

Neutral Brushes Covalently Grafted on OH-Functionalized Mica Surfaces via Surface-Initiated ATRP: Control of Grafting Density and Polymer Chain Length

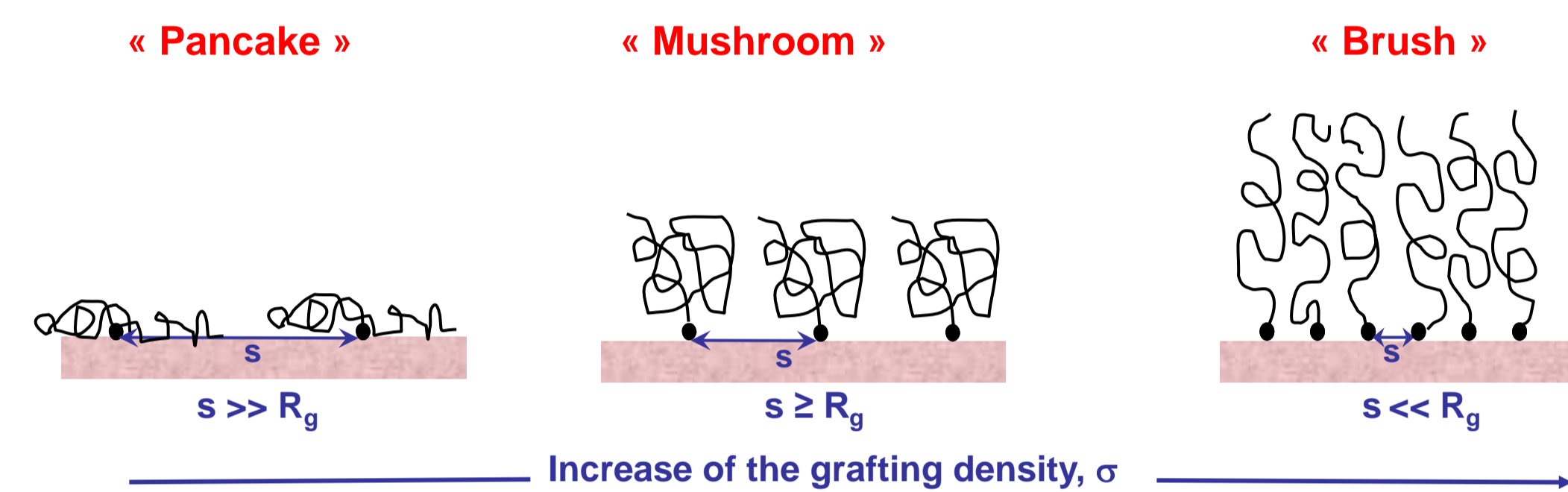
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Introduction

• Design, fabrication and characterization of polymer-bearing surfaces have attracted much attention for many potential applications ranging from nanocomposites to microelectronic devices and biological applications.¹ The different possible chemical and physical structures that polymer chains can exhibit at surfaces represent a very powerful tool to adjust **surface properties** of materials such as wettability, adhesion, lubricity, solubility.

• Surface properties depend highly on the **conformation** of the attached polymer. The conformation adopted by tethered polymers depends on the **grafting density**, polymer molecular weight, the way by which the polymer is attached to the surface, and on environmental stimuli.



