, PDEAEMA	PMMA, PHEMA, PDMAEMA, PtBA, PMA, PEGMA, PEGDMA	PMMA, PBA, PHEMA	PMMA	PMMA			
		Charged	PAA, PMAA		PMAA, PMETAC	PDMAPS					
	(Meth)acrylamides		PDMA, PAAm	PDMA	PDMA, PNIPAM	PDMA					
	Styrenic monomers	Neutral	PSt	PSt, POEOMSt	PSt	PSt	PSt	PSt	PSt		
		Charged	PNaSS				PSS				
	Pyridinic monomers		P4VP	P3VP	P4VP			P2VP			
	Amino-NCAs									PBLG, PMLG	
	Lactones									PCL, PLA, PDXO	
	Others		PAN					PI, PBD	PIB	PPEI, PEDHO	PBNE, PBNE-d

PHEMA: poly(2-hydroxyethyl methacrylate); **PHEA:** poly(2-hydroxyethyl acrylate); **PBMA:** poly(butyl methacrylate); **PDMAEMA:** poly(2-(dimethylamino)ethyl methacrylate); **PGMA:** poly(glycidyl methacrylate); **PAA:** poly(acrylic acid); **PMAA:** poly(methacrylic acid); **PDMA:** poly(N,N'-dimethylacrylamide); **PAAm:** poly(acrylamide); **PSt:** polystyrene; **PNaSS:** poly(styrene sulfonate); **P2VP:** poly(2-vinylpyridine); **P3VP:** poly(3-vinylpyridine); **P4VP:** poly(4-vinylpyridine); **PAN:** poly(acrylonitrile); **PMMA:** poly(methyl methacrylate); **PBA:** poly(butyl acrylate); **PtBA:** poly(t-butyl acrylate); **PDEAEMA:** poly(2-diethylamino)ethyl methacrylate); **POEOMSt:** poly(4-(oligoethyleneoxy)oxymethylstyrene); **PMA:** poly(methyl acrylate); **PEGMA:** poly(oligo(ethyleneglycol) methacrylate); **PEGDMA:** poly(oligo(ethyleneglycol) dimethacrylate); **PMETAC:** poly(2-(methacryloyloxy)ethyltrimethylammonium chloride); **PNIPAM:** poly(N-isopropyl acrylamide); **PDMAPS:** poly(N,N'-dimethyl(methylmethacryloyl ethyl)ammonium propane sulfonate); **PSS:** poly(4-styrene sulfonate); **PI:** polyisoprene; **PBD:** poly(butadiene); **PIB:** poly(isobutylene); **PEDHO:** poly(2-ethyl-4,5-dihydrooxazole); **PPEI:** Poly(N-propionylethyleneimine); **PBLG:** poly(γ -benzyl glutamate); **PMLG:** poly(γ -methyl L-glutamate); **PCL:** poly(caprolactone); **PLA:** poly(L-lactic acid); **PDXO:** poly(1,5-dioxepan-2-one); **PBNE:** polynorbornene; **PBNE-d:** polynorbornene-derived brushes.

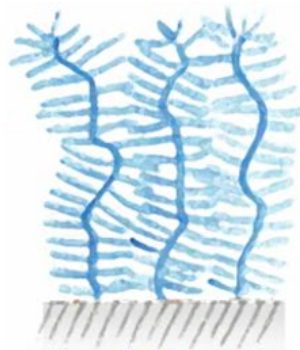
Polymer Architectures obtained via SIP



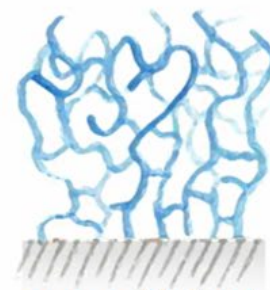
branched
brushes



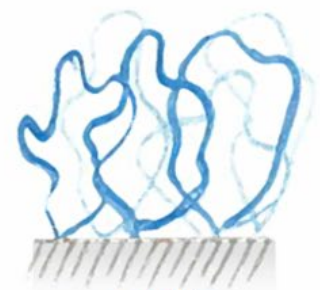
graft copolymer
brushes



bottlebrush
brushes



cross-linked
brushes



cyclic
brushes

Current Scope and Limitations of SIP



Surface-initiated Polymerizations

Radical	H_2O	O_2			
Anionic	H_2O	O_2			
Cationic	H_2O	O_2			
RO(M)P	H_2O	O_2			
Kumada	H_2O	O_2			

H_2O	water tolerant	O_2	oxygen tolerant
	metal free		external regulation
	conductive brushes		

Green color indicates tolerance (e.g., towards H_2O or O_2), **red** specifies inherent chemical incompatibility with previously attempted approaches, and **gray** implies potential possibilities, yet no current literature.

Large Scale SI-ATRP under Ambient Conditions

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Article

Surface-Initiated Controlled Radical Polymerization: Going beyond Laboratory Scale

Jakob Pagh Nikolajsen, Lukas Vogtmann Thinnesen, Orhan Altuğ Karabiber, Kim Daasbjerg, Steen Uttrup Pedersen, Mikkel Kongsfelt, and Mie Lillethorup*



Cite This: *ACS Appl. Polym. Mater.* 2023, 5, 3534–3541



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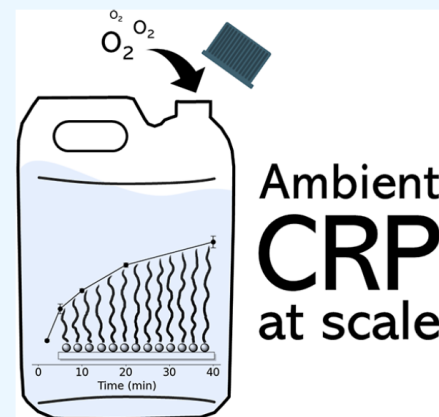
Article Recommendations



Supporting Information

ABSTRACT: Surface coatings of immobilized polymer brushes are used, e.g., as lubricants, for anti-fouling, and as adhesives. Based on surface-initiated controlled radical polymerization (SI-CRP), a fast, versatile, and enduring scaled SI-CRP (SI-CRP_{scaled}) approach for the formation of polymer brushes is reported. The chemical process is made from an easily prepared chemical solution that is reusable for more than 6 h, even in the presence of oxygen. Because an inert atmosphere is not required, the SI-CRP_{scaled} process can be carried out under ambient conditions with no significant loss of polymerization activity and viability. The high bath life of the activated solution along with an extraordinarily high brush growth rate of 10 nm per minute makes this method industrially relevant. Based on a straightforward dip coating protocol, this is the first scaled polymer brush technique successfully demonstrated on an industrial scale, enabling uniform polymer brush-functionalized materials for a broader variety of applications.

KEYWORDS: *polymer brushes, surface-initiated controlled radical polymerization (SI-CRP), thin films, long-lived, industrial scale*



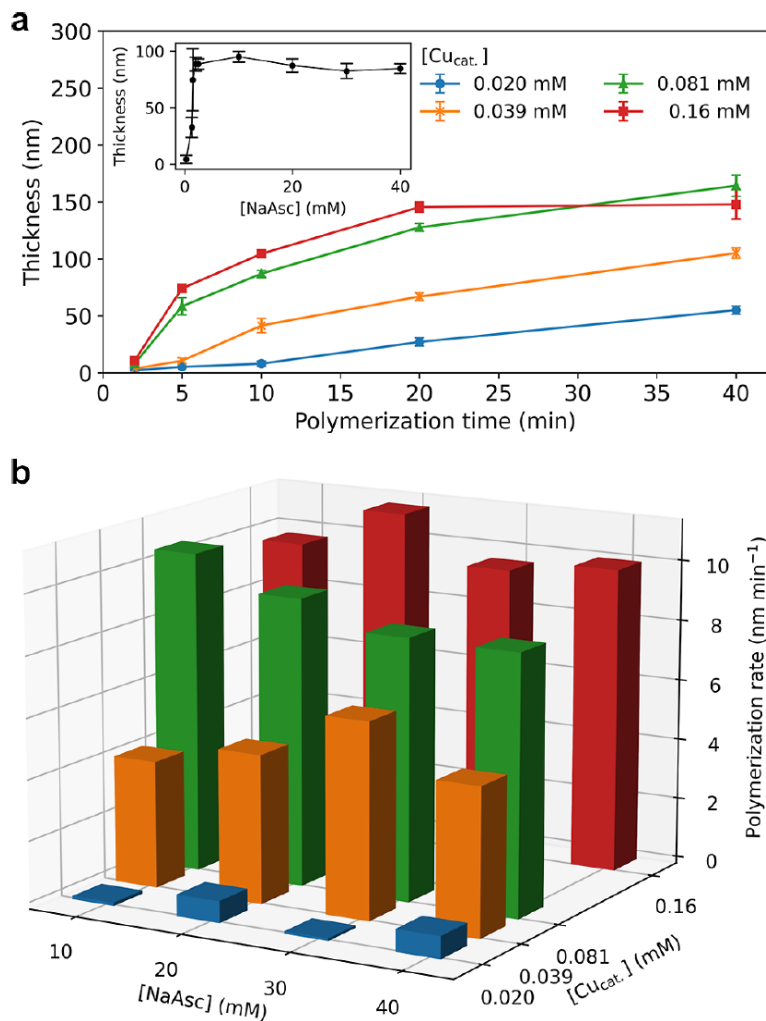


Figure 1. (a) Polymer brush thickness on a stainless-steel substrate as a function of polymerization time for SI-CRP_{scaled} comprising [MMA] = 0.7 M, [NaAsc] = 20 mM, and [Cu_{cat}] = 0.020 (●), 0.039 (×), 0.081 (▲), and 0.16 mM (■) in 100 mL water/ethanol (v/v = 1.3:1); inset shows polymer brush thickness vs [NaAsc] using [Cu_{cat}] = 0.081 mM; lines drawn to guide the eye. (b) Polymerization rates derived from data presented in (a) and Figure S1, calculated from the initial 10 min of polymerization. All data including standard deviations are available in the Supporting Information (Table S1).

CONCLUSIONS

In summary, we have demonstrated the potential of the SI-CRP technology at scale because of its good tolerance toward oxygen, high control of polymerization, fast polymerization rates, monomer versatility, and simple production setups. On the basis of the general PMMA protocol, we achieved a polymerization rate of $\sim 10 \text{ nm min}^{-1}$, exceeding similar polymerization rates for SI-polymer brushes in the literature. SI-CRP_{scaled} was shown to be compatible with a wide range of monomers, including GMA, HFDMA, ST, PFS, and HEMA. Furthermore, the DOE approach was used to optimize the polymerization with respect to concentrations of reactants, solvent systems, and oxygen reduction, thereby making it applicable for multiple uses over a bath life as long as 6 h. Finally, the potential for industrialization of SI-CRP_{scaled} was demonstrated by treating five batches of 50 A5-size samples with 10 min polymerization time per batch in a 10 L polymerization solution. Altogether, we succeeded in coating 250 samples with $\sim 90 \text{ nm}$ thick polymer brushes within 55 min, which is the first demonstrated use of a SI-CRP solution on such a scale.

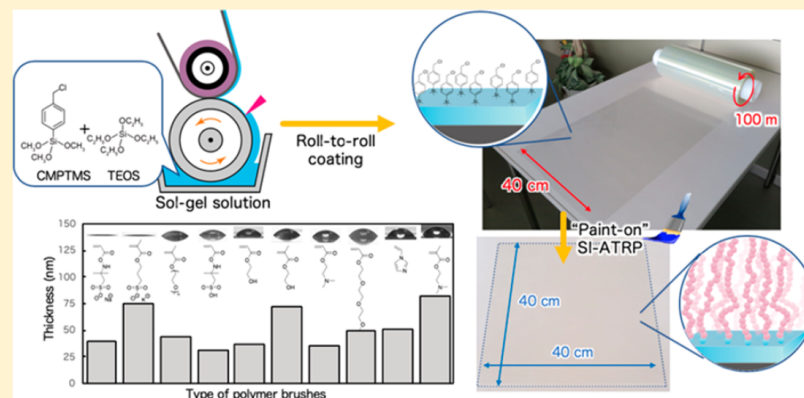
Sol–Gel Preparation of Initiator Layers for Surface-Initiated ATRP: Large-Scale Formation of Polymer Brushes Is Not a Dream

