Report on
Catalytic Scanning Probe Microscopy for the Complex Nanopatterning of Responsive Polymer Brushes
(project led within the frame of "coopération S&T internationale; bourses post-doc pour chercheurs hors UE; Sélection 2012")

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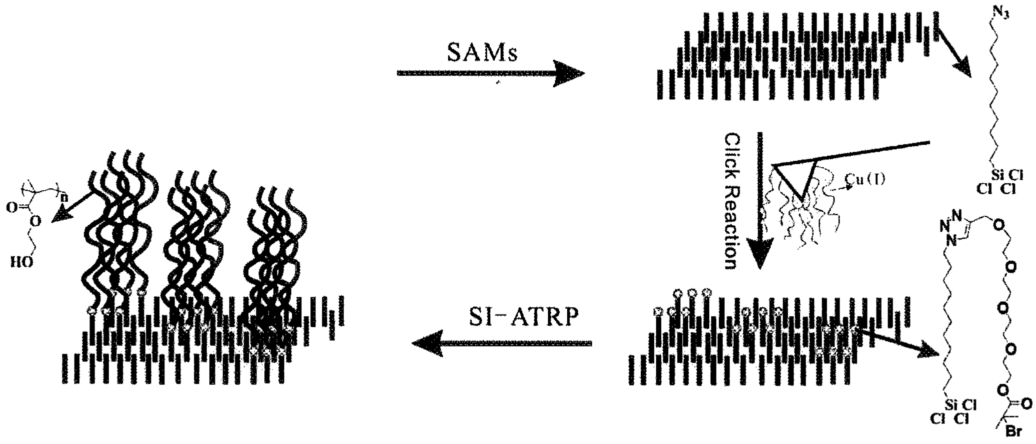
1. Introduction and short summary

This project aims at understanding local catalysis, more precisely catalysis governed by an AFM tip functionalized by metal-ligand compounds grafted in a polymer brush. The selected reaction is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) between a surface bearing azide groups and a propargyl-tetraethylene glycol ATRP initiator; from the clicked initiator, it was planned to grow polymer brushes in a subsequent step, in order to obtain tridimensional nanopatterned functional surfaces (Scheme 1).



Scheme 1. Schematic drawing of the main objectives of the project.

In the first year of the project, we have been working on the project in good compliance with our initial plans. We have mainly concentrated on the fabrication of the catalytic surfaces, and started first tests of local catalysis by AFM. It was planned to perform more detailed investigations of AFM catalysis next year; however, because Dr. Qian Ye has to go back to China earlier than planned, in order to apply for a position of associate professor, this part of the project will not be performed at this stage.

More specifically, the planned first steps of the project involved :

1. the preparation and characterization of AFM tips grafted by a catalytic brush;
2. the synthesis and characterization of the azide-ended monolayers to be used for the local reaction, as well as of the ATRP clickable initiator;
3. the realization of first SPM catalysis experiments at different scanning rates, forces, times of application, temperatures and solvents.

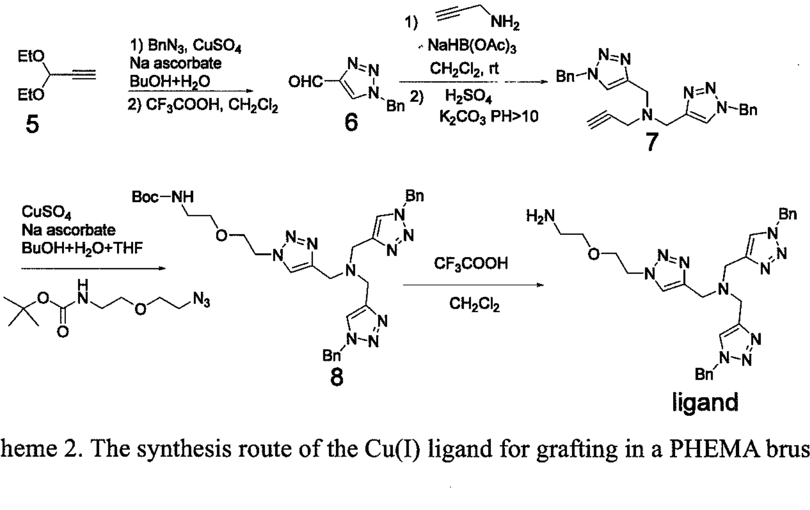
These steps were successfully performed or started. Indeed,

1. we have synthesized a ligand for complexing copper (I) in polymer brushes, then coupled it to polymer brushes grafted from AFM tips and flat Si wafers;
2. we have finished the synthesis and characterization of the azide-terminated monolayers on surfaces specially patterned for easing monitoring during AFM experiments; we have also synthesized the clickable ATRP initiator;
3. we have started AFM catalysis experiments at different scanning rates, forces, different concentration of alkyne initiator solution and different solvents (methanol, DMF and water), etc.

Details on these steps are given below.

2. The synthesis of the copper(I) ligand

In order to obtain Cu (I)-terminated AFM probes, we need first to synthesize the proper ligand, capable to complex Cu(I) and to be grafted in a polymer brush. The synthesis route is given in Scheme 2 :



Scheme 2. The synthesis route of the Cu(I) ligand for grafting in a PHEMA brush.

The different steps of the synthesis are described below :

1.1. 1-Benzyl-1H-1,2,3-triazole-4-carbaldehyde (6)

1-Benzyl-4-(diethoxymethyl)-1H-1,2,3-triazole diethylpropargyl acetal (4.90 g) and benzylazide (6.50g) were dissolved in a 1 : 1 mixture of t-BuOH/H_2O (32.0 mL). To this solution, sodium bicarbonate (0.48 g), copper(II) sulfate pentahydrate (0.48 g), and sodium ascorbate (1.50 g) were added, and the mixture was stirred at room temperature. After 16 h, EtOAc (100 mL) was added, and the organic phase was washed with saturated sodium bicarbonate (2x100 mL), brine (1x100 mL), dried over magnesium sulfate, and concentrated on a rotary evaporator. A crude product was used in the next step without purification.

