

Electronic Supporting Information

Self-Templating Surface-Initiated Polymerization: A Route to Conductive Brushes

Michał Szuwarzyński,^a Justyna Kowal,^{a,b} Szczepan Zapotoczny*^a

^aJagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland

^bUniversity of Basel, Department of Chemistry, Klingenbergstrasse 80 CH-4056, Basel, Switzerland

Corresponding author email: zapotocz@chemia.uj.edu.pl

Table of Contents

Apparatus	S1
Surface grafted polymerization	S2
Determination of the brush height using AFM	S3
FTIR spectra	S4
XPS spectra	S5
AFM images of the brushes with respective I-V plots	S6

Apparatus

Conductive Atomic Force Microscope (C-AFM) images were taken using NanoScope IV Multimode atomic force microscope (Bruker, Santa Barbara, CA) working in air using silicon nitride cantilevers with nominal spring constant of 0.2 N/m coated with 20 nm PtIr conductive layer (and 3 nm Cr adhesive underlayer) on both sides. The height images in contact mode were captured simultaneously using interleave mode. I-V plots were obtained in the selected spots varying the voltage applied between the tip and the gold surface in the range -3V to +3V.

Tapping mode AFM images were captured with the same microscope using standard silicon cantilever with nominal spring constant of 40 N/m and the tip radius <10 nm (Bruker).

Brushes thickness were measured using Woollam M-2000U Spectroscopic Ellipsometer working in the 350-1050 nm spectral range. Cauchy function was used as a fitting model. Each film was modeled as a homogeneous organic layer (application of more complex models have not brought any significantly different results).

XPS spectra were obtained using photoelectron spectrometer XPS (PREVAC, Rogów, Poland).

FTIR spectra were taken using Nicolet 6700 Spectrometer with diamond ATR accessory and DLaTGS detector.

Surface grafted polymerization

Gold substrates (200 nm of Au sputtered on glass, Ssens bv, Hengelo, The Netherlands) were cleaned in “piranha solution” (a mixture of H₂SO₄ and H₂O₂ in a 1:3 ration) (*CAUTION! “Piranha solution” should be handled with extreme care!*) and then immersed into a 1 mM methanol solution containing DTCA and ODT in 20:80 molar ratio for 24 h at room temperature. Afterwards the substrates were extensively rinsed with ethanol, dichloromethane, and methanol. As shown previously¹ the surface concentration of DTCA is very similar to the feed ratio. Such prepared gold substrates covered with SAMs were immersed into degassed ethanol solution of TPM monomer (0.5 M) and then irradiated with UV light for 30 min using Rayonet photoreactor equipped with RPR-3000 lamps with maximum emission at 300 nm. The photopolymerization of polymer brushes was performed in borosilicate glass vial cutting-off the UV radiation below 290 nm (see Figure 1a). After photopolymerization the samples were extensively rinsed with ethanol and dichloromethane. The protecting trimethylsilyl groups in the polymer brushes were cleaved (see Figure 1b) in the solution of sodium carbonate (0.5 g, 6.02 mmol, Sigma Aldrich, ≥99%) in

THF (10 mL, Sigma Aldrich, $\geq 99\%$) and methanol (10 mL, POCH, p.a.) mixture. The mixture was stirred for 24 h at room temperature and afterwards the samples were removed and rinsed with methanol. To conduct template polymerization (see Figure 1c) of the acetylene groups of the polymer brushes the substrate was immersed in toluene (1ml) and the vial was sealed with a septum, deoxygenated by the flow of nitrogen. The deoxygenated solution of the catalyst, bicyclo[2.2.1]hepta-2,5-diene-rhodium(I) chloride dimer (0.95 mg, 2 μmol , Fluka Analytical, $\geq 98\%$ Rh) and co-catalyst, triethylamine (3 μL , 20 μmol , Sigma Aldrich, $\geq 99\%$), in toluene (1 mL, POCH, p.a.) was subsequently added. The reaction was carried out for 1 h at room temperature. Then the substrate was removed and extensively rinsed with toluene and ethanol and finally dried in a stream of dry nitrogen. Doping (see Figure 1d) of the obtained brushes was performed using toluene solution of I_2 (0.01 M). The substrate was covered with the solution and left in argon atmosphere at room temperature for 3h. Then the substrate with such doped brushes (see Figure 1e) was rinsed with toluene and finally dried under vacuum.