Tomoya Sato, Gary J. Dunderdale, Chihiro Urata, and Atsushi Hozumi*^{id}

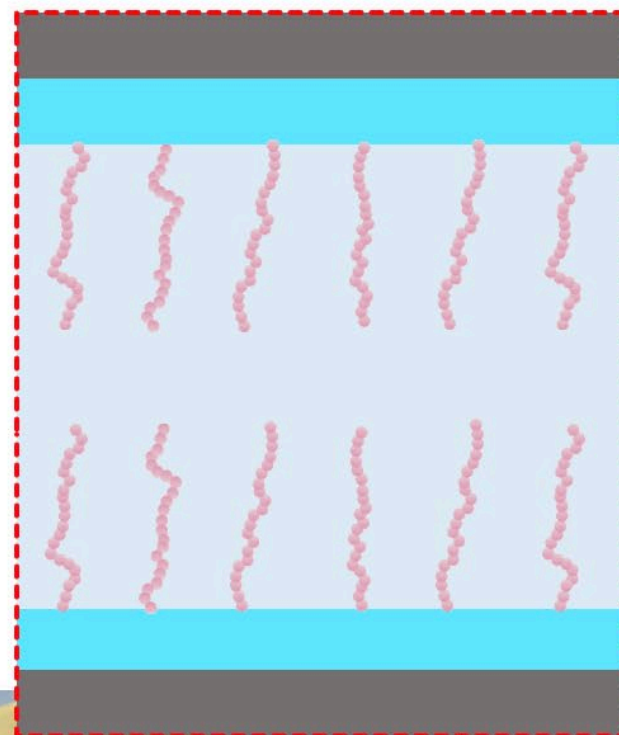
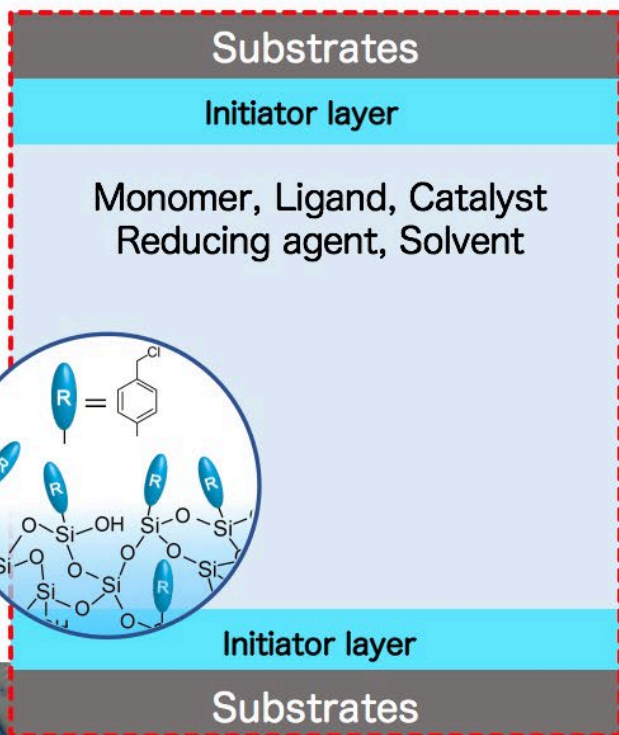
National Institute of Advanced Industrial Science and Technology (AIST), 2266-98, Anagahora, Shimoshidami, Moriyama, Nagoya 463-8560, Japan

Supporting Information

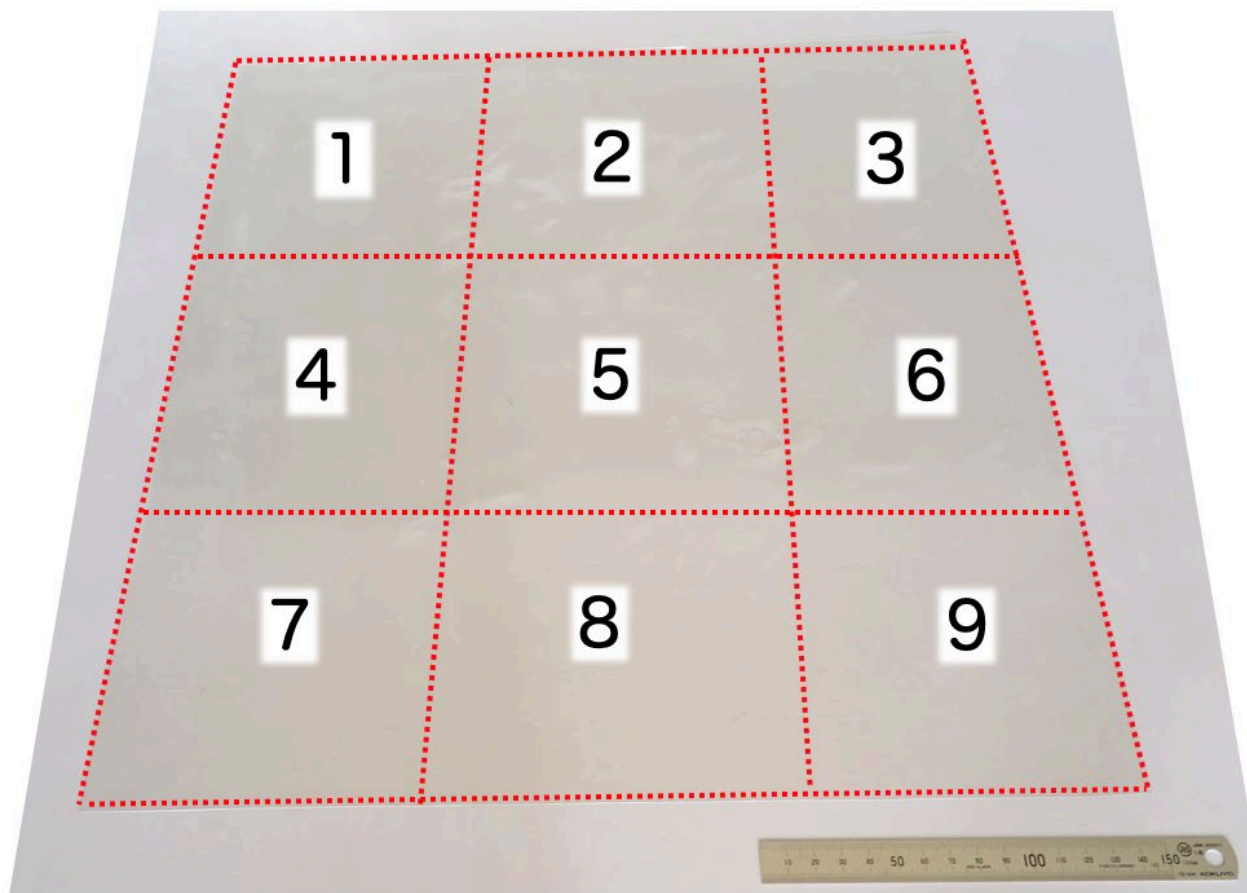
ABSTRACT: We demonstrated for the first time a facile and reproducible preparation of large-scale ($\sim 40 \text{ m}^2$) initiator layers for surface-initiated atom transfer radical polymerization (SI-ATRP) using a simple sol–gel solution of (*p*-chloromethyl)phenyltrimethoxysilane and tetraethoxysilane. Highly smooth and transparent initiator layers could be formed on various inorganic/organic substrates via a spin-, wire-bar-, or roll-to-roll-coating without any marked change in surface morphology or bulk properties at room temperature. Combining the advantages of this sol–gel approach and subsequent “paint on” SI-ATRP using a variety of waterborne monomers, we have succeeded in the formation of polymer brushes on large-scale real-life substrates (i.e., maximum $50 \times 50 \text{ cm}^2$) under ambient conditions (room temperature and open to the air) without any complicated apparatus or harsh reaction conditions.



"Paint on" SI-ATRP



"Paint on" SI-ATRP



Area No.	Thickness (nm)	Water θ_s (°)
1	87.2	53
2	78.7	53
3	79.0	52
4	79.5	55
5	85.8	52
6	76.4	55
7	76.1	55
8	79.6	55
9	74.5	54
Average	79.7	54

Figure S6. Average dry thicknesses and water θ_s values measured at nine different points on pDMAEMA brushes grafted from iCMPTMS-covered PET roll film (roll-to-roll coating, 40 × 40 cm²).

Large-Scale and Environmentally Friendly Synthesis of pH-Responsive Oil-Repellent Polymer Brush Surfaces under Ambient Conditions

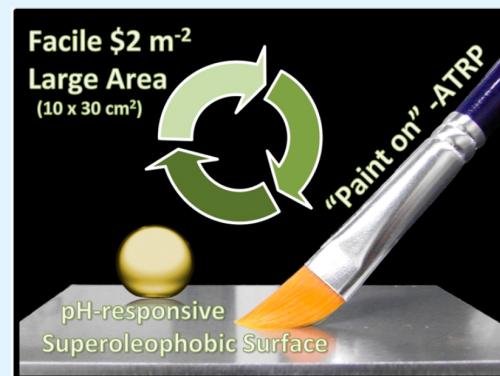
Gary J. Dunderdale, Chihiro Urata, Daniel F. Miranda, and Atsushi Hozumi*

Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimoshidami, Moriyama, Nagoya 463-8560, Japan

S Supporting Information

ABSTRACT: Contrary to conventional ATRP, aqueous A(R)GET-ATRP at ambient temperature without deoxygenating reaction solutions is an extremely facile method to create polymer brushes. Using these techniques, extremely thick poly[2-(dimethylamino)ethyl methacrylate] polymer brushes can be prepared (~ 700 nm), or reaction solutions can be low chemical-content, consisting of 99% v/v water. Based on these techniques, we have also developed an easy and inexpensive method, referred to as “paint on”-ATRP, that directly pastes reaction solutions onto various large-scale real-life substrates open to the air. The resulting brush surfaces possess excellent oil-repellent properties, which can be activated or deactivated in response to solution pH.

KEYWORDS: poly[2-(dimethylamino)ethyl methacrylate], polymer brush, ATRP, superoleophobic, pH-responsive, large scale



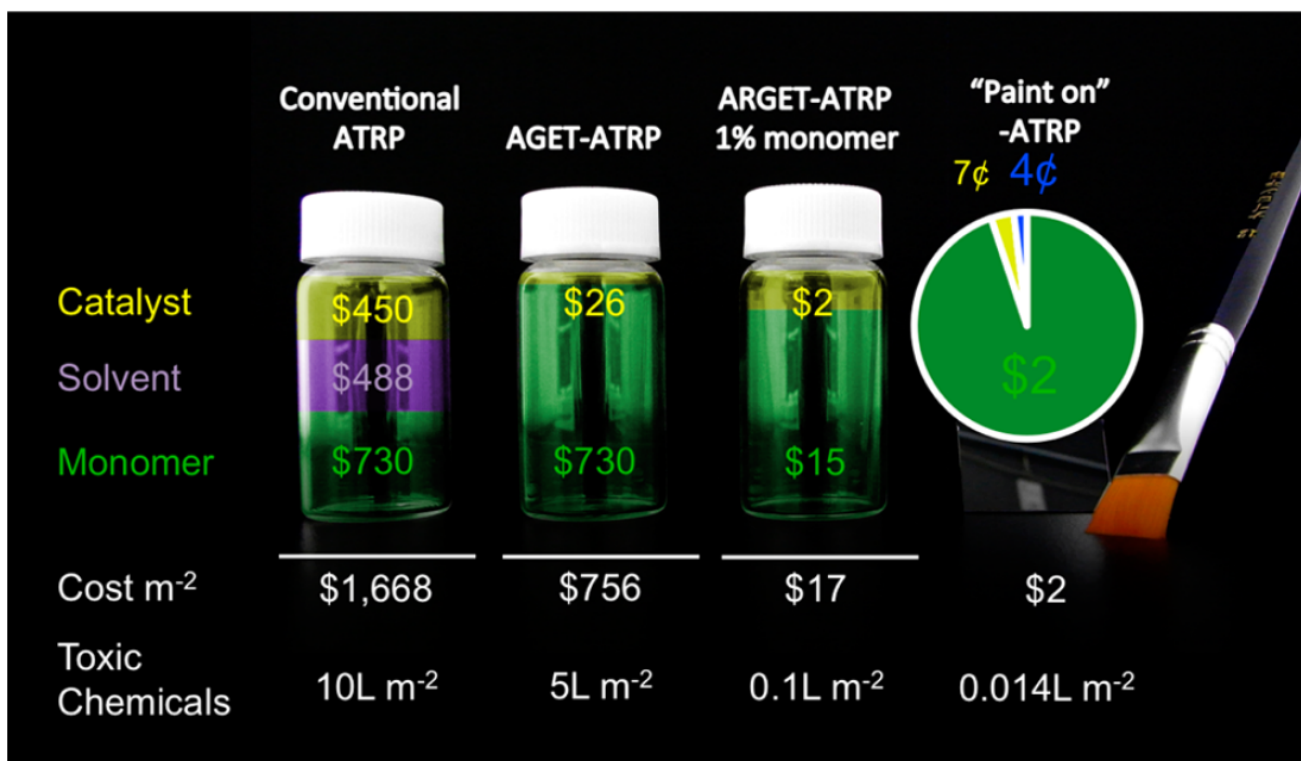


Figure 2. Costs of polymer brushes created using conventional ATRP, AGET-ATRP, ARGET-ATRP and “paint on”-ATRP. Green indicates cost of monomer, purple cost of organic solvent, yellow cost of catalyst, and blue cost of ascorbic acid. The total cost per square meter is shown at the bottom, along with the amount of toxic chemicals used.

What is a polymer brush (and when is a brush a brush....)?