To a solution of aforementioned crude product in CH_2Cl_2 (25 mL), 10 mL water and 2.5 mL TFA was added. The reaction mixture was stirred for 6 h at room temperature. EtOAc (100 mL) was added, and the organic phase was washed with saturated $NaHCO_3$ (3x100 mL), brine (1x100 mL), dried over MgSO4, and the solvents were removed and obtained the product as a beige solid (7.05 g, 98% over 2 steps).

1.2. N,N-Bis[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]prop-2-yn-1-amine (7)

Propargylamine (0.25 g) and 6 (1.88 g) were stirred in CH_2ClCH_2Cl (50 mL). Sodium triacetoxyborohydride (2.50 g) was added. After the addition, the reaction was stirred at room temperature for 2 days. The mixture was then treated by 0.5mol/L H_2SO_4 (60 mL), and stirred for 15 min until all excess borohydride was quenched. The reaction was adjusted to be PH>10 with K_2CO_3 and water, and stirred well. The organic phase was separated and extracted with CH_2Cl_2 (3x100 mL), and the combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude solid, which was then purified by column chromatography to give a white powder (1.12 g, 62%).

1.3. BOC-ligand (8)

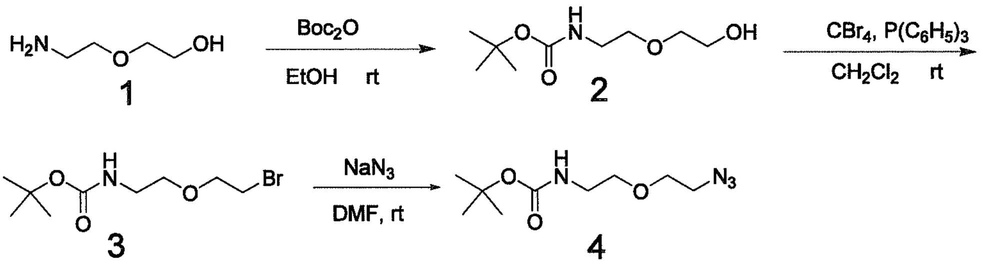
The product (7) 500 mg and the product (4) 333mg were dissolved in a 1: 1: 1 mixture of t-BuOH/H_2O/THF (18 mL). To this solution, copper(II) sulfate pentahydrate (16mg), and sodium ascorbate (50 mg) were added, and the mixture was stirred at room temperature for overnight. After 16 h, EtOAc (100 mL) was added, and the organic phase was washed with saturated sodium bicarbonate (2x100 mL), brine (1x100 mL), dried over magnesium sulfate, and concentrated on a rotary evaporator. A crude product was purified by column chromatography to give 720mg product (91%).

1.4. The target product-ligand

To a solution of the above product BOC-ligand (200mg) in 10 mL anhydrous

CH_2Cl_2 at room temperature was added TFA (0.24ml) portion wise. The mixture was stirred for overnight. After completion of reaction evidenced by TLC analysis, the solvent was washed with saturated K_2CO_3 solution (50ml) and extracted with CH_2Cl_2, dried over magnesium sulfate. The mixture was filtered and the filtrate was concentrated to obtain product 141mg (97%).

This reaction scheme required the synthesis of tert-butyl 2-(2-azidoethoxy)ethylcarbamate (4), which is described below (Scheme 3) :



Scheme 3. The synthesis route of tert-butyl 2-(2-azidoethoxy)ethylcarbamate

1.5. tert-butyl (2-(2-hydroxyethoxy)ethyl)carbamate (2)

*To a solution of 2-(2-aminoethoxy)ethanol 1 (1.0 g) in anhydrous EtOH (20 mL) was added Boc_2O (2.18 g) at 0 °C. After stirring at room temperature for 2 h, the mixture was evaporated and then extracted with CH_2Cl_2 (3x20 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under vacuum to obtain the product **2** as a colorless oil (1.93 g, 99%).*

1.6. tert-butyl3-bromopropylcarbamate (3)

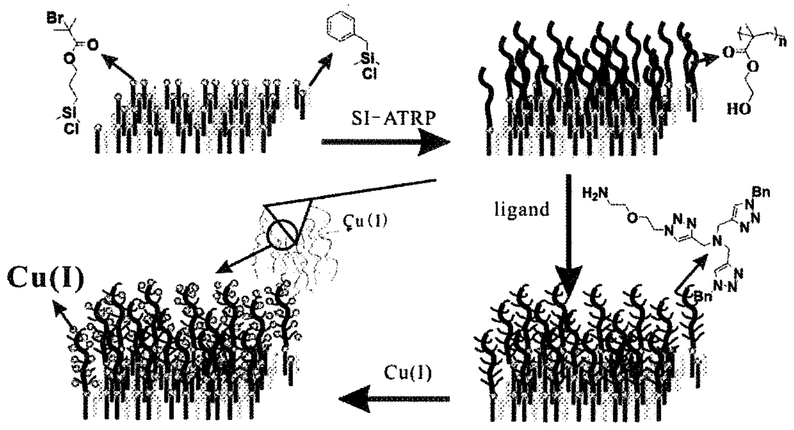
*To a solution of tert-butyl (2-(2-hydroxyethoxy)ethyl)carbamate (2) (5 g) in dichloromethane (200 mL) was added triphenylphosphine (9.63 g) followed by carbon tetrabromide (12.18 g) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography to give the product **3** (4.9g, 70.7%).*