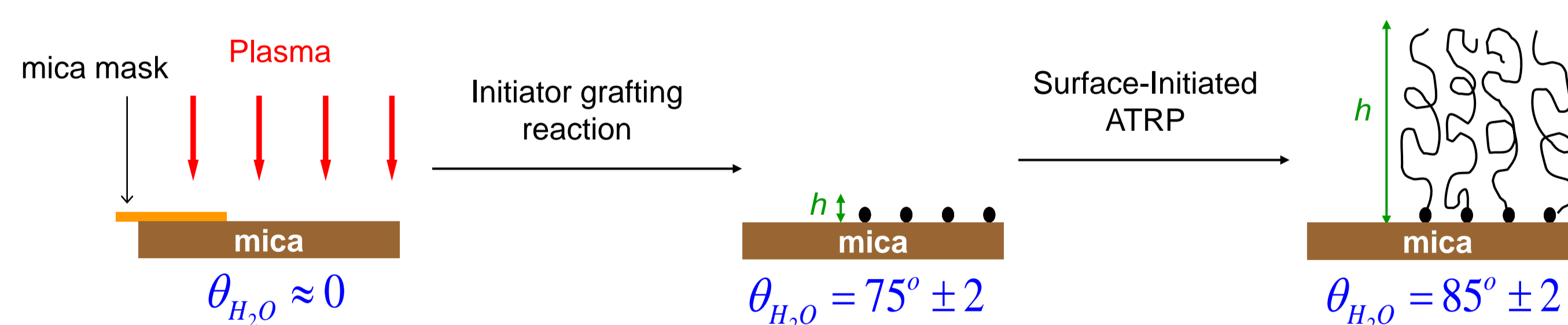
• Among all methods for functionalizing surfaces, **surface-initiated polymerization (SIP)** is the most appropriate approach for chemically binding polymers to substrates along a wide range of grafting densities.²

Objective and Strategies

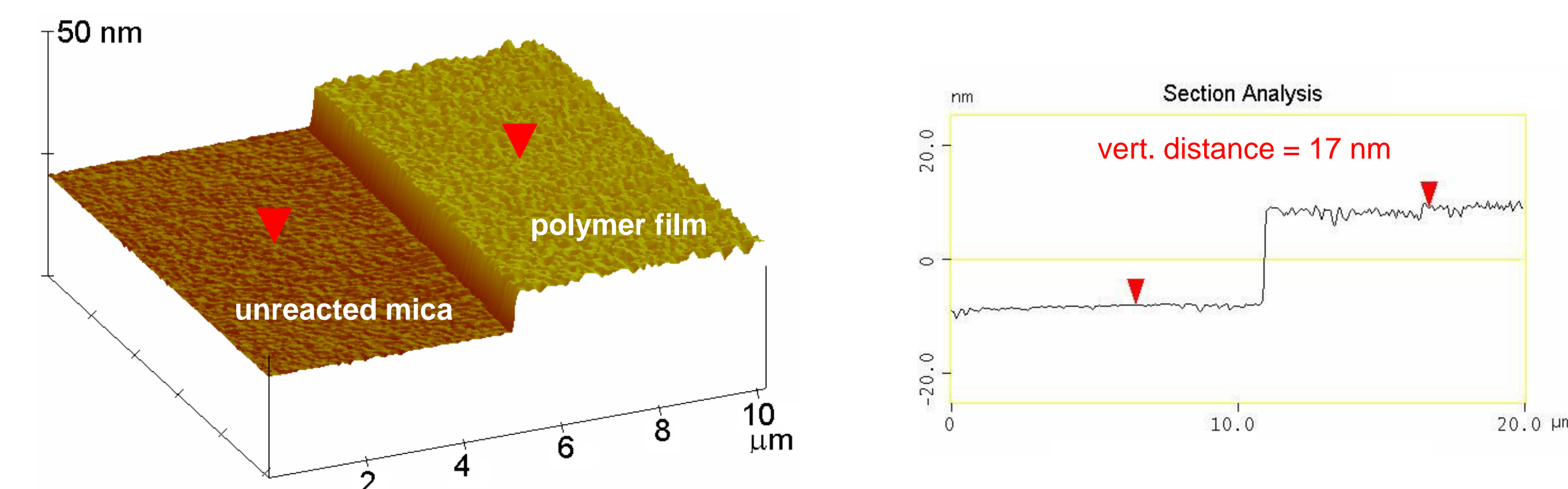
• Our objective is to examine the correlations between physical properties of end-grafted polymers and surface properties for specifically controlling the surface properties. Our work is focused on **friction properties** of end-grafted polyelectrolytes.²

• Molecular interactions between polymer-bearing surfaces and their environment can be studied via force measurement using the **surface forces apparatus (SFA)**. Mica is the most reliable substrate for accurate force measurements.