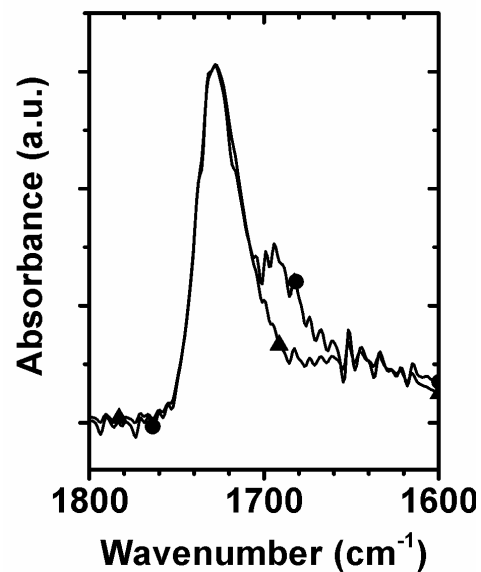
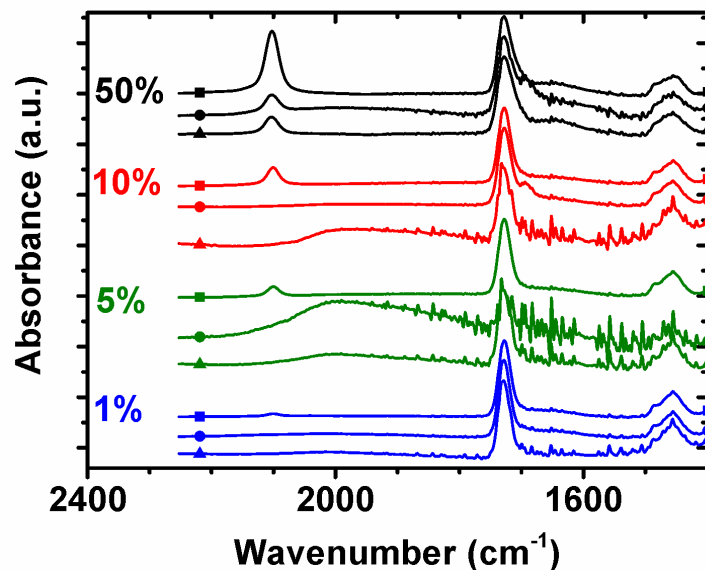
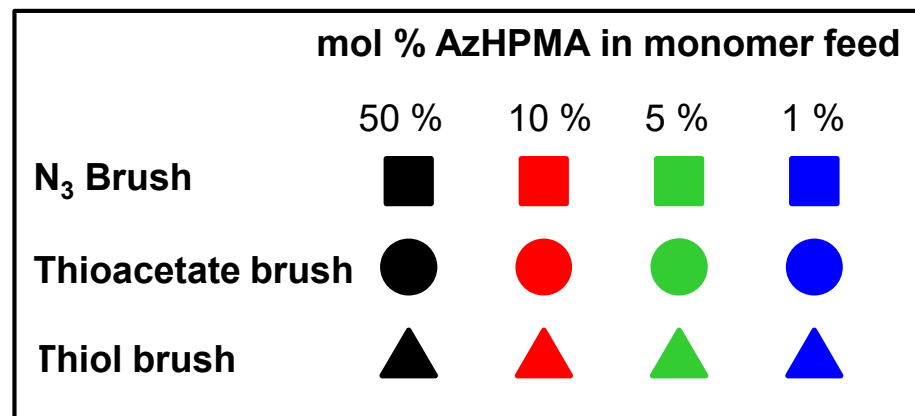
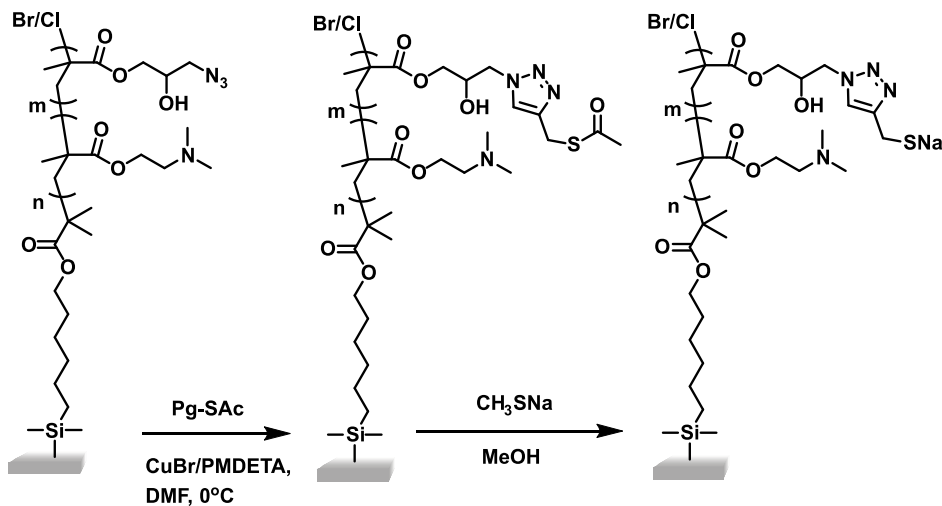
Making polymer brushes

Characterizing polymer brushes

What are polymer brushes good for ?

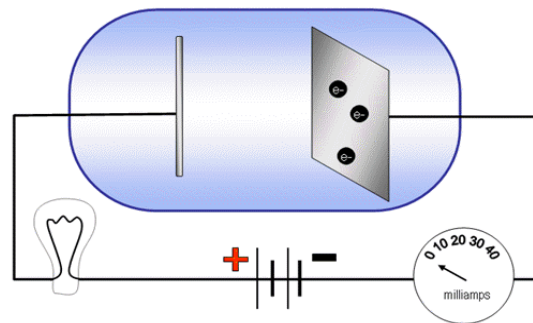
Chemical Composition

FTIR Spectroscopy

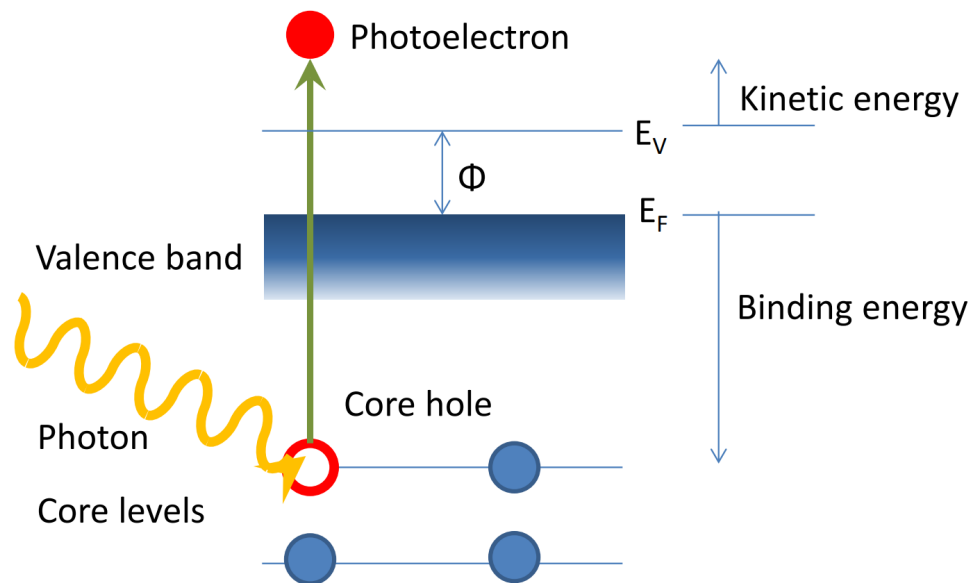


X-Ray Photoelectron Spectroscopy (XPS)

Photoelectric effect
Einstein, Nobel Prize 1921



Photoelectric effect



$$KE = h\nu - BE - \phi$$

$h\nu$: Incident light energy (known)

KE: Kinetic energy (measured)

BE: Binding energy (calculated)

ϕ : Photoelectric workfunction (known)

XPS is also referred to as Electron Spectroscopy for Chemical Analysis (ESCA)

X-Ray Photoelectron Spectroscopy (XPS)

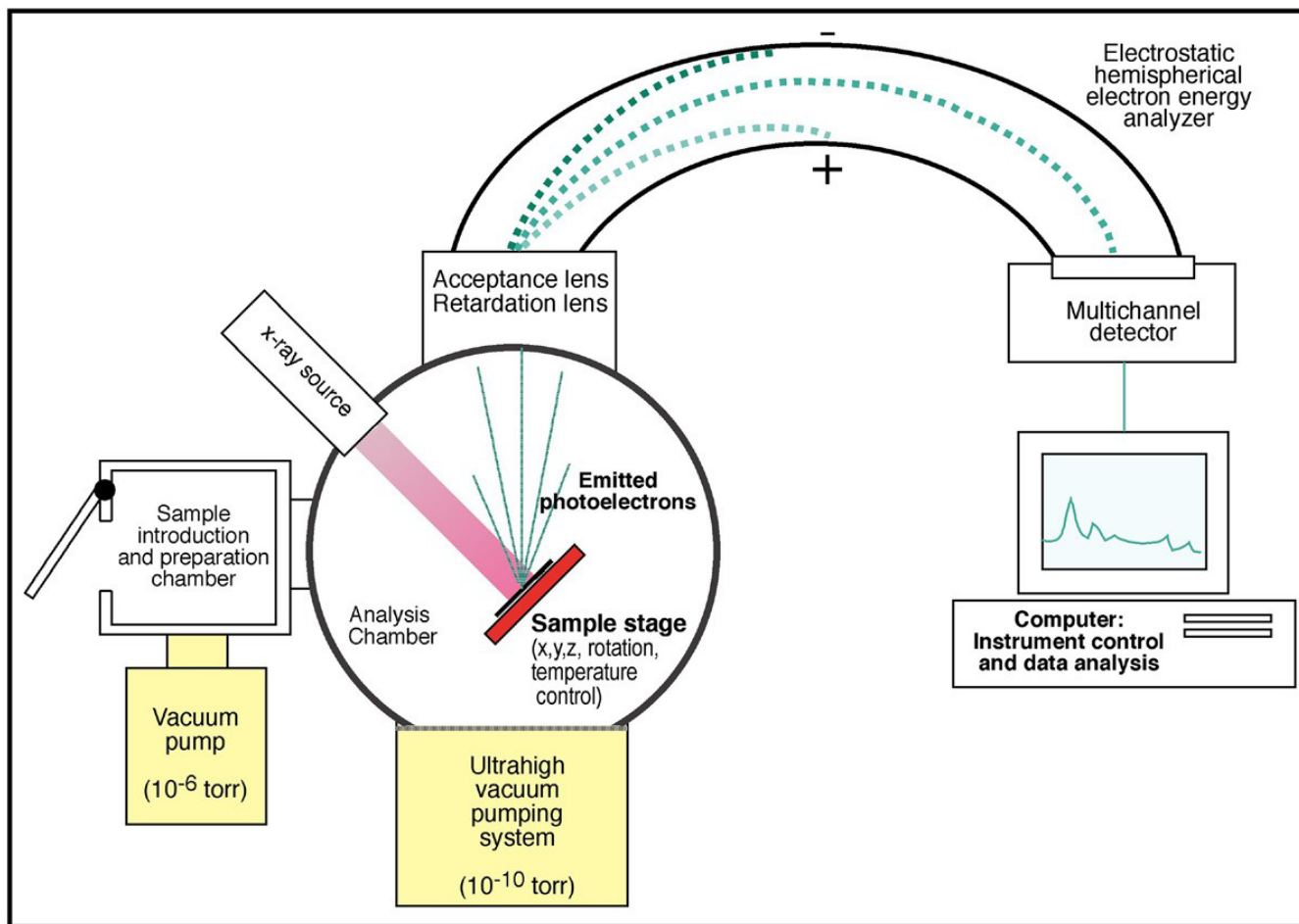
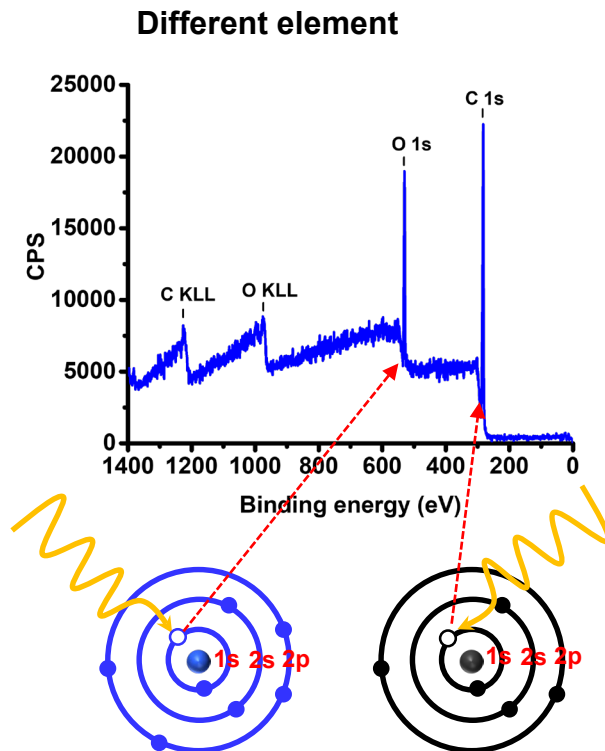


FIGURE I.1.5.6 Schematic diagram of a mono-chromatized ESCA instrument.

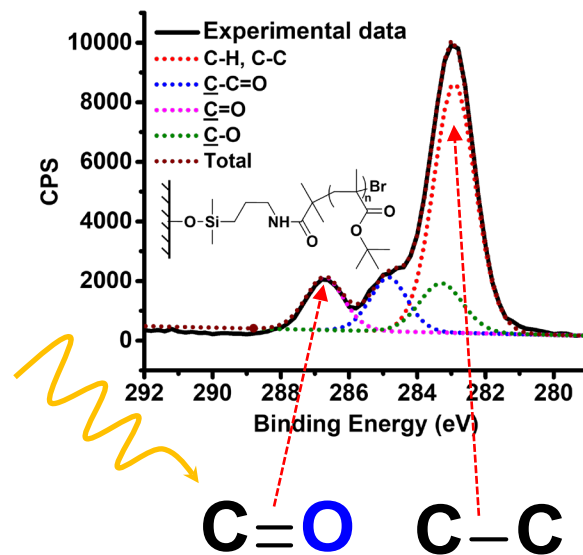
XPS-Data analysis

Binding energy is determined by

- 1: Interaction between electron and nucleus (type of element).
- 2: Chemical bonding state.