1.7. tert-butyl 2-(2-azidoethoxy)ethylcarbamate (4)

*To a solution of tert-butyl3-bromopropylcarbamate (3) (1.49 g) in DMF (5.5 mL) was added sodium azide (431mg) at room temperature. The reaction mixture was heated to 70°C and stirred for 24 h, The mixture was evaporated with H_2O (9x50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under vacuum to obtain the product **4** as colorless oil (1.27 g, 99%).*

3. Functionalization of the AFM tip with the ligand grafted in a brush

In order to obtain Cu(I)-terminated AFM probes, we need to modify the AFM tip with a polymer brush before linking the ligand in the brush, and incorporating Cu(I). The route we developed is given in Scheme 4. Details on each step are given in the sequel. Of note, the synthesized catalytic brushes grafted onto flat Si wafers were also tested as catalysts; a publication on this topic is currently in preparation.



Scheme 4. The functionalization of AFM tip with ligand

3.1. The synthesis of ATRP initiator

Allyl-2-bromo-2-methylpropionate (0.3 mL) was mixed with dimethylchlorosilane (2 mL) in a flame dried Schlenk flask. Chloroplatinic acid (6 mg) was added to the solution and the reaction mixture was stirred at room temperature under nitrogen in the dark for 24 hours. The crude reaction mixture was purified by vacuum distillation after the reaction completed monitored by NMR.

3.2. AFM tip pretreatment and modification

The AFM tip were cleaned by plasma etching and then immediately installed in a Teflon holder and transferred into a Schlenk tube. The whole system was sealed and heated at 80°C. Three cycles of vacuum/Ar were performed. The ATRP initiator (20 μL) was then injected and the reaction was carried out at 80°C for 2 h. The AFM tips were removed, rinsed with toluene, and dried under a flow of nitrogen.

Different ratios of ATRP initiator silane:benzylchlorodimethylsilane were tested (10:0, 7:3, 5:5 and 3:7), in order to obtain polymer brushes of varying grafting densities.

3.3. Grafting poly(2-hydroxyethyl methacrylate) (PHEMA) polymer brushes on AFM tip via Surface-Initiated Polymerization

In a typical SI-ATRP, 15 mL of HEMA monomer and 15 mL of deionized *water mixture were placed in a Schlenk tube under Ar flow for 15 min; then, 206 mg of CuCl, 135 mg of* $CuBr_2$ *and 915 mg of bipyridyl were added into the Schlenk tube and purged with Ar flow again; The solution was stirred under Ar for 15 min until a homogeneous dark-brown solution formed.*

A tube containing AFM tip-initiator were sealed and subject to three vacuum/Ar cycles. The growth of the polymer brushes was initiated by the injection of the previously described solution (2.5 mL solution per sample). 5h later, the AFM tips were taken out of the polymerization solution and washed with deionized water and methanol, then dried under a flow of nitrogen.

3.4. Incorporation of the ligand

Reactions were performed in a glove box. The PHEMA-AFM tips were immersed in a solution of N,N'-disuccinimidyl carbonate (DSC; 0.10 mmol per AFM tip) and Et_3N *(0.20 mmol per AFM tip) in DMF (2.5 mL per AFM tip)for 24 h. The samples were then removed, washed with DMF, and immersed into a solution containing ligand (0.015 mmol per AFM tip) and* Et_3N *(0.05 mmol per AFM tip) in DMF (2.5mL per AFM tip). After 24 h of reaction, the samples were washed thoroughly with DMF, deionized water and methanol, then dried under a flow of nitrogen, to give ligand-PHEMA-AFM tips.*

3.5. Incorporation of CuCl

The AFM tips (ligand-PHEMA-AFM tips) were immersed in a solution of CuCl (0.05 mmol per AFM tip) in THF (3 mL per AFM tip) for 3h. The samples were then removed and washed with THF, deionized water and methanol, then dried under a flow of nitrogen.

3.6. The characterization of these samples

We have conducted all experiments on silicon wafers for characterization purposes, because AFM tips are too small to be monitored. Various characterization techniques including ellipsometry, X-ray reflectivity (XRR) measurements, and X-ray photoelectron spectroscopy were used to characterize Cu(I)-ligand-PHEMA-Si wafers.

Table 1. Average thickness of PHEMA-Si, ligand-Si and Cu(I)-ligand-Si samples for different (ATRP silane:benzyl silane) ratios (in order to tune the chain grafting density of the brush).

	ATRP silane:benzyl silane ratios			
Average thickness (nm)	100:0	70:30	50:50	30:70
PHEMA-Si	58	39	32	26
Ligand-PHEMA-Si	98	73	76	44
Cu-ligand-PHEMA-Si	116	83	87	50

Table 1 provides the average thickness for PHEMA-Si, ligand-PHEMA-Si and Cu(I)-ligand-PHEMA-Si samples for various (ATRP silane : benzyl silane) ratios (100:0, 70:30, 50:50, 30:70), as obtained by ellipsometry. From the table, we can see clearly that the thickness increases when modifying the PHEMA-Si surface with ligand and incorporating Cu(I), indicating the proper incorporation of the various components along the synthesis pathway