• To develop robust self-lubricating surfaces, our approach is to **covalently bind polymers on OH-functionalized mica via surface-initiated ATRP**.

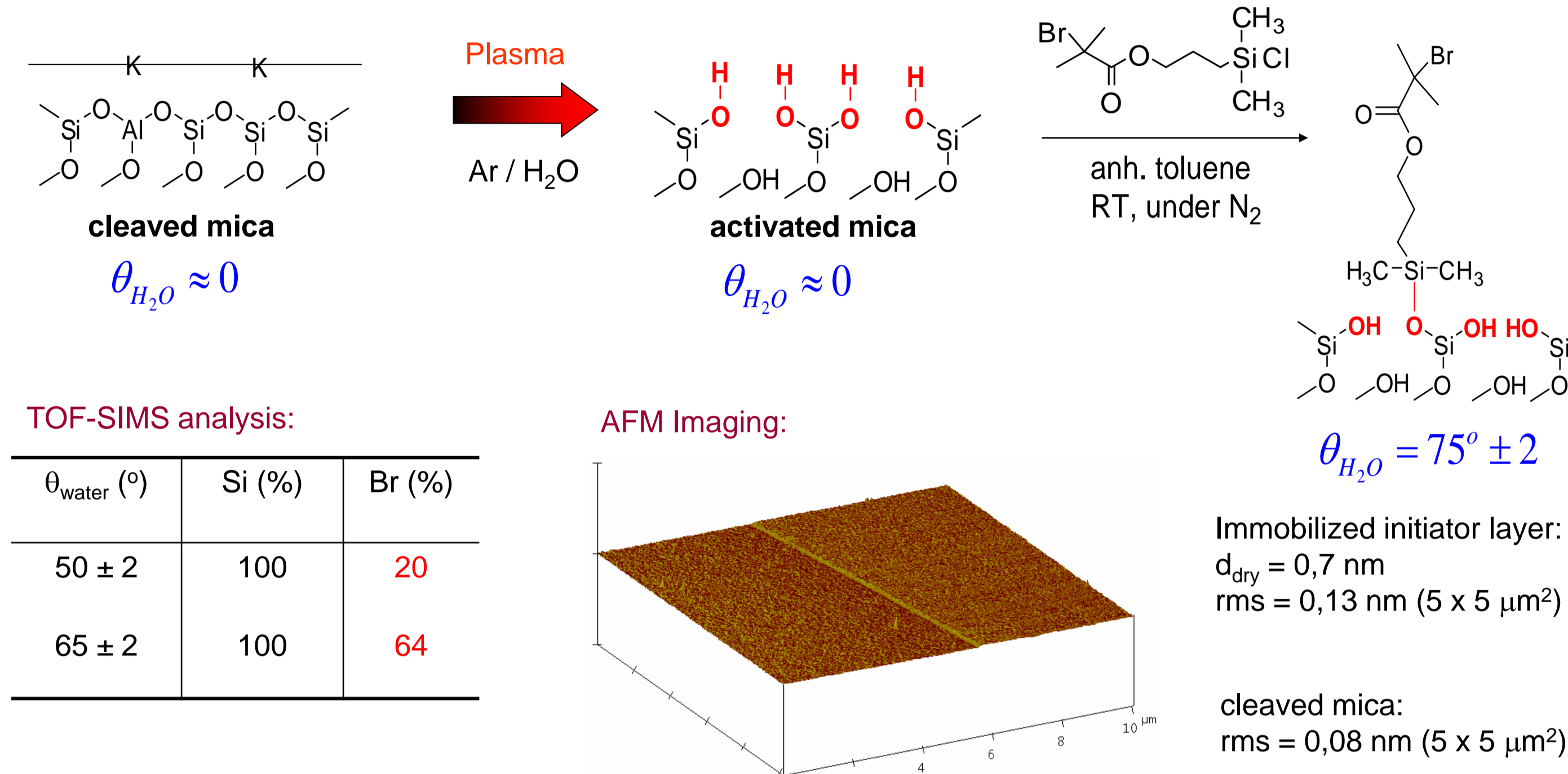


• The thickness of a grafted layer can be quantified by the **step-height method**: a mask of mica protects a cleaved surface from subsequent chemical reactions and by removing it, a step-height difference between the unreacted and the reacted portion of the surface can be measured by AFM.³