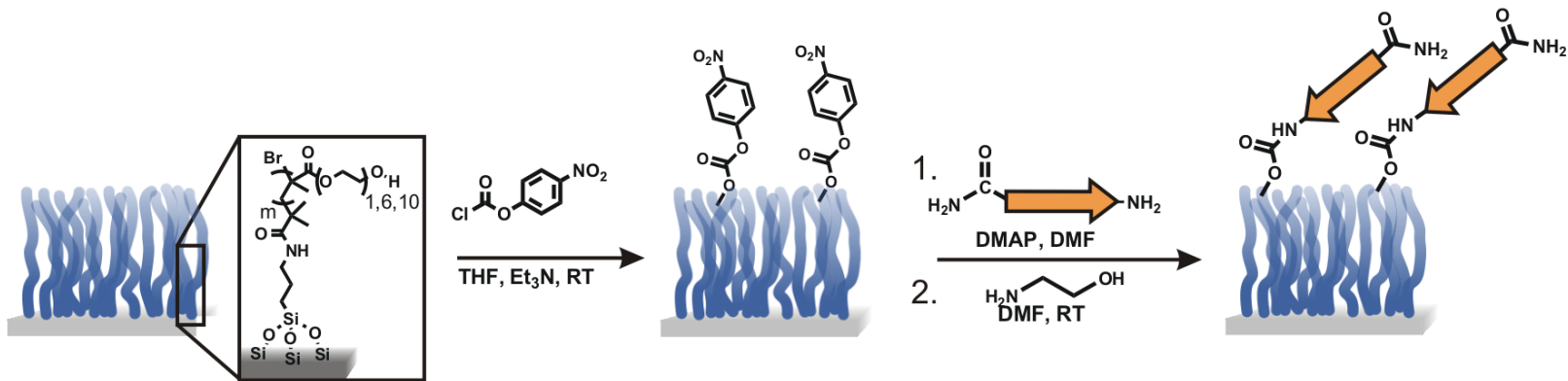
Different chemical state
Intensity \propto concentration



XPS can be used to analyze:

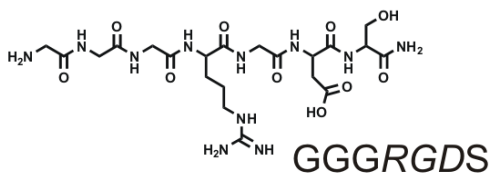
- 1: Elemental identification and chemical state of element.
- 2: Relative composition of the constituents in the surface region.

Brush Functionalization



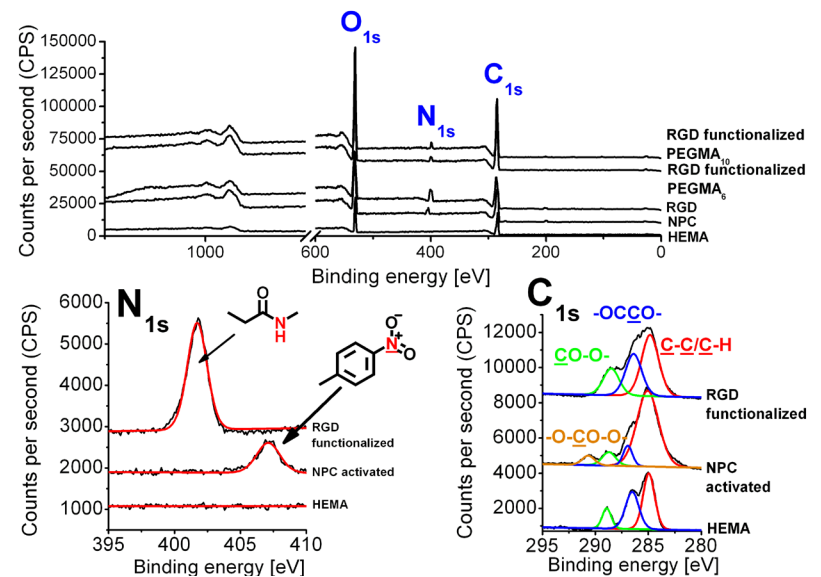
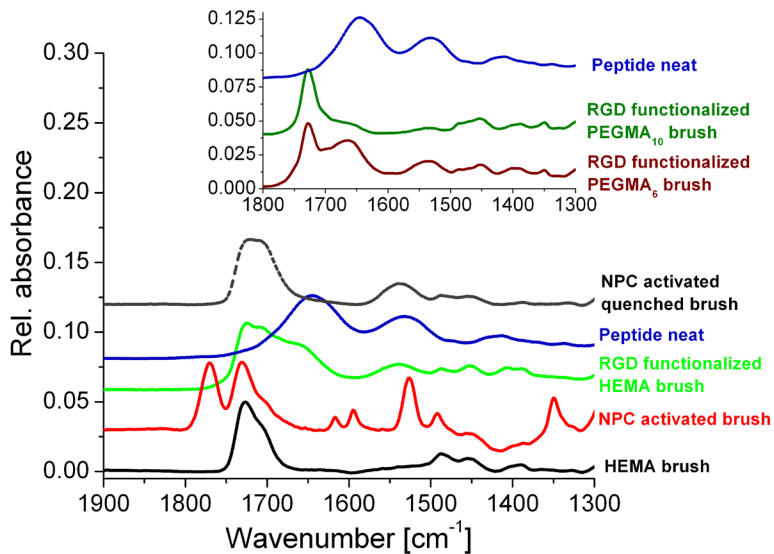
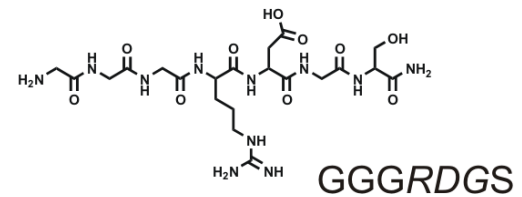
Cell Adhesion:

RGD



Negative Control:

RDG



Characterization of Structural Parameters

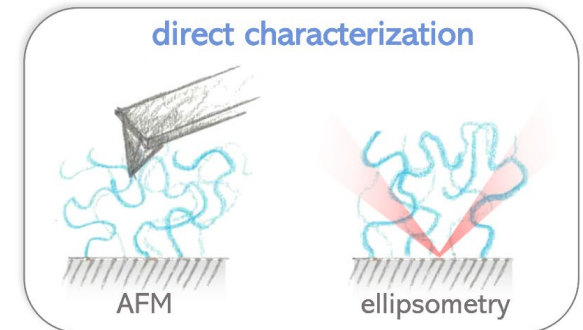
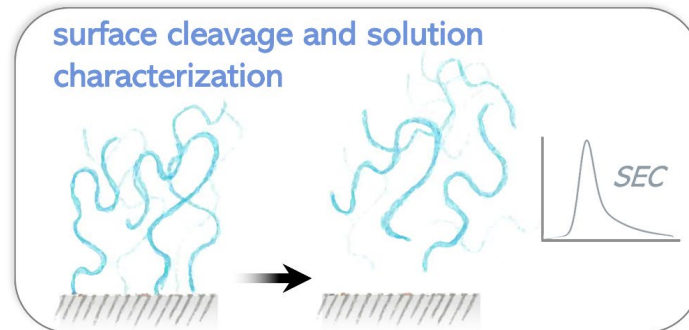
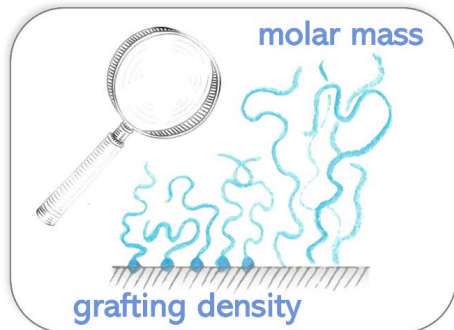
Key structural parameters of polymer brushes are the **molar mass** of the surface-anchored polymers, and the **grafting density** (σ).

Grafting density
(nm^{-2}):

$$\sigma = \frac{h \rho N_A}{M_n}$$

h : dry film thickness of the brush
 ρ : polymer density
 N_A : Avogadro's constant
 M_n : number-average molecular weight of the polymer grafts

When the dry film thickness or mass of polymer brushes are known, any experiment that provides information about σ also affords the M_n of the polymer grafts, and vice versa.



Determining Polymer Brush Dry Film Thickness

Polymer brushes grafted from or onto nanoparticles:

- Thermogravimetric analysis (TGA)

Polymer brushed grafted from or onto planar substrates:

- Atomic force microscopy (on patterned brushes)
- Ellipsometry

TGA of Polymer Brush Grafted Nanoparticles

Scheme 1. Synthesis of Loop PMMA Brushes via SI-ATRP of MMA and Subsequent Chain-End Modification and Loop-Closure Metathesis

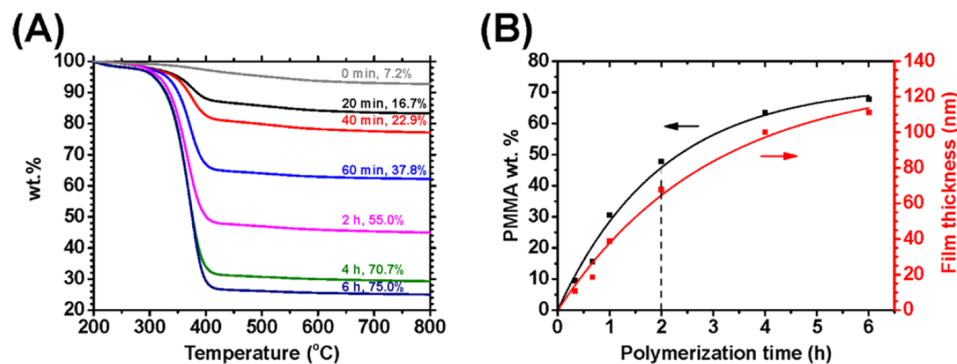
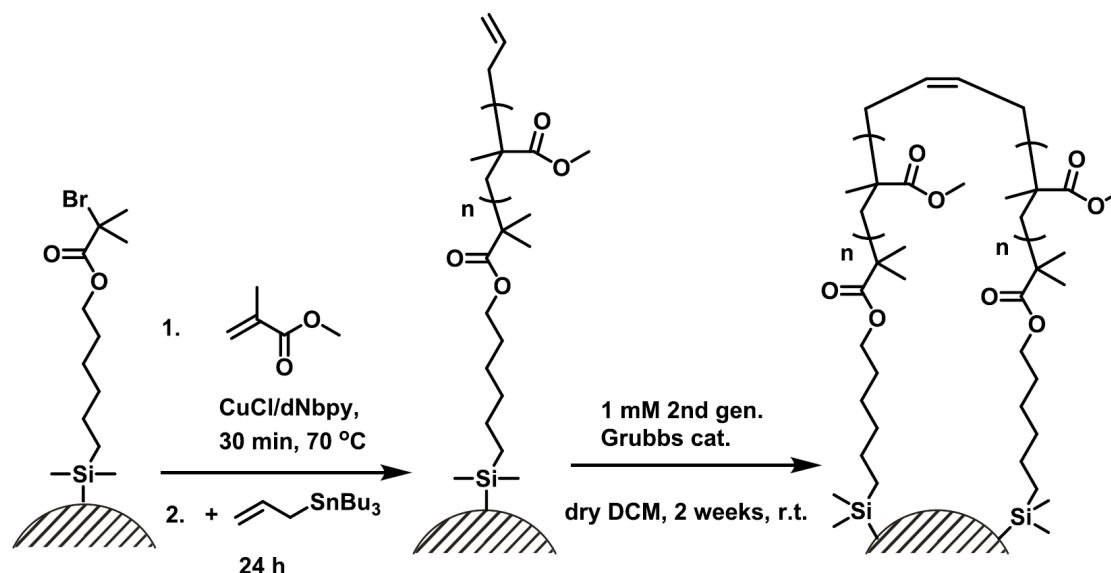
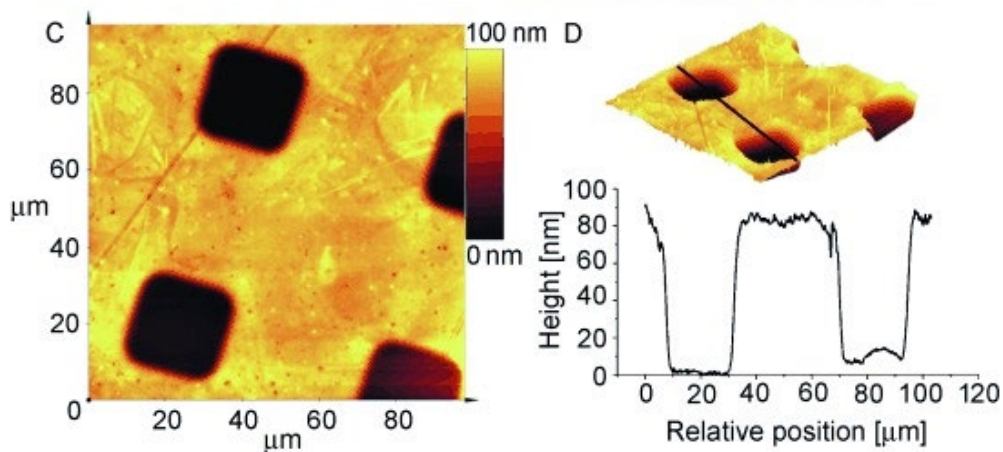
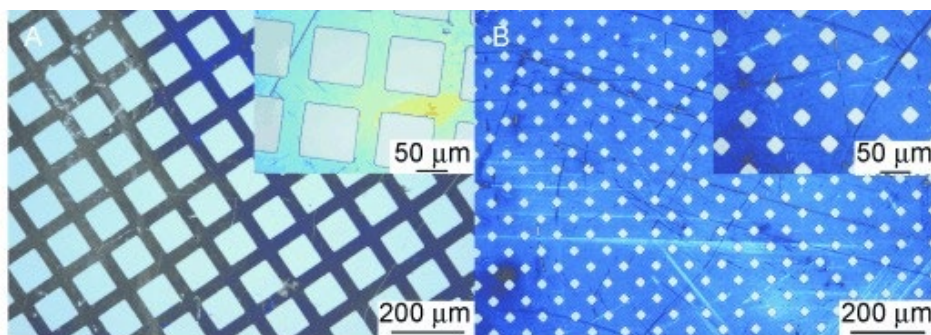
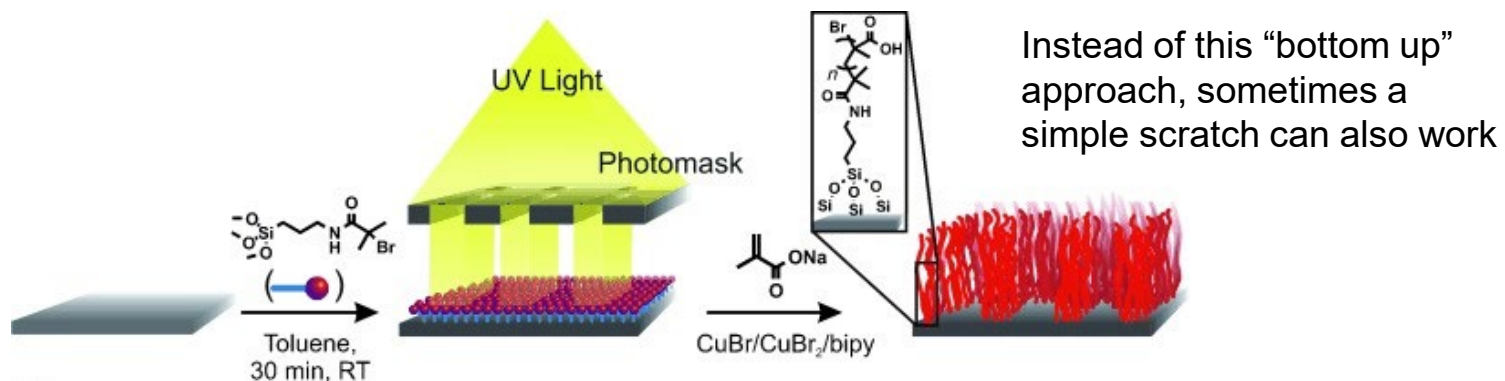