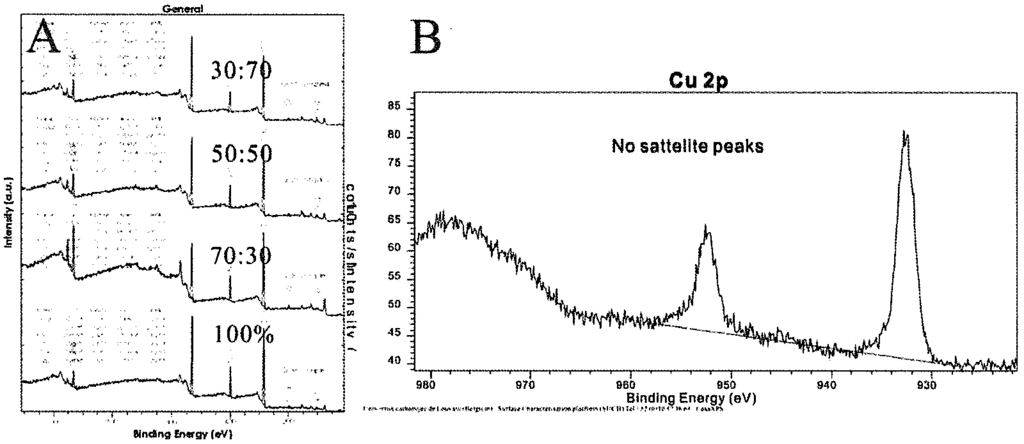


Figure 1. (A) XPS survey spectra of Cu(I)-ligand-PHEMA-Si samples for different (ATRP silane : benzyl silane) ratios (100:0, 70:30, 50:50, 30:70). (B) High-resolution XPS spectrum of the Cu(I) 2p region of Cu(I)-ligand-Si samples.

Successful polymer grafting and Cu(I)-ligand complexation were also proved by XPS. Figure 1A displays the XPS spectra of Cu(I)-ligand-brush-Si samples at different ratios. Surface chemical composition data of these surfaces are summarized in Table 2. Successful linking of ligand and loading of Cu(I) were confirmed by the presence of N and Cu(I) 2p signals. Moreover, the number of Cu(I) loaded per ligand can be obtained from the ratio of Cu/N as listed in Table 2; two Cu(I) are computed for each ligand for the sample (100%), three Cu(I) for each ligand for the samples (70:30) and (50:50), and only one Cu(I) for each ligand for the sample (30:70). These variations indicate that the complexing of Cu onto the ligand is not trivial, but occurs substantially in all samples.

Table 2. Surface analysis results of Cu(I)-ligand-brush-Si samples for different (ATRP silane : benzyl silane) ratios (100:0, 70:30, 50:50, 30:70).

Sample	XPS atomic concentration (%)			
	[Cu]	[N]	[N/11]	[Cu/ligand]
100:0	1.9	10	0.91	2.1
70:30	3.2	10.1	0.91	3.4
50:50	2.7	9.4	0.85	3.1
30:70	0.9	7.9	0.71	1.3

4. Preparing the azide-monolayer grafted on a patterned surface

In an AFM tip catalysis experiment, the catalytic tip is scanned over the substrate to initiate a local reaction. Afterwards, the surface is rinsed and dried before being imaged with the AFM. As the produced drawing are relatively small (ca. 10 µm long lines), it is important to build some landmarks on the substrate surfaces to find easily the places where the catalysis was attempted; therefore, we prepared patterned surfaces functionalized by an azide monolayer, as described below.

4.1. The preparation of patterned surfaces

We have used a TEM grid to reproduce its grid on silicon squares. (1) 200nm thick silicon oxide was grown on a silicon wafer. (2)Then the wafer was diced into 1 cm^2 *squares and the TEM grid was stuck on each sample surface with carbon tape. (3) 20 nm chromium layer was evaporated on the samples. (4) TEM grids were removed and the substrates were rinsed with acetone to remove the residual carbon tape. The silicon oxide was removed via plasma (HF), while the Cr-protected layers were not affected. (5) Finally, the chromium layer was removed with standard chromium etchant for 2 h, then washed with deionized water and methanol, then dried under a flow of nitrogen. The resulting pattern is shown in Figure 2. Each array is identified by a letter.*

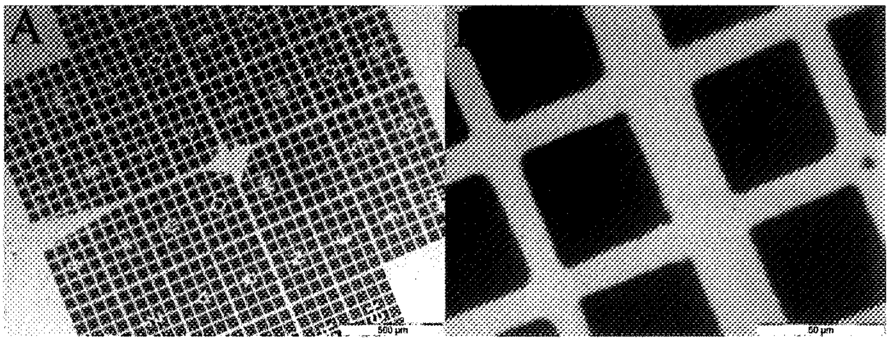
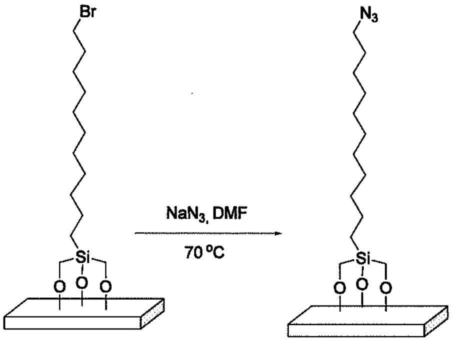


Figure 2. The substrates were patterned with TEM grids to form arrays of protruding SiO_2 squares identified by a letter.