Determination of the brush height using AFM

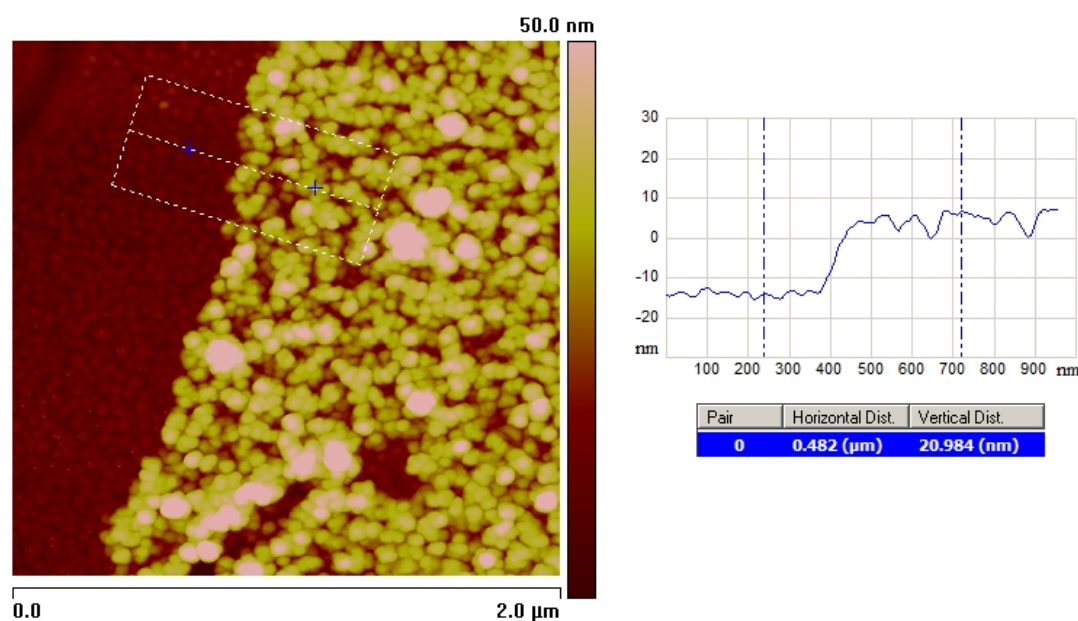


Figure S1. Tapping mode AFM measurements of poly(TPM) at the edge of the scratched area.

The thickness of the brushes was measured by AFM. First, the brushes were locally removed by gentle scratching the surface with the tip of a Teflon tweezers. Then, tapping mode AFM image was taken at the edge of the scratched area. The averaged depth of the observed well was taken as the brush thickness (Fig. S1).