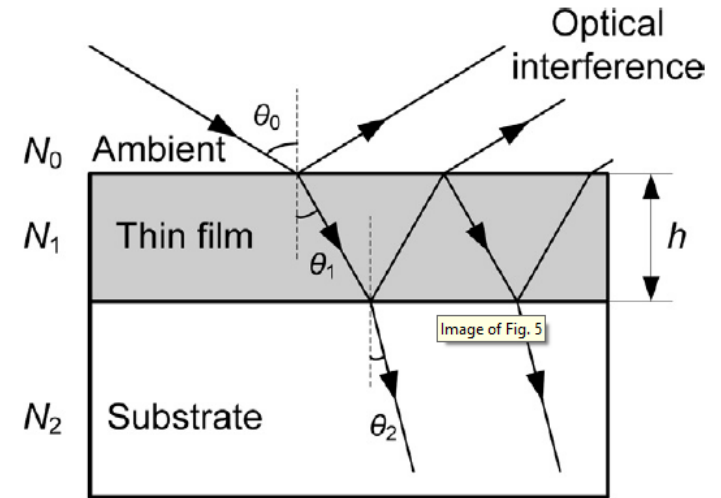
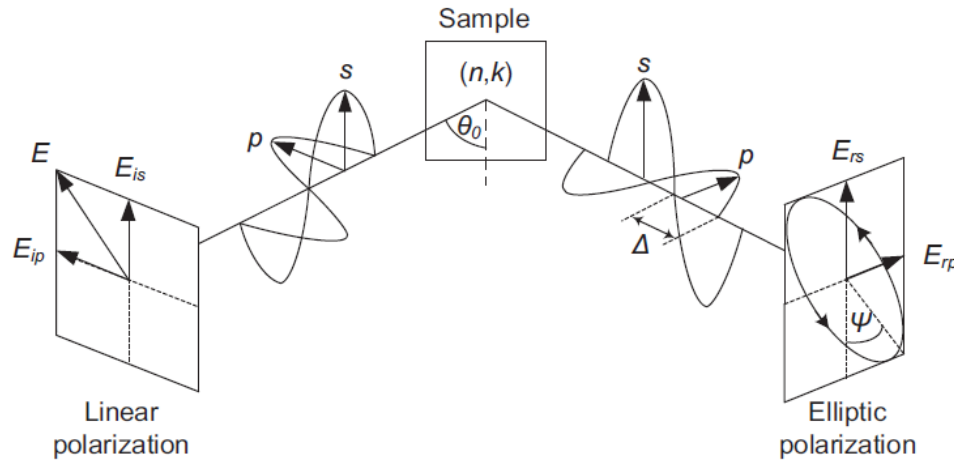
Figure 2. (A) TGA curves of PMMA-grafted silica nanoparticles ($\phi = 332$ nm) prepared by SI-ARGET-ATRP at different polymerization times. A heating ramp of 10 °C/min was used. (B) TGA weight loss between 200 and 800 °C and dry PMMA brush film thicknesses as a function of polymerization time.

AFM Analysis of Micropatterned Polymer Brushes



Ellipsometry - Interaction of Light and Matter

Polarized light interacts with sample upon reflection



Complex reflectance ratio

$$\rho = \frac{r_s}{r_p} = \tan \Psi * e^{i\Delta}$$

r_s and r_p : amplitudes of s and p component, after reflection normalized to their initial value

Ψ : amplitude ratio upon reflection

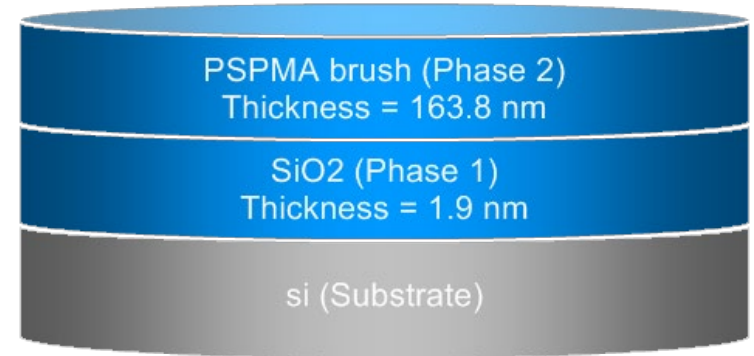
Δ : phase shift

The change of polarization upon reflection on the surface can be expressed in terms of the two angles Ψ and Δ , which is the typical outcome of an ellipsometric measurement, usually measured as a function of wavelength, angle of incidence or both.

Ellipsometry - Data Fitting

Structure of sample has to be known or needs to be assumed

most models are based on the assumption that the sample is composed of a **small number of discrete, well-defined layers that are optically homogeneous and isotropic**



The complex reflectance ratio ρ can be expressed in terms of n_i , k_i (complex refractive index) and d_i (thickness)

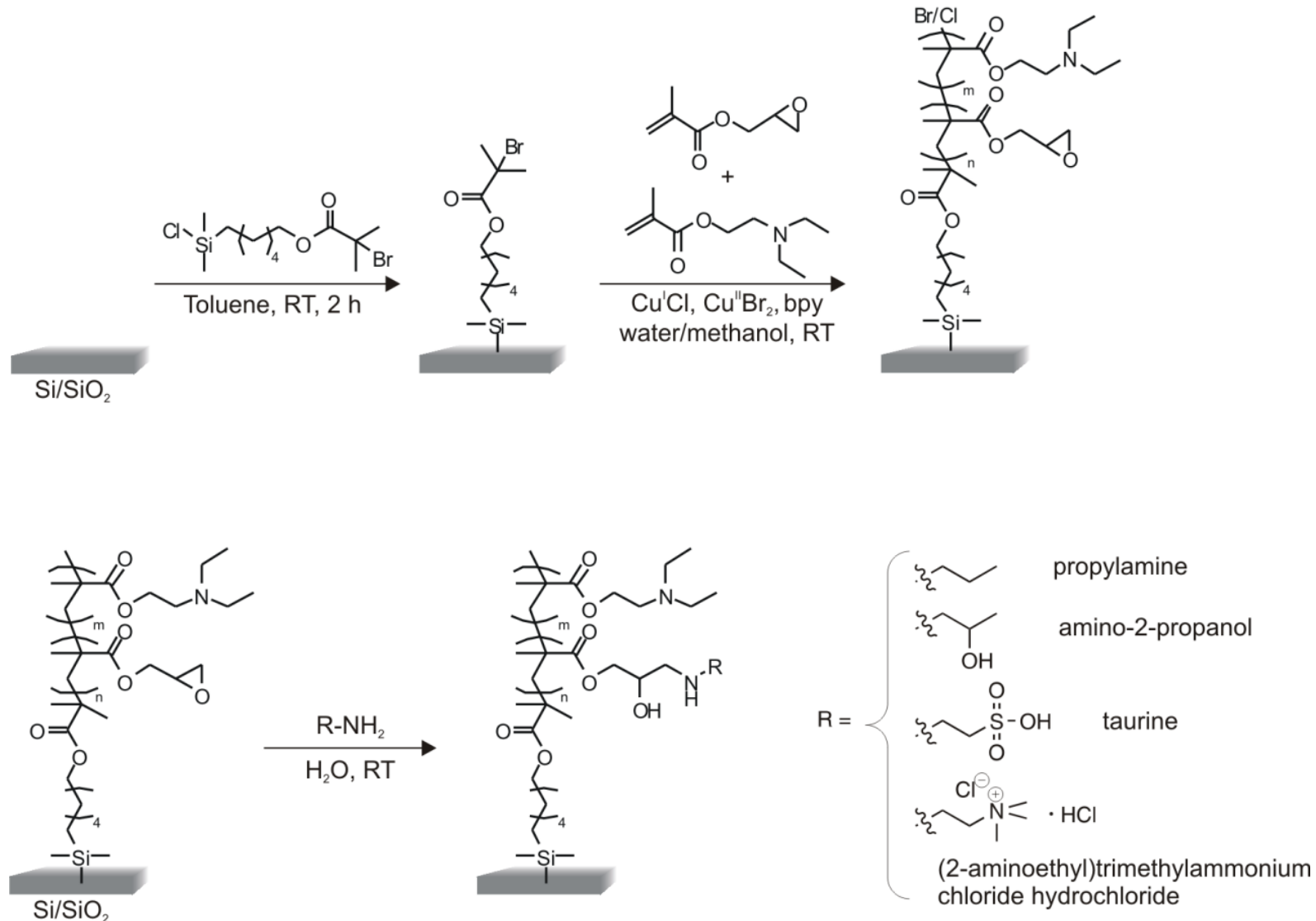
- > n_i and k_i are functions of the wavelength
- > dispersion laws are mathematical functions modelling the optical properties of a material (e.g. *Cauchy's equation*)
- > ellipsometry software usually also provides a database with optical properties for a wide range of materials

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

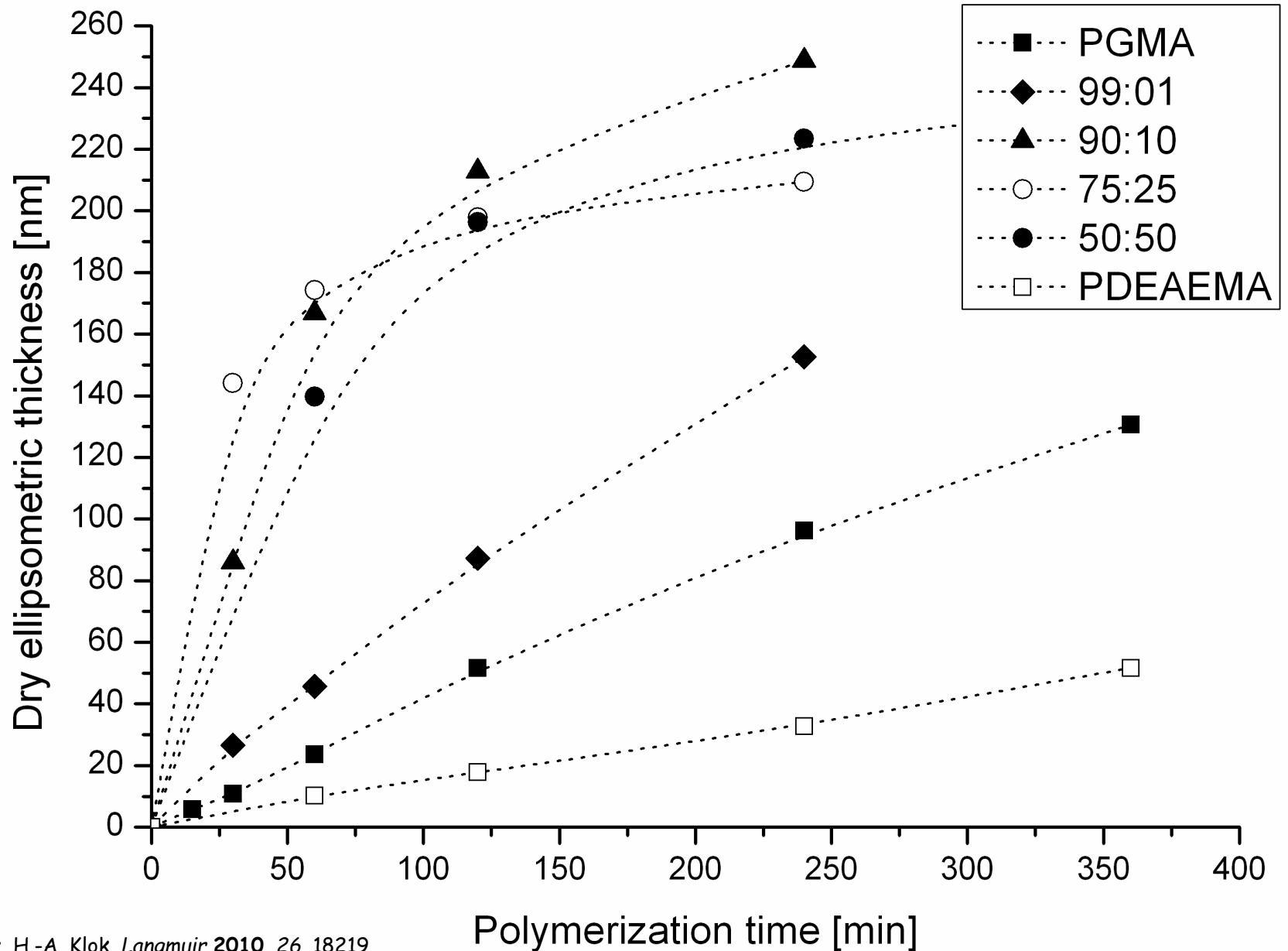
$$k(\lambda) = D + \frac{E}{\lambda^2} + \frac{F}{\lambda^4}$$