4.2. Preparation of the azide-monolayer grafted substrate surface (Scheme 5)

The resulting pattern surfaces were immersed in a piranha bath (Caution! Handle with care, piranha can cause severe burns) for 45 min (H_2SO_4 *(98%)/*H_2O_2*(30%)) and then washed with Milli-Q water, dried with nitrogen. Reactions were performed in a glove box. Each patterned substrate was functionalized by immersion in 3 ml toluene solution of 11-bromoundecyltrichlorosilane (1 µL/mL) in distilled toluene at room temperature for 2h. After reaction, the samples were washed with toluene and dried with nitrogen (the thickness was 1.5 nm by XRR). Then the samples were* *put into 0.1 mol/L anhydrous DMF of sodium azide in a glove box at 70 ^{o}C. After 60 h of reaction, the samples were removed and washed with DMF, deionized water and methanol, then dried under a flow of nitrogen, to give azide-monolayer-patterned surfaces (the thickness was 1.3 nm by XRR on flat wafers).*

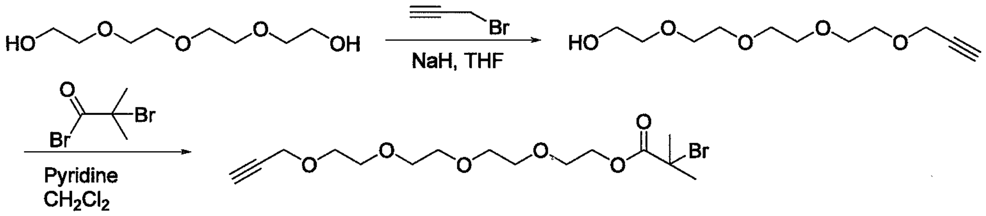


Scheme 5. The preparation of azide-monolayer on patterned surfaces

5. AFM catalysis

In order to seek suitable conditions for the AFM reaction, we first performed the click reaction in homogeneous conditions on azide monolayer-grafted Si wafers, with a copper catalyst dissolved in ethanol. The clicked molecule was an ATRP initiator bearing an alkyne group on one end, whose synthesis is described below. Next, we started the study of the local clicking of this initiator on the azide monolayer, using the copper/ligand catalytic complex immobilized on an AFM tip. Details are given in what follows.

5.1. The synthesis of the alkyne initiator



Scheme 6. The synthesis route of the alkyne initiator

To a solution of 6 g tetraethylene glycol in dry THF at 0°C under nitrogen atmosphere, 1.36g of 60% NaH in oil was carefully added and after 15 min, 3.79 ml of 80% toluene solution of propargyl bromide was slowly added. Mixture was stirred at 0°C for another 3 h, and then allowed to warm to room temperature for overnight. Then solvent was evaporated and residue extracted with ethyl acetate and after removal of the solvent product was purified using flash chromatography on silica gel. (yield 3.75g, 52%). To a solution of 1.5 g *the above product in dry CH_2Cl_2 (65 ml) at 0°C under nitrogen atmosphere, 0.77 ml pyridine and 0.98 ml 2-bromoisobutyl bromide were carefully added slowly. Mixture was stirred at 0°C for 30min, and then allowed to warm to room temperature for overnight. Then solvent was evaporated and this crude product was purified by column chromatography to give target product alkyne initiator (2.47g, 98%).*

5.2 Homogeneous click reaction on an azide monolayer-grafted Si wafer

The azide-monolayer-Si surfaces were immersed in a solution of alkyne initiator (5 mmol per sample) in ethanol (3 mL per sample), then $CuSO_4$ was added (0.1 mmol per sample) together with sodium ascorbate (1 mmol per sample). After 5h of reaction, the samples were washed thoroughly with methanol, deionized water and methanol and immersed into EDTA/NH_4OH solution for 5 min before drying under a flow of nitrogen (the final thickness is 2.3 nm by XRR, showing that the grafting occurred but was moderate). From these surfaces, a PHEMA brush was grown by ATRP, obtaining a final thickness of 52 nm, showing that the initiator was properly clicked on the surface.

5.3. Local AFM catalysis experiments

With all the elements in hand, we then started to study local catalysis. To this end, we grew a PHEMA brush from an AFM tip, and modified it by the Cu(I)/ligand system. We then used this tip to perform catalytic tests; the characterization of the resulting surfaces in reading mode is presented in Figures 3 to 7, after experimental details .

Experimental details :

(1)Cu (I)-ligand were attached to V-shaped Si3N4 cantilevers and to their tips via PHEMA brushes activated with DSC as described above. (2) Depending on the alkyne to be reacted on the azide monolayer and on the experiment to be performed, two different concentrations (5mmol and 50mmol) alkyne initiator solutions were prepared and used in preliminary tests.

In a representative AFM nanolithography experiment, AFM catalysis and AFM characterizations were performed at identical positions before and after each indicated chemical treatment. In our experiment, the solvent in the AFM cell was 50 mM EtOH-H_2O and DMF-H_2O solution of alkyne initiator and 1-2 x 1-2 mm^2 squares (256 lines per square) were scanned in contact (writing) mode with a constant rate of 2µm/s or 4µm/s with a gradually increased force (ca. 20, 40, 60, 80 and 100 nN).

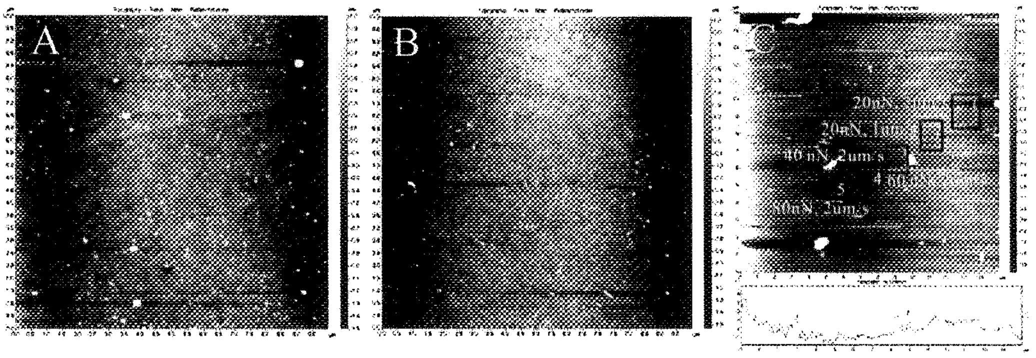


Figure 3. AFM topography of patterned surfaces. (A) azide monolayer; (B) and (C) Topography images after writing 1µmx1µm squares at different scan rates and forces in EtOH-H_2O solution using a bare AFM tip.