Immobilized initiator on mica³

• Mica is chemically inert \Rightarrow **Activation of mica surfaces providing hydroxyl sites** is carried out by plasma discharge in water vapor.⁴

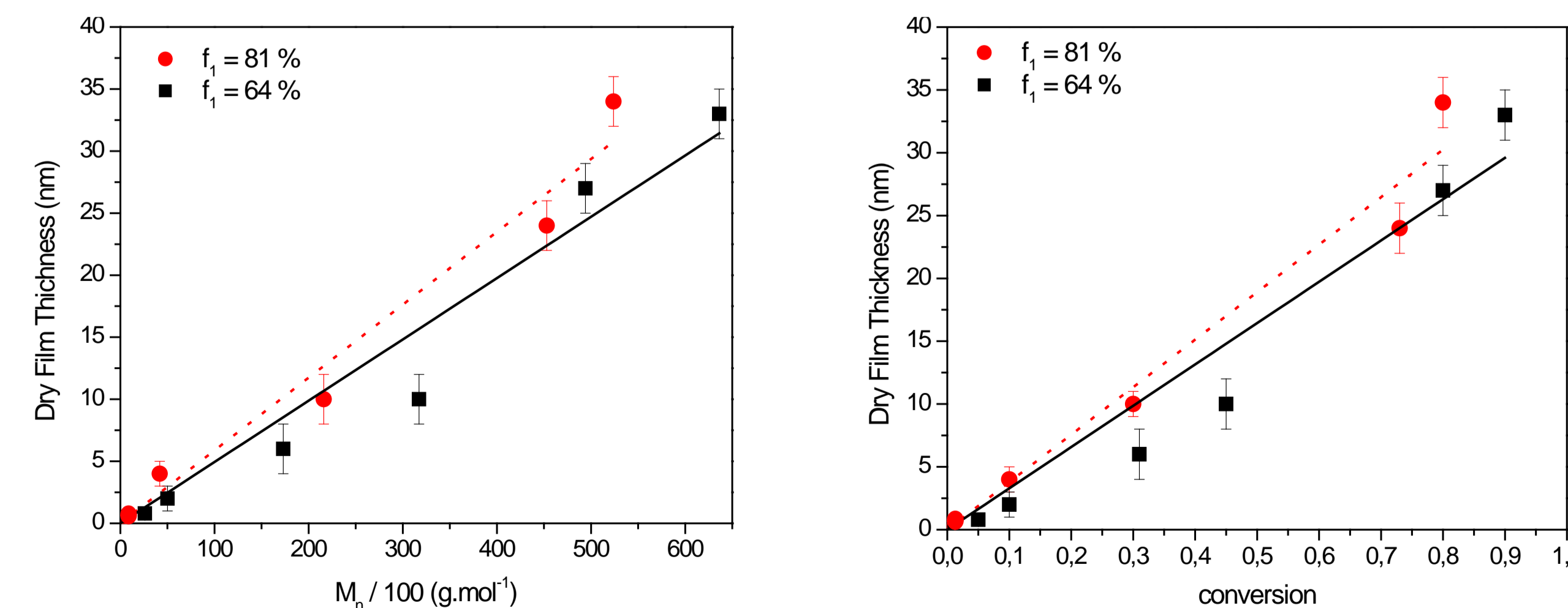


Controlled Surface-Initiated ATRP onto mica

• The thickness of the polymer film is dictated by the concentration of free initiator in solution.

immobilized initiator substrate	ATRP conditions		grafted polymer substrate	
surface coverage (%)	[free initiator] (mM)	M_n of free polymer ($g \cdot mol^{-1}$)	Thickness (nm)	water contact angle (°)
57	20	1870	$0,5 \pm 0,2$	61 ± 2
61	10	17 300	6 ± 1	79 ± 2
63	5	47 000	33 ± 2	84 ± 2

• The polymer film thickness increases linearly with the molecular weight of the “free” polymer and the monomer conversion indicating that **ATRP of grafted PtBA from mica surfaces is well controlled**.