Cauchy's equation

Post-Polymerization Modification of PGMA Brushes



Surface-Initiated Polymerization



Determining M_n and Grafting Density

Surface-Cleavage of Polymer Brushes and Solution Characterization

- mostly using HF or TBAF
- works well from nanoparticles
- for planar surface, sufficiently large surface area is needed
- cleaved polymer can be analyzed using standard polymer characterization, e.g. GPC

On-Demand Degrafting and the Study of Molecular Weight and Grafting Density of Poly(methyl methacrylate) Brushes on Flat Silica Substrates

Rohan R. Patil,[†] Salomon Turgman-Cohen,[‡] Jiří Šrogl,[†] Douglas Kiserow,^{†,§} and Jan Genzer^{*,†}

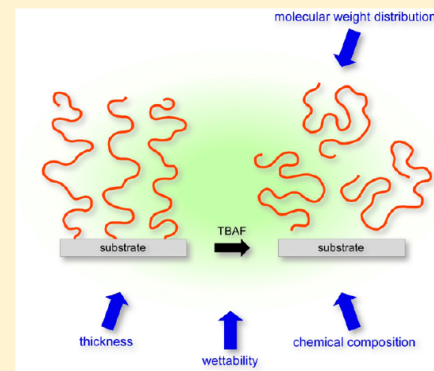
[†]Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States

[‡]Department of Chemical Engineering, Kettering University, Flint, Michigan 48504, United States

[§]US Army Research Office, Research Triangle Park, North Carolina 27709-2211, United States

Supporting Information

ABSTRACT: We report on degrafting of surface-anchored poly(methyl methacrylate) (PMMA) brushes from flat silica-based substrates using tetrabutylammonium fluoride (TBAF) and determining their molecular weight distribution (MWD) using size exclusion chromatography (SEC). The grafted PMMA layer was synthesized using surface-initiated atom transfer radical polymerization (SI-ATRP) of MMA for polymerization times ranging from 6 to 24 h. X-ray photoelectron spectroscopy, ellipsometry, and time-of-flight secondary ion mass spectrometry were employed in tandem to characterize the degrafting process. The SEC eluograms were fit to various polymer distributions, namely Zimm–Schulz, ATRP in continuous stirred tank reactor, Wesslau, Schulz–Flory, and Smith et al. The ATRP model gives the best fit to the experimental data. The dry PMMA brush thickness and the number-average molecular weight (obtained from the MWD) suggest that the grafting density of the PMMA grafts is independent of polymerization time, indicating well-controlled/living growth of MMA. The observed polydispersity index (PDI) was higher than that generally observed in bulk grown polymers under similar conditions, indicating an effect due to chain confinement and crowding. We detect small but noticeable dependence of the polymer brush grafting density on the inhibitor/catalyst ratio. Higher inhibitor/catalyst ratio offers better control with lower early terminations, which results in a small increase in the apparent grafting density of the chains.



Solution Characterization of Cleaved PMMA

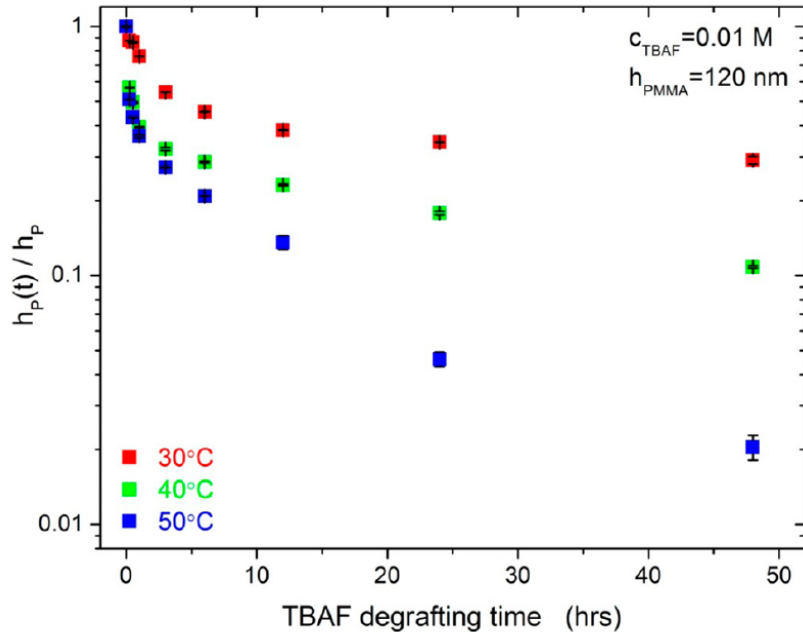


Figure 4. Relative brush thickness (i.e., time-dependent thickness normalized by the initial thickness) of a PMMA brush as a function of TBAF degrafting time at three different temperatures. The original dry thickness of the PMMA brush was ~ 120 nm, and the concentration of the TBAF solution was 0.01 M.

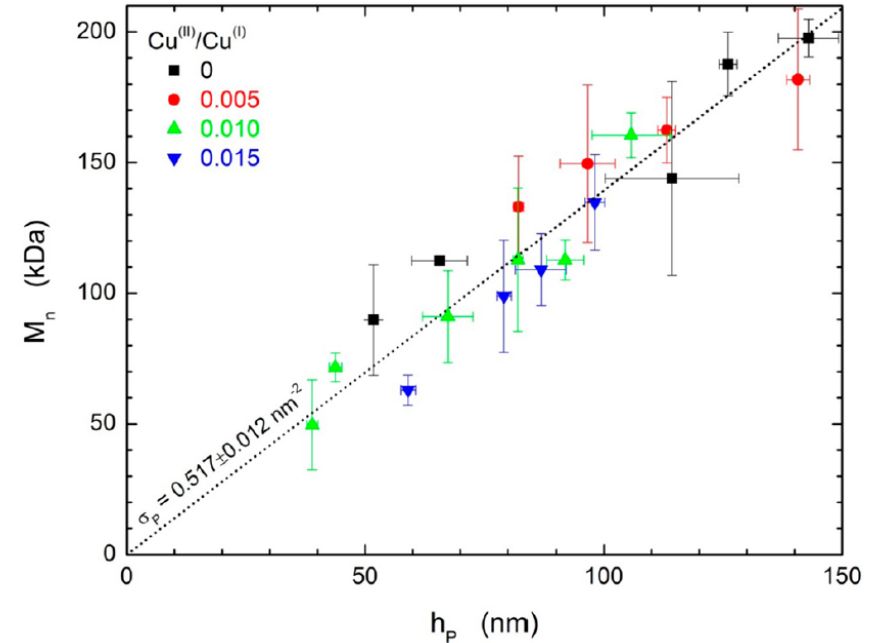


Figure 8. Number-average molecular weight (M_n) as a function of dry PMMA brush thickness (h_p) for four ATRP catalyst ratios. The dotted line is a linear fit passing through the origin.

$$\text{Note: } M_n = \frac{h \rho N A}{\sigma}$$

Sacrificial Initiator - Fact or Fiction ?

- Sometimes a **sacrificial initiator** (e.g. ethyl 2-bromoisobutyrate) is added to the reaction mixture for the growth of polymer brushes via SI-ATRP.
- Does analysis of the polymer generated by the sacrificial initiator provide insight into the molecular weight of the polymer grafts ?

Chemical Reviews

Review

Table 6. Overview of Polymer Brushes that Have Been Cleaved from Silicon Oxide Substrates Using Hydrofluoric Acid (HF) and Their Molecular Characteristics

Polymer Brush	Substrate Geometry	Cleaved Polymer Brush ^a			Free Polymer ^b		SI-CRP Technique
		M_n (kDa)	M_w/M_n	Grafting density (σ) (chains/nm ²)	M_n (kDa)	M_w/M_n	
Methacrylates							
PBMA	Nanoparticles	2300	1.16	-	-	-	AGET ATRP ³⁰⁸
PBzMA	Nanoparticles	~48	~1.4	0.47	~48	~1.4	ATRP ¹¹⁹⁴
PHEMA	Nanoparticles	9.3	1.12	-	-	-	ATRP ⁷⁰⁵
PHPMAM	Mesoporous	11.5	1.28	-	-	-	RAFT ¹⁹⁵
PMAA	Nanoparticles	41	1.11	0.65	-	-	RAFT ²⁰⁹
PMPC	Nanoparticles	20.9	1.72	0.066	-	-	ATRP ²⁰³⁸
PPEGMA	Nanoparticles	125.4	1.32	0.79	-	-	ATRP ¹¹²⁹
PTMSPMA	Nanoparticles	24.86	1.31	0.16	-	-	ATRP ¹⁹⁴⁹
		71.2	1.48	0.20	-	-	ATRP ¹²⁶⁶
		68.9	1.90	0.32	-	-	ATRP ²⁰⁵⁷
PSBMA	Nanoparticles	206	1.21	0.071	-	-	ATRP ²⁰⁶⁰
		23.8	1.27	0.129	-	-	ATRP ²⁰³⁸
	Planar	176	1.80	0.080	365	1.74	ATRP ³²⁹
		79.9	1.38	0.26	-	-	ATRP ¹²⁶⁶
PDMAEMA	Nanoparticles	98.7	3.11	0.14	-	-	ATRP ⁶⁷⁹
		36.15	1.14	0.077	-	-	ATRP ¹⁰⁷³
PDEAEMA	Mesoporous	23.6	1.14	-	-	-	ATRP ¹²¹¹
		17	1.31	-	21.3	1.34	ATRP ¹⁶⁷⁹
		9.69	1.18	-	-	-	ATRP ⁸¹⁴
		62	2.5	0.10	-	-	ATRP ²³⁶
		105.1	~1.5	0.37	~65	~1.4	AGET ATRP ³³⁸
		222	1.51	0.93	228	1.54	ARGET ATRP ¹⁷³⁷
		191	~1.27	0.5	~205	~1.28	ATRP ²⁴⁶
		48.7	1.47	0.36	90.8	1.60	RAFT ²⁰⁴
		~510	~1.2	0.45	~480	~1.3	ATRP ⁴⁶⁶
PMMA	Nanoparticles	17.89	1.2	-	-	-	ATRP ³⁰²
		410	1.20	-	-	-	AGET ATRP ³⁰⁸
		27000	1.17	-	-	-	AGET ATRP ³⁰⁸
		40.2	1.34	-	-	-	ATRP ³²⁷
		62.4	1.47	0.54	-	-	AGET ATRP ¹⁷³⁹
		205	<1.3	0.07	-	-	RAFT ²⁰⁸
		108	1.24	-	-	-	ATRP ¹⁵⁷¹
	Mesoporous	54.22	1.6	0.05	-	-	ATRP ³⁰²
		43.72	1.4	0.05	63.73	1.12	ATRP ³⁰²
Acrylates							
PtBA	Nanoparticles	24.2	1.09	0.20	21.0	1.10	RAFT ¹⁸⁷
PBBEA	Mesoporous	29.2	1.80	-	-	-	ATRP ¹³¹⁹
PAPBA-PA	Porous beads	-	-	-	-	-	ATRP ²¹³³
PMA	Nanoparticles	2400	1.18	-	-	-	AGET ATRP ³⁰⁸
PMA (loops)	Nanoparticles	53 (M_p)	2.0	-	~100 (M_p)	-	RAFT ²⁰⁶
		31 (M_p)	-	-	80 (M_p)	-	RAFT ²⁰⁷
PCPPUA	Porous beads	3.85	1.15	-	-	-	ATRP ¹¹³⁰
PBA	Nanoparticles	79.4	1.29	-	-	-	AGET ATRP ¹⁰⁸⁷
		100	1.07	0.31	105	1.24	RAFT ²⁰⁴

Sacrificial Initiator - Fact or Fiction ?

		205	<1.3	0.07	-	-	RAFT ²⁰⁸	
		108	1.24	-	-	-	ATRP ¹⁵⁷¹	
	Mesoporous	54.22	1.6	0.05	-	-	ATRP ³⁰²	
		43.72	1.4	0.05	63.73	1.12	ATRP ³⁰²	
Acrylates								
	PtBA	Nanoparticles	24.2	1.09	0.20	21.0	1.10	RAFT ¹⁸⁷
	PBBEA	Mesoporous	29.2	1.80	-	-	-	ATRP ¹³¹⁹
	PAPBA-PA	Porous beads	-	-	-	-	-	ATRP ²¹³³
	PMA	Nanoparticles	2400	1.18	-	-	-	AGET ATRP ³⁰⁸
	PMA (loops)	Nanoparticles	53 (M_p)	2.0	-	~100 (M_p)	-	RAFT ²⁰⁶
			31 (M_p)	-	-	80 (M_p)	-	RAFT ²⁰⁷
	PCPPUA	Porous beads	3.85	1.15	-	-	-	ATRP ¹¹³⁰
	PBA	Nanoparticles	79.4	1.29	-	-	-	AGET ATRP ¹⁰⁸⁷
			100	1.07	0.31	105	1.24	RAFT ²⁰⁴
Acrylamides								
		Nanoparticles	113	1.33	0.31	106	1.33	RAFT ²⁰⁴
			64	1.25	0.55	-	-	ATRP ⁸¹⁷
			7.4	1.19	0.36	7.2	1.19	ATRP ¹⁰⁶¹
	PNIPAM	Mesoporous	2.8	~1.26	-	-	-	ARGET ATRP ¹³⁰⁶
		Porous beads	13.3	3.13	0.125	-	-	ATRP ²³⁹⁵
		Monoliths	9.7	2.23	0.072	-	-	ATRP ²³⁹⁵
		Planar	42.3	1.11	1.2	44	1.13	ATRP ³³⁷
Styrenic								
			17.2	1.17	-	18	1.21	ATRP ¹⁶⁷⁹
			9.1	1.09	-	-	-	ATRP ²⁴⁹⁶
			~220	1.3	0.2	~130	1.6	RAFT ²⁰⁴
			88.8	1.37	0.2	-	-	ATRP ²³⁷
			20	1.27	0.24	-	-	ATRP ³⁰⁷
		Nanoparticles	7.58	1.22	-	-	-	ATRP ⁸¹⁶
			12.7	1.25	-	-	-	RAFT ²¹⁰
	PS		96.9	1.10	-	-	-	ATRP ³¹¹
			119	<1.3	0.047	-	-	RAFT ²⁰⁸
			80.4	1.32	0.5	-	-	ARGET
			203	~1.2	0.55	-	-	ATRP ^{1080,2492}
			24.8	2.1	0.2	24.5	1.22	NMP ⁴⁸⁷
		Mesoporous	3.27	9.7	-	18.92	1.15	ATRP ³⁰²
		Planar hole array	~72	~1.32	-	-	-	ATRP ⁵⁵⁵
	PSS(Na)	Nanoparticles	23.8	1.7	-	-	-	ATRP ¹¹⁴⁴

Sacrificial Initiator - Fact or Fiction ?