As shown in Figure 3, we can see that the patterned surfaces are very flat before and after modification with the azide monolayer. When we wrote 1 µm x 1 µm squares over the azide monolayer- surface using a bare AFM tip at different scan rates and forces in EtOH-H_2O solution, the bare AFM tip may destroy the surface and then remove the monolayer, although signs of such a mechanical degradation were only seen above a force of 60 nN.

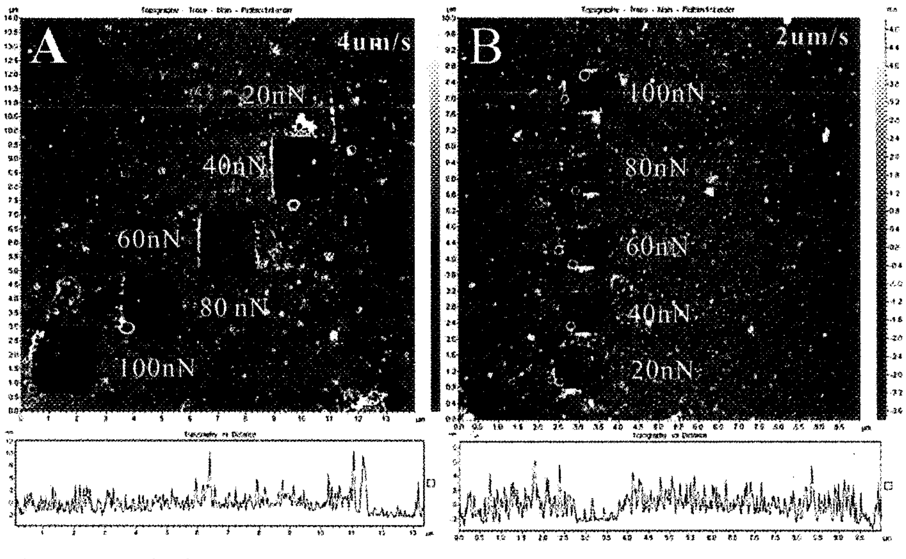


Figure 4. Topography image: 2 µm x 2 µm squares written at different forces in 5mmol alkyne initiator using a Cu(I)-functional AFM tip in EtOH-H_2O (1:1) solution (A) and DMF-H_2O (1:1) solution (B).

We have then tried to write squares at different forces in 5mmol alkyne initiator using a Cu(I)-functional AFM tip in different mixture solutions (EtOH-H_2O and DMF-H_2O). Five different scan forces were tested (20, 40, 60, 80, 100 nN) and the result showed that the surface was etched away by the tip. Since this was not seen in the absence of alkyne initiator, we hypothesized that the alkyne initiator adsorbs on the surface, and is removed locally by the scanned tip. We also changed the scan rates (five different scan speeds were tested) and the results remained the same (Figure 5).

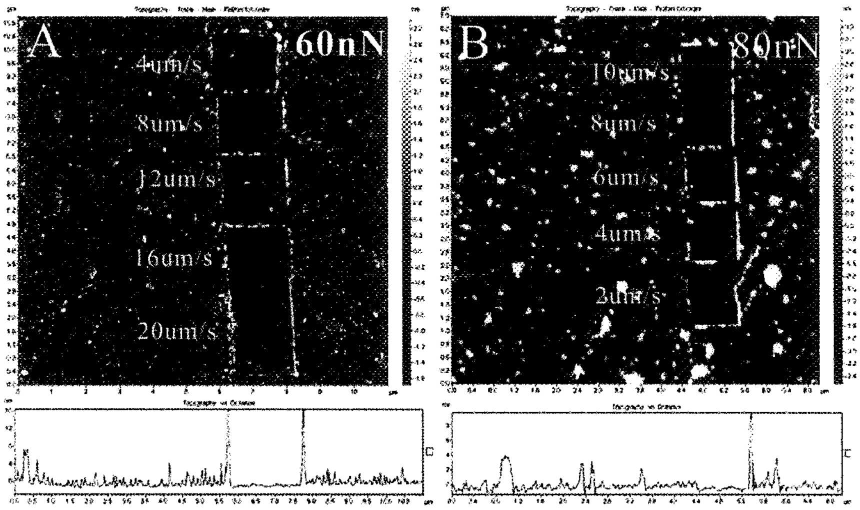


Figure 5. Topography images: 2 μm x 2 μm squares written at different scan rates in 5mmol alkyne initiator using a Cu(I)-functional AFM tip in EtOH-H_2O (1:1) solution (A) and DMF-H_2O (1:1) solution (B).

We have also tried to change the alkyne initiator concentration from 5 mmol to 50 mmol and then wrote squares at different force and scan rates in different solutions (EtOH-H_2O and DMF-H_2O) using a Cu(I)-functional AFM tip. The results (Figure 6 and Figure 7) showed a local modification in the phase images, but did not indicate topographical changes. These experiments thus require further investigations before conclusions be drawn.