FTIR spectra

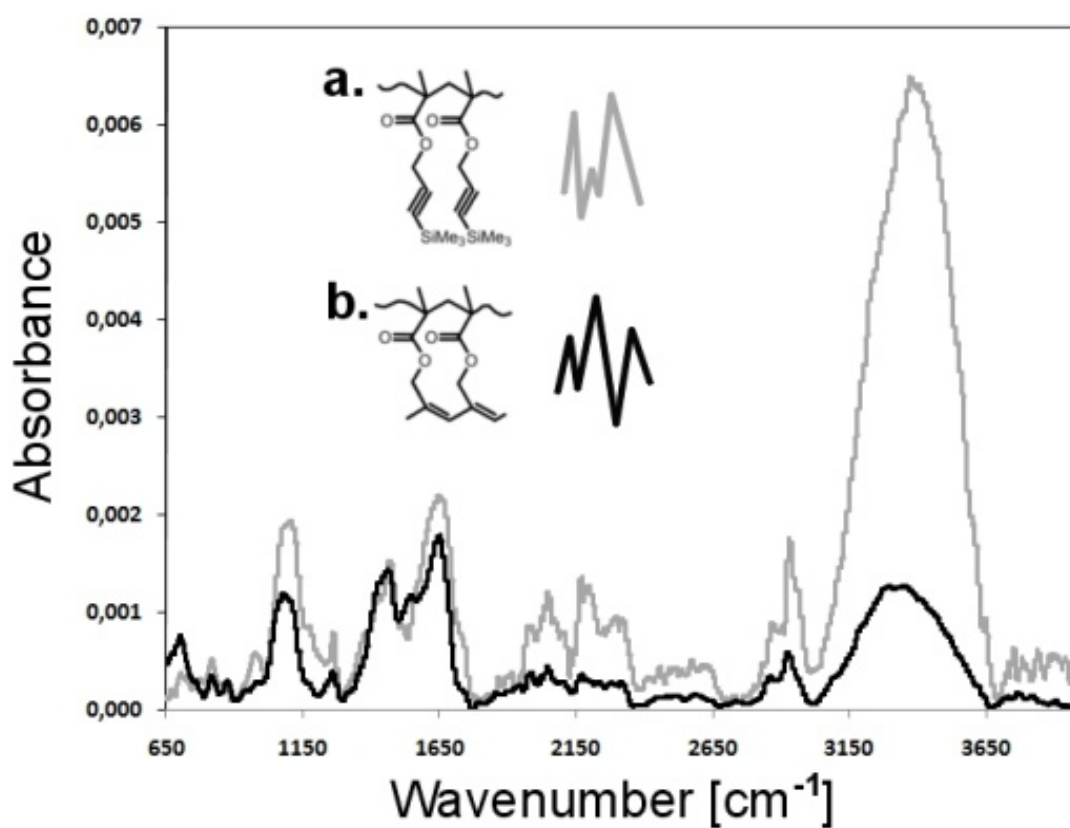


Figure S2. FTIR-ATR spectra obtained for the brushes before (a. - grey) and after (b. - black) polymerization of acetylene groups.

XPS spectra

Fig. S3 A. shows the spectrum with maximum binding energy at 619 eV and 630.5 eV, which are characteristic for iodine I⁻ that is present in the doped brushes (no traces of I₂).

The ratios between carbon atoms in C-C and C-H bonds to carbon atoms in oxygen neighbourhood were determined based on the intensities of the respective deconvoluted bands. For poly(TPM) brush it was found to be $83.4/16.6 = 5.0$ (Fig. S3 B). Such relation roughly corresponds (with ca. 20% deviation due to weak signals) to the ratio between 8 carbon atoms in C-C and C-H bonds to 2 carbon atoms (O-C=O, C-O-C) in the structure of the protected mer (see Figure 1b) and it is not lower than 4 that would suggest some deprotection taking place during the polymerization procedure.