Table 7. Overview of Polymer Brushes that Have Been Cleaved from Silicon Oxide Substrates Using Reagents Other than Hydrofluoric Acid (HF) and Their Molecular Characteristics

Polymer Brush	Substrate Geometry	Cleaving Agent	Cleaved Polymer Brush ^a			Free Polymer ^b		SI- CRP Technique
			M_n (kDa)	M_w/M_n	Grafting density (σ) (chains/nm ²)	M_n (kDa)	M_w/M_n	
Methacrylates								
PLMA	Planar	UV	900	2.0	0.13	-	-	ATRP ²⁴⁴
PMETAC	Planar	H ₂ SO ₄	101	1.29	0.20	130	1.15	ATRP ²⁵¹
PMMA	Planar	tetrabutyl ammonium fluoride (TBAF)	200	1.15	0.52	-	-	ATRP ⁸⁴²
PDMAEMA	Nanoparticles	<i>p</i> -toluenesulfonic acid	17.8	1.12	-	-	-	ATRP ²⁴⁷
PTMSPMA	Nanoparticles		7.9	1.14	0.20	-	-	ATRP ²⁴⁸
Acrylates								
PAA	Planar	Tris(hydroxymethyl) aminomethane buffer	-	-	-	-	-	ATRP ²⁵²
PMA	Nanoparticles	AIBN	~12.5	~1.6	-	~21	~1.3	RAFT ²⁰⁵
Acrylamides								
	Planar		~6.3	-	-	-	-	ATRP ²³⁸²
PNIPAM	Porous beads	NaOH	18.9	2.69	0.133	-	-	ATRP ²³⁹³
			16.1	2.94	0.106	-	-	ATRP ²³⁹⁶
PNTBAM	Porous beads		4.7	1.77	0.080	-	-	ATRP ²³⁹⁶
Styrenic								
	Planar	UV	70	1.9	0.44	-	-	ATRP ²⁴⁴
		<i>p</i> -toluenesulfonic acid	37.3	1.26	0.83	26.6	1.28	ATRP ²⁴⁰
PS	Mesoporous	-	240.8	1.30	-	-	-	SET/SARA ⁹⁸
	Nanoparticles	-	156.9	1.29	-	-	-	SET/SARA ⁹⁸
		<i>p</i> -toluenesulfonic acid	16.1	1.13	-	19.1	1.35	ATRP ²⁴⁹
Block copolymers								
PMMA- <i>b</i> -PMDPAB	Planar	Ammonium bifluoride (NH ₄ HF ₂)	140	1.22	-	130	-	ATRP ²⁵³
PMA- <i>b</i> -PS	Nanoparticles	AIBN	21.4	1.42	-	18.7	1.53	RAFT ²⁰⁵
PTMSPMA- <i>b</i> -PHFBMA	Nanoparticles		26.8	1.27	0.20	-	-	ATRP ^{248,250}
PS- <i>b</i> -PTMSPMA	Nanoparticles	<i>p</i> -toluenesulfonic acid	41.1	1.24	-	-	-	ATRP ²⁴⁹
Random copolymers								
PPEGMA- <i>co</i> -PPEGMEMA	Nanoparticles		165.8	1.28	-	-	-	ATRP ⁵⁰⁹
PNIPAM- <i>co</i> -PAPTAC- <i>co</i> -PNTBAM	Porous beads		15.8	1.67	0.09	5.1	1.27	ATRP ²³¹⁸
PNIPAM- <i>co</i> -PMBAM	Porous beads		9.1	2.68	0.021	-	-	ATRP ²³⁹⁶
PNIPAM- <i>co</i> -PNTBAM	Porous beads	NaOH	18.6	1.89	0.067	-	-	ATRP ²³⁹⁶
PNIPAM- <i>co</i> -PDMAEMA- <i>co</i> -PNTBAM	Monoliths		12.9	2.53	0.072	-	-	ATRP ¹³²¹
PNIPAM- <i>co</i> -PAA- <i>co</i> -PNTBAM	Porous beads		17.4	3.13	0.11	-	-	ATRP ¹³²¹
	Monoliths		13.8	1.48	0.169	-	-	ATRP ⁶²⁶
	Porous beads		12.1	1.53	0.131	-	-	ATRP ⁶²⁶

^aResults refer to values corresponding to the highest number-average molecular weight (M_n) obtained by the cited authors for cleaved polymer brushes. ^bBulk or solution polymers produced simultaneously or under the same reaction conditions. The superscripts are references to the relevant publications.

Determining M_n and Grafting Density

Direct characterization of molar mass and grafting density

- No brush cleavage needed
- Techniques:
 - Single molecule atomic force microscopy
 - Analysis of swollen polymer films thicknesses

Study of the Polydispersity of Grafted Poly(dimethylsiloxane) Surfaces Using Single-Molecule Atomic Force Microscopy[†]

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Single-molecule atomic force microscopy (AFM) was used to study the statistical distribution of contour lengths (polydispersity) of polymer chains grafted to a surface. A poly(dimethylsiloxane) (PDMS) monolayer was grafted on a flat silicon substrate by covalently bonding Cl-terminated PDMS ($M_w = 15000\text{--}20000$) to an OH-silicon surface and characterized using contact angle measurements, ellipsometry, and single-molecule AFM. A model for the single-chain dynamics is presented. The statistical distributions of the polymer contour lengths were found to depend on the concentration of the PDMS polymer used in the grafting solutions. Shifts of the statistical distributions toward higher contour lengths indicated preferential adsorption of longer chains with increasing PDMS:CH₂Cl₂ volume ratios of 0.005–0.16. The gel permeation chromatography (GPC) profile was found to correlate with the most dilute (0.005 volume ratio) AFM data. The polydispersity index (PI) calculated using AFM data was found to be 1.56 compared to 1.62 by GPC. A surface grafted with two PDMS polymer samples of average molecular weights, 3000 and 15000–20000, was found to have a bimodal distribution of contour lengths, with peaks corresponding to the two grafting samples.

Single-Molecule Atomic Force Microscopy

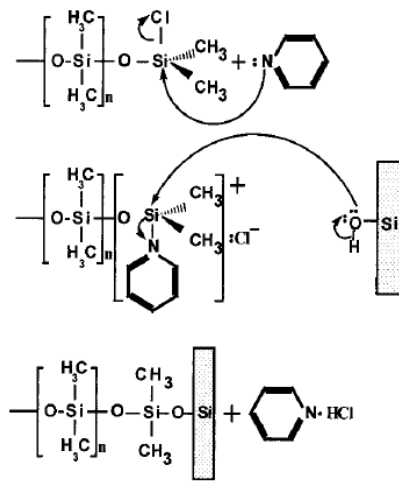


Figure 2. Mechanism for grafting Cl-terminated PDMS on a silicon surface.²¹

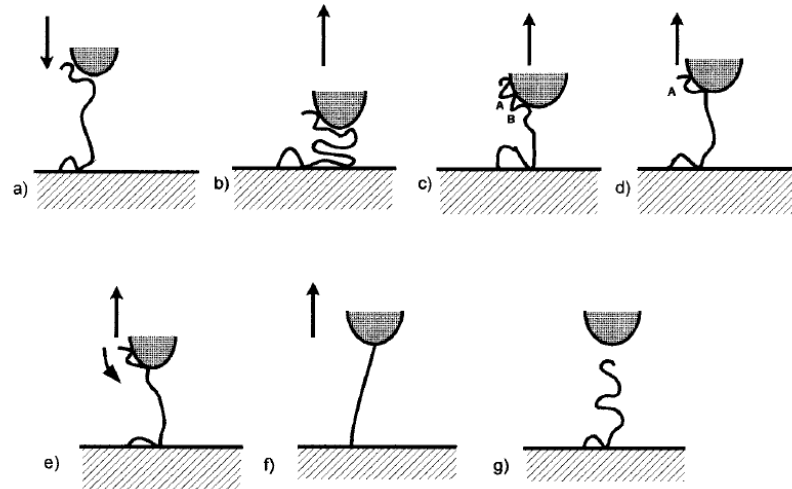


Figure 1. Stages of tip-polymer interaction. (a) Before interaction with the tip, the polymer, grafted to the surface at one end, is in a brush state, again with a small number of monomers on the surface which separate the adsorbed chain into a series of loops and a tail. (b, c) The AFM tip, when it comes into contact with the surface, also creates a collection of contacts with the polymer that lead to a distribution of loops and a tail. Other tip-surface contacts are also formed, whose release may be described by a well-known JKR contact mechanism,²² and are illustrated here. (d, e) The process of separating the tip and surface creates a stress on the polymer chain. This stress is at first released by sliding the polymer chain along one of the surfaces. This causes monomer-surface contacts to collect. (f) At some point of tip separation from the surface, no more stress can be released by such sliding or snakelike motion, and significant stretching of the chain occurs. (g) Finally, complete rupture of the chain from the tip follows, with the sudden rupture of the collected monomer-surface contacts.

Single-Molecule Atomic Force Microscopy

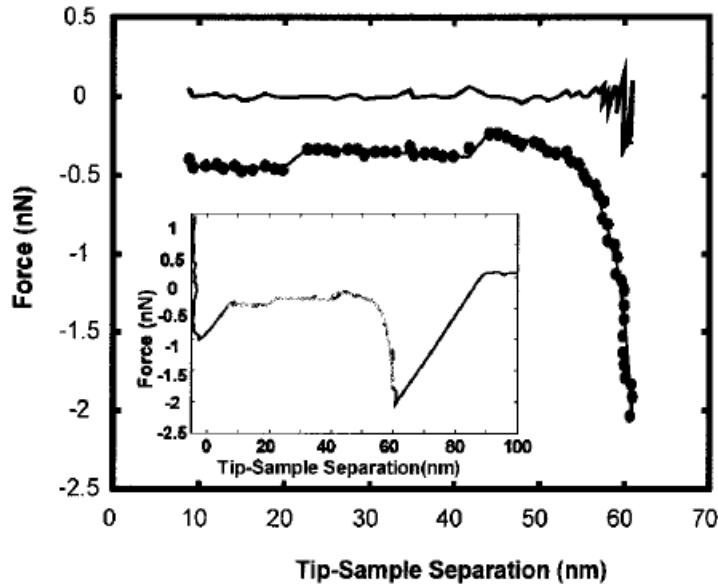


Figure 4. Force plot with a primary adhesion and a secondary adhesion due to PDMS stretching. The flat, steplike profile is caused by the chain sliding on the tip, as described in the text. The persistence length obtained from fitting the hybrid model is 0.13 nm, suggesting that, unlike in Figure 3, a loop is being stretched. The error between the data and the fitted values is indicated by the line above the fitted data. The inset shows the entire force plot.

Model for Nonlinear Extension of the Chain. The extension of the chain can cause non-Gaussian distributions of its end-to-end length. We calculate the forces required to generate such conformations using the wormlike chain (WLC) model. This model describes a polymer chain as consisting of N bonds with fixed lengths l joined in a linear succession. The WLC model maintains the angles at the bond junctions fixed, but the dihedral angles are free to rotate.^{8,9,10a,12,32} The elastic restoring force of the polymer chain, F_{chain} (nN), is calculated as follows:

$$F_{\text{chain}} = \frac{k_{\text{B}}T}{p} \left(\frac{1}{4(1 - r/L_{\text{contour}})^2} - \frac{1}{4} + \frac{r}{L_{\text{contour}}} \right) \quad (2)$$

where r (nm) is the end-to-end distance of the polymer chain, k_{B} is the Boltzmann constant, T is the temperature, p is the persistence length (nm), and L_{contour} is the contour length (nm) of the polymer chain.

Single-Molecule Atomic Force Microscopy

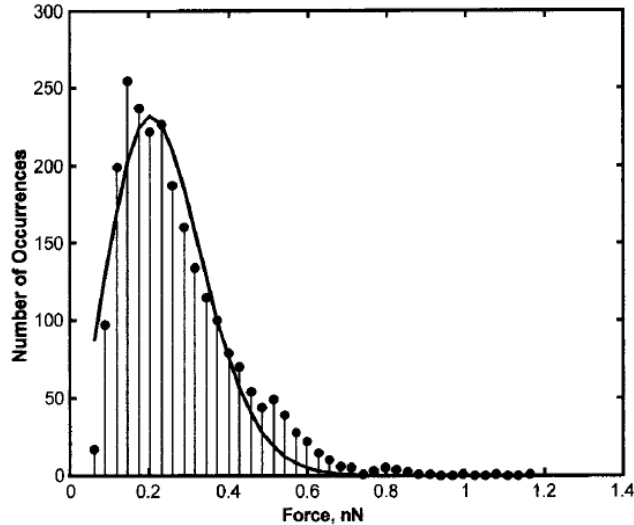


Figure 5. Statistical distribution of polymer stretching rupture forces observed between the AFM tip and the PDMS monolayer at the surface.