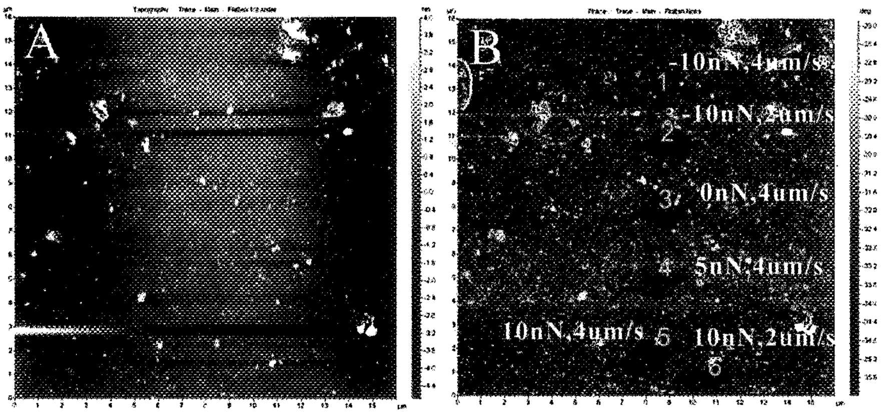


Figure 6. Topography A and phase B images: 2 μm x 2μm squares written at different scan rates and forces in 50 mmol initiator EtOH-H2O solution (1:1) using a Cu(I)-functional AFM tip.

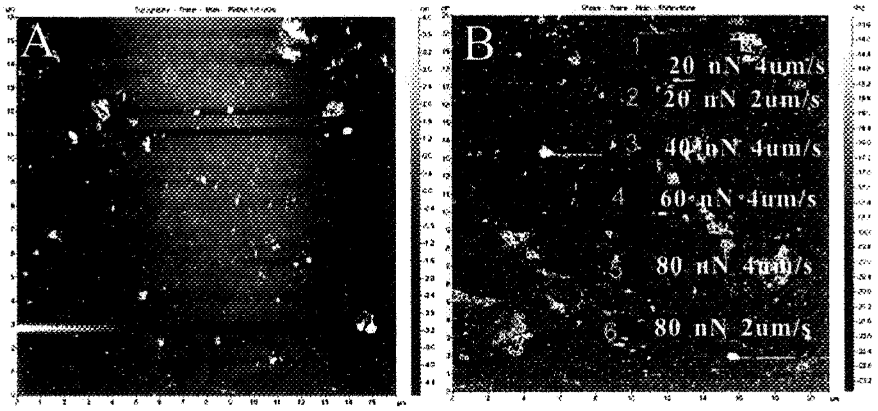


Figure 7. Topography A and phase B images: 2 µm x 2µm squares written at different scan rates and forces in 50 mmol initiator DMF-H2O solution (1:1) using a Cu(I)-functional AFM tip.

Conclusions and perspectives

Summing up, we have prepared polymer brushes including a copper(I) ligand, which we have successfully grown both from flat Si surfaces and from AFM tips. In parallel, we have prepared a clickable ATRP initiator, which we have clicked in the presence of Cu(I) onto azide self-assembled monolayers. We have also successfully grown polymer brushes from this clicked ATRP initiator. Then, we have attempted to use similar catalyst-modified AFM tips for the local clicking of the ATRP initiator on the azide monolayer. Different conditions of grafting were used, but these tests proved to be complex; we are thus not yet at a stage where we can clearly delineate the conditions leading to the local grafting of the initiator.

Because Dr. Qian Ye has to leave earlier than expected, the AFM part of the work will be delayed until further opportunities arise. However, the polymer brushes including a catalytic moiety are by themselves interesting systems, and we have thus started in parallel a thorough study of the effect on the catalytic activity of the brushes of parameters controlling the brush architecture (such as the chain density, or the amount of grafted ligand). This part of the work is ongoing, and will be pursued in collaboration with Dr. Qian Ye by Dr. Antony Fernandes, who is post-doctoral fellow of the FNRS in our laboratory. This work will be published shortly.

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Sélection 2012

Short summary of the work done by Dr. Qian Ye

Project title : Catalytic Scanning Probe Microscopy
for the Complex Nanopatterning of Responsive Polymer Brushes

Keywords : *catalysis; polymer brushes; atomic force microscopy*

Our project initially aimed at understanding local catalysis, more precisely the local clicking of reagents on a surface, initiated by a catalytic micro-device placed in contact with the surface. By moving the catalytic device, chemical patterns can thus be drawn at a very small scale on the surface. Different applications of such patterns are possible; in the project, we considered especially the fabrication of surfaces displaying a complex tridimensional topography, which could be used for instance for counterfeiting applications. The micro-device which is considered is the tip of an atomic force microscope (AFM) functionalized by catalytic metal-ligand compounds grafted in a polymer brush. The selected reaction is the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) between a surface bearing azide groups and a propargyl-tetraethylene glycol ATRP initiator, from which it becomes possible to grow polymer brushes from the patterned surface in a second step.

During the first year of the project, we have thus prepared and characterized polymer brushes including a Cu(I) ligand, which we have successfully grown both from flat Si surfaces and from AFM tips. In parallel, we have prepared a clickable ATRP initiator, which we have clicked in the presence of Cu(I) onto azide self-assembled monolayers. We have also successfully grown polymer brushes from this clicked ATRP initiator. Then, we have attempted to use similar catalyst-modified AFM tips for the local clicking of the ATRP initiator on the azide monolayer. Different conditions of grafting were used, but these tests proved to be complex and require further work for a complete understanding of the phenomena. Because Dr. Qian Ye has to leave earlier than expected in order to apply for an associate professor position, this part of the work is delayed until further opportunities arise.