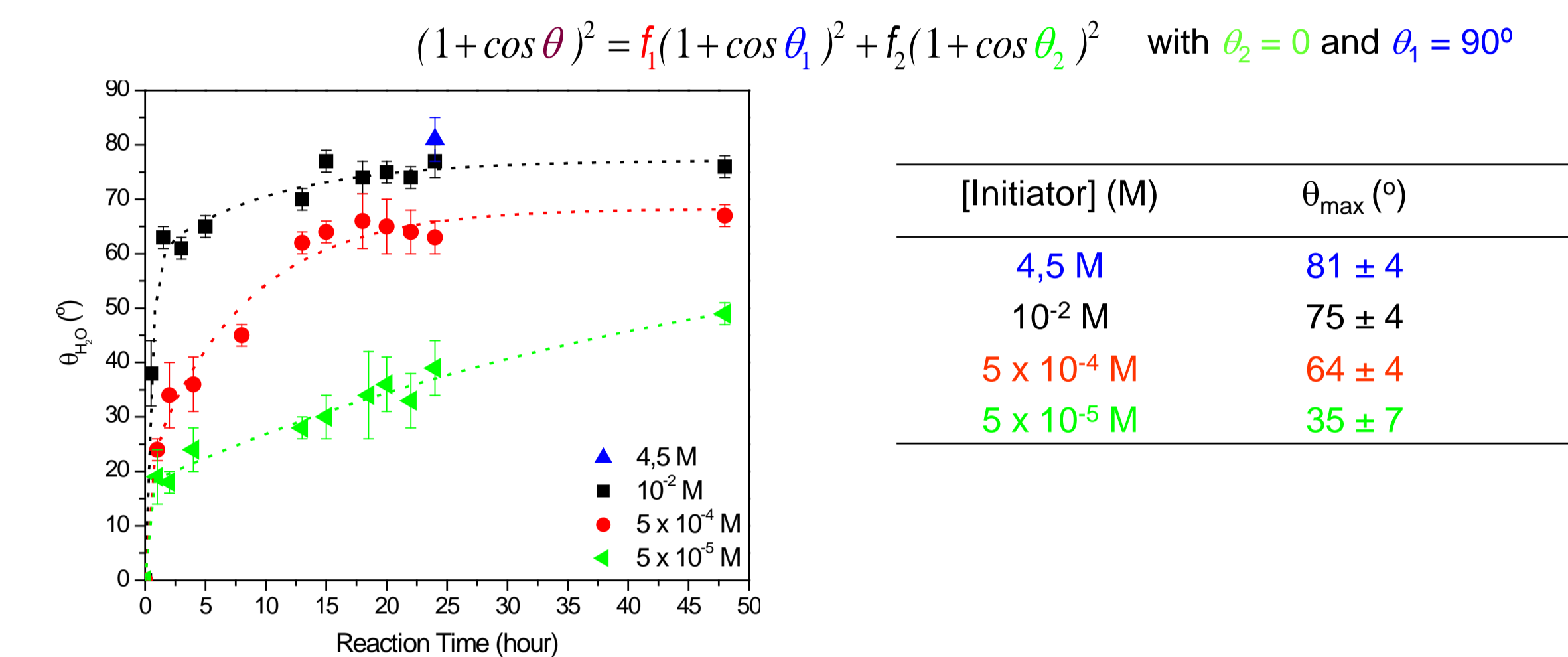
• Surface-Initiated ATRP can be re-initiated allowing further chain extension of pre-existing polymers.