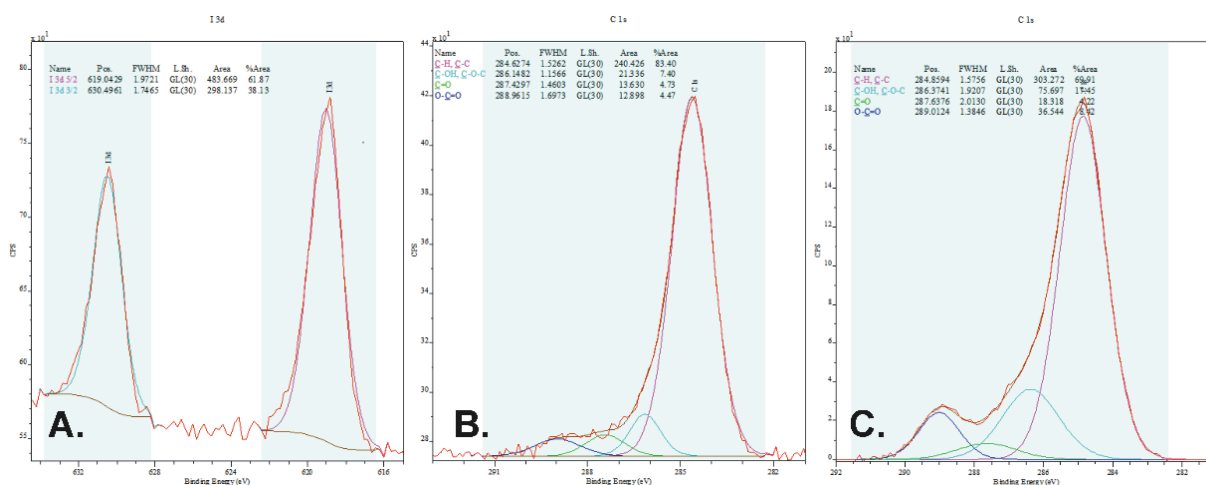


Figure S3. XPS spectra for: A. - doped conjugated brushes (iodine, I 3d), B. - poly(TPM) brushes (carbon, C 1s), C. – conjugated brush after template polymerization (carbon, C 1s).

After removal of the protecting groups the proportion between the respective carbons changed significantly (see Figure S3 C) to $69.9/30.1 = 2.3$ that corresponds (with 8% deviation) to the proportion between 5 (C-C, C-H) and 2 (O-C=O, C-O-C) carbon atoms in one mer structure of the ladder-type polymer (Figure 1d).

AFM images of the brushes with respective I-V plots

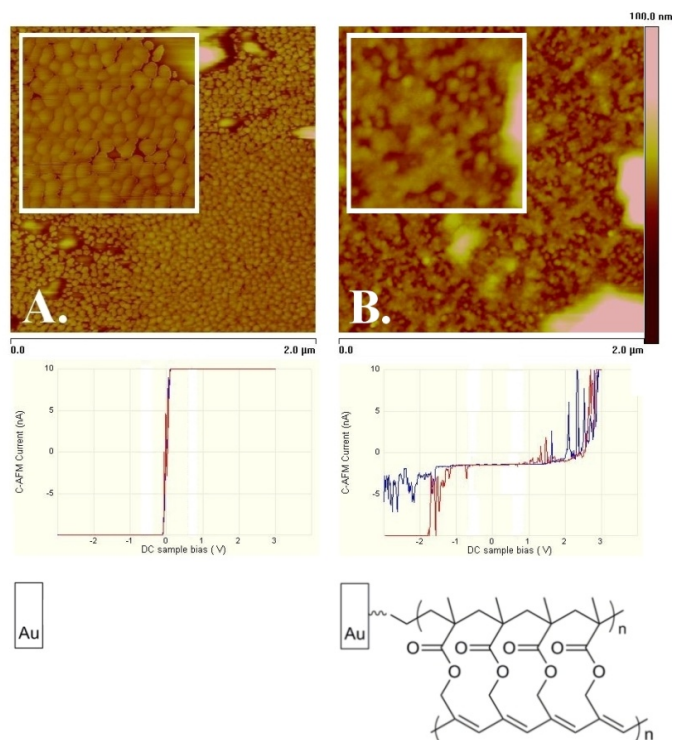


Figure S4. Contact mode AFM height images and the selected I-V plots for: A. - poly(TPM) brushes deformed by AFM tip due to scanning at high load (I-V plot is typical for highly conductive metallic contact since the tip reaches gold surfaces), B. - brushes after template polymerization (I-V plot is typical for semiconductors).

¹ Benetti, E. M.; Reimhult, E.; de Bruin, E.; Zapotoczny, S.; Textor, M.; Vancso, G.J. *Macromolecules*, **2009**, *42*, 1640-1647.