However, the polymer brushes including a catalytic moiety are by themselves interesting systems, and we have thus started in parallel a thorough study of the catalytic activity of the brushes depending on parameters which control the brush architecture (such as the chain density, or the amount of grafted ligand). This part of the work is ongoing and will be published shortly; it is pursued in collaboration with Dr. Qian Ye by Dr. Antony Fernandes, who is post-doctoral fellow of the FNRS in our laboratory. This work reveals that polymer brushes are ideally suited to immobilize in a recyclable way organometallic catalytic systems, and that the efficiency can be increased by a proper decrease of the chain grafting density of the brush.

Coopération S&T internationale; bourses post-doc pour chercheurs hors UE

Sélection 2012 - Dr. Qian Ye

Titre du projet : Catalytic Scanning Probe Microscopy
for the Complex Nanopatterning of Responsive Polymer Brushes

Commentaires sur le bénéfice du séjour et la perspective d'une collaboration plus étroite

Bénéfice du séjour :

Le projet du Dr. Qian Ye a été très fructueux pour l'UCL, malgré la réduction de sa durée initiale. En effet, bien que tous les objectifs du projet n'aient pas été atteints, le Dr. Qian Ye a néanmoins mis en place un ensemble d'éléments (molécules, procédures) qui ont une portée bien plus large qu'initialement prévu. En effet, nous développons dans le cadre du PAI 'Functional Supramolecular Systems' une activité d'hétérogénéisation de catalyseurs homogènes au sein de brosses de polymères. Les molécules créées par le Dr. Qian Ye sont directement utilisables dans ce cadre, et nous avons d'ailleurs avancé dans une étude allant dans ce sens. Ces éléments seront par ailleurs intégrés dans une thèse actuellement menée dans le laboratoire, en co-tutelle avec l'Université de Waterloo (Canada). Les premiers résultats devraient être publiés dans les 6 mois.

Perspective d'une collaboration plus étroite :

Le Dr. Qian Ye a interrompu son séjour plus tôt que prévu, de manière à postuler dans de bonnes conditions à un poste de professeur associé de l'institut de chimie physique de l'Académie des Sciences de Chine, à Langzhou. En cas de succès, ceci serait bien évidemment de nature à prolonger la collaboration entreprise. Cet effet est renforcé par la présence à Lanzhou d'un autre de nos anciens post-docs, le Prof. Xiaowei Pei; les liens entre notre institut et Lanzhou sont donc assez forts. Quoi qu'il en soit, dans un premier temps, le Dr. Qian Ye interagira avec le Dr. Antony Fernandes, chargé de recherches du FNRS dans notre laboratoire, afin de finaliser l'étude des propriétés catalytiques des brosses réalisées.

UCL Université catholique de Louvain
***EPL** Ecole polytechnique de Louvain*

Institute of Condensed Matter and Nanosciences (IMCN)
Bio & Soft Matter (BSMA)
Qian Ye, post-doctoral scientist

M. Bernard Delhausse
Politique scientifique fédérale
Avenue Louise 231
1050 Bruxelles

Your ref : coopération S&T internationale; bourses post-doc pour chercheurs hors UE
Sélection 2012

Louvain-la-Neuve, April 28, 2014

Dear Mr. Delhausse,

Thank you very much for your help in granting funds to me for supporting my postdoctoral research in the group of Prof. Alain Jonas at the Universite catholique de Louvain.

In the past year, I have been working on the project with rather good results, and I plan to collect these results in a coming publication. However, I would like to stop the grant earlier than planned, due to personal reasons. Indeed, I need to go back to China this May to apply for an associate professorship this June in Lanzhou Institute of Chemical Physics Chinese Academy of Sciences. I already missed one chance last year. I hope you agree with my request to terminate this grant after 12 months, on May 6, 2014. My supervisor, Professor Alain Jonas, agreed with this earlier termination.

I sincerely apologize for any inconveniences caused by this abrupt action and beg for your understanding. Thank you again for your assistance.

Best wishes,

Qian Ye QIAN YE
叶谦

For approval, Prof. Alain Jonas

UCL Université catholique de Louvain
Institute of Condensed Matter and Nanosciences (IMCN)

Alain Jonas, full professor

M. Bernard Delhausse
Politique scientifique fédérale
Avenue Louise 231
1050 Bruxelles

Louvain-la-Neuve, le 30 avril 2014

Cher Monsieur Delhausse,

Veuillez recevoir ci-joint le rapport d'activité du Dr. Qian Ye, qui a bénéficié d'une bourse 'coopération S&T internationale' de la politique scientifique fédérale dans le cadre de la sélection 2012. Vous trouverez également dans le dossier le résumé en une page des travaux menés, ainsi que des commentaires sur l'intérêt des travaux réalisés et les perspectives de collaboration. Ces documents vous ont par ailleurs déjà été envoyés sous format électronique.

Comme vous le savez, le Dr. Qian Ye a souhaité interrompre son séjour plus tôt que prévu, au 6 mai 2014. Sa lettre de motivation, contresignée par moi-même, est également annexée à ce courrier. Le départ anticipé du Dr. Qian Ye n'a pas permis d'atteindre tous les objectifs initialement prévus; néanmoins, le travail réalisé est déjà suffisamment avancé que pour permettre la rédaction d'une publication sur un thème plus général. L'interruption anticipée n'est donc pas trop problématique de mon propre point de vue, même si je n'ai évidemment pas été enchanté quand l'intéressé m'en a fait part il y a 3 semaines. Néanmoins, je n'ai pas souhaité créer de difficultés, l'intérêt de préserver de bonnes relations en vue de collaborations futures étant premier.

En vous souhaitant une bonne réception de ces documents, je vous prie d'accepter, cher Monsieur Delhausse, mes salutations courtoises.

Alain Jonas

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05. V. 2014