[free initiator] (mM)	Initial film thickness (nm)	Final film thickness (nm)	Increase in film thickness (nm)
5	10 ± 2	10 ± 2	0
3	6 ± 2	17 ± 2	11
1	17 ± 2	31 ± 3	14

Control of the grafting density

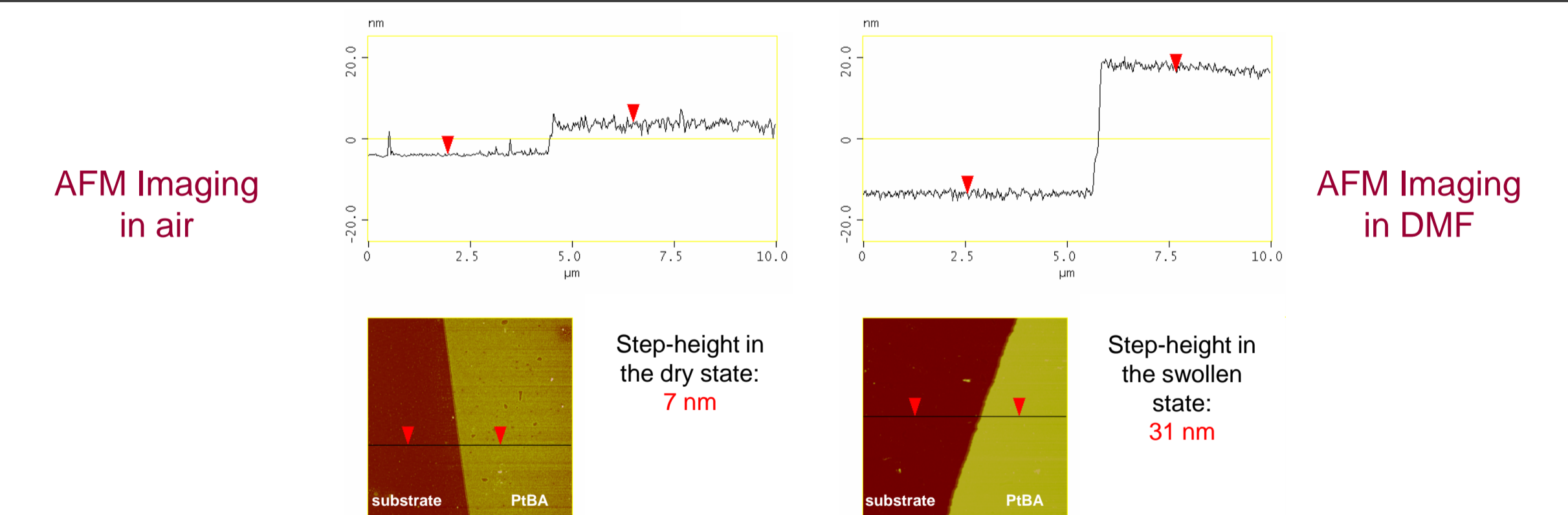
• We developed a new method to tune the initiator density. The **control of the grafting density** is ensured either by the **initiator concentration** or by the **reaction time**.

• The fraction of grafted initiator, f_1 , is determined by water contact angle measurement:



• The initiator surface coverage dictates the **polymer grafting density**.
• The dry thickness of the polymer film increases with increasing grafting density.
• The degree of swelling decreases with increasing grafting density.

immobilized initiator substrate	M_n ($g \cdot mol^{-1}$) ^b	grafted polymer substrate				
θ_{water} (°)	f_1 (%)	θ_{water} (°)	h (nm)	σ ($chain \cdot nm^{-2}$)	% increase in thickness	
			in air	in DMF		
46	38	83	7 ± 2	31 ± 2	0,08	371
66	67	86	27 ± 2	33 ± 2	0,34	22
78	85	84	34 ± 2	36 ± 2	0,41	6



Conclusion & References

- Unprecedented example of surface-initiated ATRP on activated mica substrates to yield **polymers that are covalently grafted onto mica**.
- The **polymer film thickness is controlled** via surface-initiated ATRP in the presence of free initiator in solution.
- The **surface coverage** of the immobilized initiator is **controlled by the reaction time or the concentration**.
- The **polymer grafting density** depends on the immobilized initiator density.

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2. Giasson, S. et al., *Nature* 2003, 425, 163-165
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4. Liberelle, B. and Giasson, S., *Langmuir*, 2007, 23, 9263; Liberelle, B., Banquy X., Giasson, S., *Langmuir*, 2008, 24, 3280

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