Using AFM results of contour lengths (L_i), we convert them to molecular weights using the following equation:

$$M_i = \frac{74L_i}{0.28 \text{ nm}} \quad (3)$$

Here, 74 is the molecular weight of one siloxane monomer and 0.28 nm is the length of one monomer. Average M_n and M_w are calculated as follows:

$$\bar{M}_n = \frac{1}{N} \sum M_i \quad (4)$$

$$\bar{M}_w = \frac{\sum_i M_i^2}{\sum_i M_i} \quad (5)$$

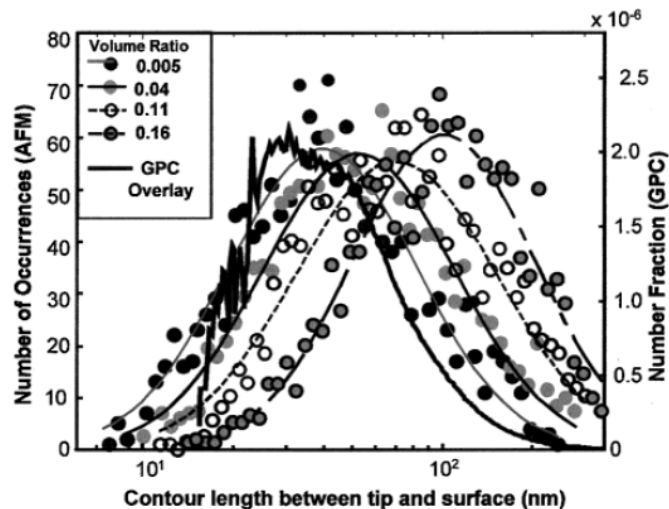


Figure 6. GPC profile overlaid with the AFM statistical distributions of contour length between the tip and surface for different PDMS: CH_2Cl_2 volume ratios indicated in the plot. See the text for further explanation.

Analysis of Swollen Polymer Brush Thicknesses

Alexander-de Gennes model

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Classification
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ADSORPTION OF CHAIN MOLECULES WITH A POLAR HEAD A SCALING DESCRIPTION

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(Reçu le 24 mars 1977, accepté le 4 mai 1977)

Résumé. — L'adsorption de molécules en chaînes à une interface est étudiée en supposant que chaque molécule présente un point d'interaction localisé sur la chaîne (du type tête polaire) et une interaction uniforme de ses monomères avec la surface. Une description en terme de lois d'échelles des configurations de chaînes et des interactions est discutée. L'existence d'une attraction de surface uniforme affecte profondément le diagramme de phase. Un régime bidimensionnel de faible densité et une phase haute densité avec les chaînes confinées dans des cylindres étroits peuvent être rencontrés. La transition entre les deux phases est du premier ordre. Les lois de puissance pour la densité à l'interface, l'épaisseur de la couche et la pression de surface sont dérivées. Le comportement des lipides et agents de surface à chaînes courtes est qualitativement semblable et il est suggéré qu'une interaction de surface uniforme peut aussi jouer un rôle important dans ce cas.

Abstract. — The adsorption of chain molecules at an interface is investigated assuming that the molecule has both a polar head type of attraction localized on the chain and a uniform interaction of the chain monomers with the surface.

A scaling description of the chain configurations and interactions is used. It is shown that the presence of a uniform surface attraction changes the phase diagram drastically. Both a low density two-dimensional regime and a high density phase with the chains confined in narrow cylinders can occur. The transition between the two phases is first order. Power laws for the surface density, layer thickness and surface pressure are derived. The qualitative similarity with the behaviour observed for short chain lipids and surfactants is also noted and it is suggested that a uniform surface interaction may also play an important role there.

Macromolecules 1980, 13, 1069-1075

1069

Conformations of Polymers Attached to an Interface

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ABSTRACT: We discuss the conformations and the concentration profiles for long, flexible chains (N monomers per chain) grafted at one end on a solid surface (fraction of surface sites grafted σ). The chains are immersed either in a pure (good) solvent or in a solution of the same polymer (P monomers per mobile chain, volume fraction ϕ). It is assumed that the polymer does *not* adsorb on the wall surface. The zone occupied by the grafted chain may contain a large fraction of mobile P chains: we call this a mixed case (M), as opposed to the unmixed case (UM). Also the chains may be stretched (S) or unstretched (US). The combination of these two criteria gives four possible regimes. Using scaling laws, we locate the domains of existence of these four regimes in terms of the variables σ and ϕ . High σ values may be hard to reach by grafting but could be obtained with block copolymers at an interface between two immiscible solvents.

Analysis of Swollen Polymer Brush Thicknesses

Alexander-de Gennes model

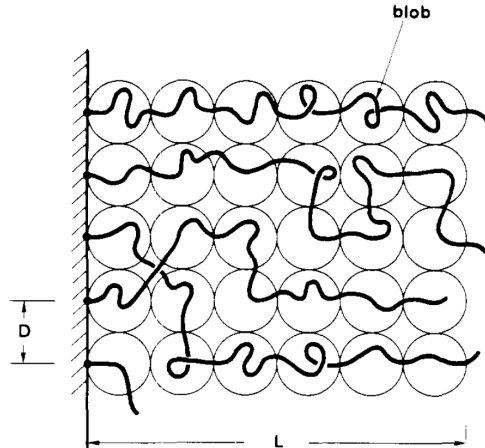


Figure 5. Strongly stretched situation for a grafted layer in good solvent. The chains are mainly stretched along the norm to the wall.

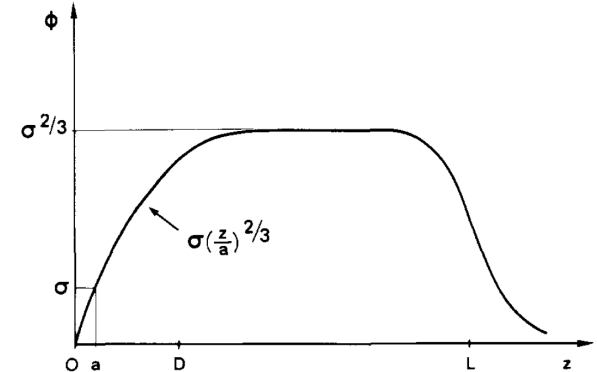


Figure 6. Concentration profile for a grafted layer immersed in a good solvent in the overlapping regime.

P.G. de Gennes, *Macromolecules* **1980**, *13*, 1069-1075

$$\sigma = a^{-2} \cdot \alpha \left(\frac{2n}{1-3n} \right)$$

a = monomer size;
 α = swelling ratio;
 n = solvent quality
 ($n = 0.5$ for θ -solvents)

$$\sigma = a^{-2} \cdot \left(\frac{h_{dry}}{h_{swollen}} \right)^2$$

in a θ -solvent

$$\alpha = \frac{h_{swollen}}{h_{dry}}$$

$h_{swollen}$ and h_{dry} can be obtained, for example, from ellipsometry or AFM

With h_{dry} and σ , M_n follows from:

$$\sigma = \frac{h \rho N A}{M_n}$$

Analysis of Swollen Polymer Brush Thicknesses

Milner-Witten-Cates Model

Macromolecules 1988, 21, 2610-2619

Theory of the Grafted Polymer Brush

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Received October 5, 1987*

ABSTRACT: We calculate the free energy of surfaces coated with grafted polymers in a solvent. We use a self-consistent field (SCF) method appropriate for weak excluded-volume interactions and at moderately high surface coverage. We give the exact solution for the "classical limit" of our SCF equations which shows that, at high molecular weight, the concentration profile approaches a parabolic form rather than the step-function suggested by Alexander and de Gennes. Accordingly, the energy required to slightly compress the brush varies as the cube of the compression distance. An extension of the method to the good-solvent, semidilute regime is described.

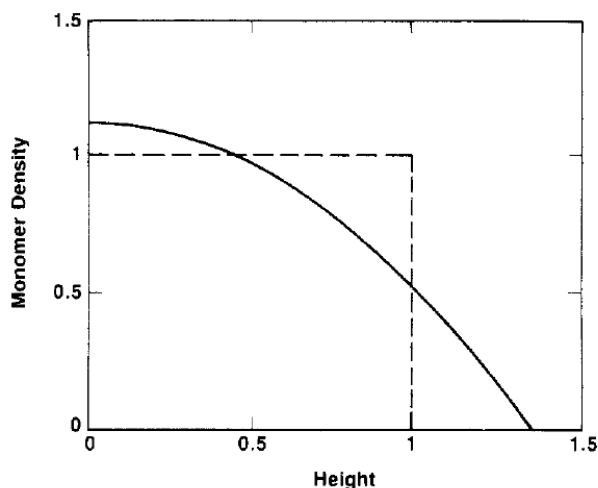


Figure 2. Density profiles $\phi(z)$ of the parabolic brush and the step-function Ansatz at equal coverage σ and molecular weight N .

Analysis of Swollen Polymer Brush Thicknesses

Milner-Witten-Cates Model

Milner-Cates model defines the degree of polymerization as

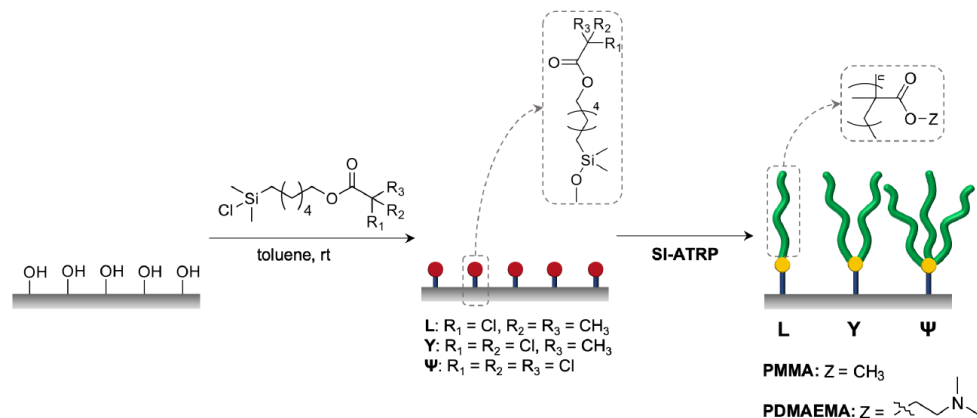
$$N = \left(\frac{\pi^2 M_0 v}{12 \rho N_A \omega} \right)^{1/2} \cdot h_{swollen}^{3/2} \cdot h_{dry}^{-1/2}$$

where M_0 is the monomer molecular weight, ρ the bulk polymer density, $v = (3/a^2)$ with a as the Kuhn length, N_A Avogadro's number, and ω is the excluded volume parameter.

$h_{swollen}$ and h_{dry} can be obtained, for example, from ellipsometry or AFM

With h_{dry} and M_n , σ follows from:
$$\sigma = \frac{h \rho N_A}{M_n}$$

Analysis of Linear, Y- and Ψ-Shaped Brushes



Scheme 1: Synthesis of L-, Y-, and Ψ-shaped PMMA and PDMAEMA brushes via atom transfer radical polymerization from a homologous series of surface-attached initiators.

Table 1: Swelling ratios (α) and grafting densities (σ) of linear, Y-, and Ψ-shaped PMMA and PDMAEMA brushes obtained using the box model to fit ellipsometric data of swollen polymer brushes and by applying the Alexander-deGennes model to determine grafting densities.

		h_{dry} [nm]	$h_{swollen}$ [nm]	α [-]	σ [chains/nm ²]
PMMA	Linear	54 ± 4	187 ± 2	3.4 ± 0.3	0.15 ± 0.02
	Y-shaped	54 ± 5	111 ± 6	2.1 ± 0.2	0.41 ± 0.08
	Ψ-shaped	52 ± 7	152 ± 13	3.0 ± 0.5	0.20 ± 0.06
PDMAEMA	Linear	48 ± 6	224 ± 14	4.7 ± 0.7	0.08 ± 0.02
	Y-shaped	52 ± 1	155 ± 6	3.0 ± 0.1	0.20 ± 0.02
	Ψ-shaped	34 ± 1	135 ± 3.4	4.0 ± 0.2	0.11 ± 0.01

Table 2: Swelling ratios (α), number-average degree of polymerization (N) and grafting densities (σ) of linear, Y-, and Ψ-shaped PMMA and PDMAEMA brushes obtained using the gradient model to fit ellipsometric data of swollen polymer brushes, and by applying the Milner-Cates model to determine number-average degrees of polymerization (N) and grafting densities (σ).

		h_{dry} [nm]	$h_{swollen}$ [nm]	α [-]	N [-]	σ [chains/nm ²]
PMMA	Linear	54 ± 4	260 ± 2	4.8 ± 0.4	6098 ± 255	0.06 ± 0.01
	Y-shaped	54 ± 5	172 ± 10	3.2 ± 0.3	3301 ± 325	0.12 ± 0.02
	Ψ-shaped	52 ± 7	255 ± 31	5.0 ± 0.9	6102 ± 1176	0.06 ± 0.02
PDMAEMA	Linear	48 ± 6	239 ± 17	5.0 ± 0.7	5734 ± 717	0.05 ± 0.01
	Y-shaped	52 ± 1	184 ± 5	3.5 ± 0.1	3691 ± 170	0.08 ± 0.01
	Ψ-shaped	34 ± 1	151 ± 2	4.5 ± 0.2	3430 ± 104	0.06 ± 0.01