2D laser lithography on silicon substrates via photoinduced copper-mediated radical polymerization

Supplementary material

LAUN, Joachim; De Smet, Yana; Van de Reydt, Emma; KRIVCOV, Alexander; Trouillet, Vanessa; Welle, Alexander; Möbius, Hildegard; Barner-Kowollik, Christopher & JUNKERS, Tanja (2018) 2D laser lithography on silicon substrates via photoinduced copper-mediated radical polymerization. In: CHEMICAL COMMUNICATIONS, 54 (7), p. 751-754.

DOI: 10.1039/c7cc08444g
Handle: http://hdl.handle.net/1942/25575

Supporting Information

2D Laser Lithography on Silicon Substrates via Photoinduced Copper-Mediated Radical Polymerization

Joachim Laun,[a] Yana De Smet,[a] Emma Van de Reydt,[a] Alexander Krivcov,[b] Vanessa Trouillet,[c,d] Alexander Welle,[d,e] Hildegard Möbius,[b] Christopher Barner-Kowollik,[f,g,h]* and Tanja Junkers[a,i]*

[a] Polymer Reaction Design Group, Institute for Materials Research (IMO), Universiteit Hasselt, Martelarenlaan 42, 3500 Hasselt, Belgium
E-mail: tanja.junkers@uhasselt.be

[b] University of Applied Sciences Kaiserslautern, 66482 Zweibrücken, Germany

[c] Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[d] Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[e] Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[f] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000 Brisbane, Australia
E-mail: christopher.barnerkowollik@qut.edu.au

[g] Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76128 Karlsruhe, Germany

[h] Institut für Biologische Grenzflächen (IBG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[i] IMEC associated lab IMOMEC, Wetenschapspark 1, 3590 Diepenbeek, Belgium

1. Materials and Methods

1.1 Materials

Sulphuric acid (95%, Analytical Reagent Grade), hydrochloric acid (37%, Analytical Reagent Grade), ammonia (25% Laboratory Reagent Grade), absolute ethanol (Analytical Reagent Grade), dimethyl sulfoxide (Analytical Reagent Grade), and toluene (Analytical Reagent Grade) were purchased from Fisher. Hydrogen peroxide (35 wt.%), triethylamine (99+%), 2-bromoisobutyryl bromide (98%), sodium sulfate (99+%), and copper dibromide (99+%) were purchased from Acros. 10-undecan-1-ol (>98%) and 2-hydroxyethyl acrylate (>95%) were purchased from TCI. t-Butyl acrylate (98%), oligo(ethylene glycol) methyl ether acrylate, [2-(Acryloyloxy)ethyl]trimethylammonium chloride solution 80 wt. % in water, and trichlorosilane (99%) were purchased from Sigma Aldrich. Tetrahydrofuran (HPLC grade) was bought from VWR, and tris[2-(dimethylamino)ethyl]amine (99+%) from Alfa Aesar. All monomers were passed over basic alumina prior to use. All other chemicals were used as purchased.

1.2 Methods

1.2.1 X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a K-Alpha+ XPS spectrometer (Karlsruhe; *ThermoFisher Scientific*, East Grinstead, UK). Data acquisition and processing using the *Thermo Avantage* software is described elsewhere.[1] All samples were analyzed using a microfocused, monochromated Al K_α X-ray source (400 µm spot size). The K-Alpha+ charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: $\pm$0.2 eV) and Scofield sensitivity factors were applied for quantification.[2] All spectra were referenced to the C 1s peak attributed to C–C, C–H at 285.0 eV binding energy which has been controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respectively. The K-alpha+ snapmap option was used to image an area of 3 × 3 mm^2 with an X-ray spot of 300 µm. (10 iterations were run in order to reach a better statistic). A principal component analysis of the spectra was conducted.

1.2.2 Grazing angle attenuated total reflection Fourier-transform infrared (GAATR-FTIR)

Grazing Angle Attenuated Total Reflection Fourier-Transform Infrared (GAATR-FTIR) spectra were obtained from the dry polymer layers using a *Frontier* FTIR spectrometer (*PerkinElmer*) equipped with an MCT detector and a *Veemax III* attachment (*PIKE Technologies*). For the collection of the spectra, a resolution of 4 cm^{-1} was selected.

1.2.3 Time-of flight secondary ion mass spectrometry

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) was performed on a *TOF.SIMS5* instrument (*ION-TOF GmbH*, Münster, Germany. This spectrometer is equipped with a Bi cluster primary ion source and a reflectron type time-of-flight analyzer. UHV base pressure was < $5 \cdot 10^{-9}$ mbar. For high mass resolution the Bi source was operated in the "high current bunched" mode providing short Bi_3^+ primary ion pulses at 25 keV energy, a lateral resolution of approx. 4 µm, an a target current of 0.25 pA. The short pulse length of 1.1 ns allowed for high mass resolution. The primary ion beam was rastered across a 500 × 500 μm^2 field of view on the sample, and 128 × 128 data points were recorded. Primary ion doses were kept below 10^{11} ions·cm^{-2} (static SIMS limit). If charge compensation was necessary an electron flood gun providing electrons of 21 eV was applied and the secondary ion reflectron tuned accordingly. Spectra were calibrated on the omnipresent C^-, C_2^-, C_3^-, or on the C^+, CH^+, CH_2^+, and CH_3^+ peaks. Based on these datasets the chemical assignments for characteristic fragments were determined. For imaging large fields of view the sample stage and the primary beam were scanned. For depth profiling a dual beam analysis was performed in non-interlaced mode: The primary ion source was again operated in "high current bunched" mode with a scanned area of 500 × 500 μm^2 (2 frames with 128 × 128 data points) and a sputter gun (operated with Ar_{1600}^+ ions, 5 keV, scanned over a concentric field of 750 × 750 μm^2, target current 0.3 nA) was applied to erode the sample for 2 scans followed by a 0.5 s pause. This approach allows the argon cluster ion dose density to be >250 times higher than the Bi ion dose density, is preserving molecular structures in the sample during erosion and is therefore highly suited for polymeric materials.

1.2.4 Nuclear Magnetic Resonance

^1H NMR spectra were recorded in deuterated chloroform and methanol, respectively, applying a pulse delay of 15 s with Oxford Instruments Ltd. NMR spectrometers (300 and 400 MHz).

1.2.5 Atomic Force Microscopy

The atomic force microscopy (AFM) measurements were performed on a Dimension Icon instrument (Bruker) using an ASYELEC tip. Tip dimensions were 28 ± 10 nm in radius and 14 ± 4 µm in height. The resonance frequency was 70 kHz. Topography was measured in tapping mode. To locally remove the polymer, the same tip was used in contact mode with higher push force. The process was repeated multiple times for a complete removal of the polymer in the area of interest.

1.2.6 Profilometry

A Dektak stylus profilometer XT (Bruker) was employed with a 2 µm stylus and 1 mg stylus force. 9500 data points per millimeter were recorded.

2. Procedures

2.1 Synthesis of undec-10-en-1-yl 2-bromo-2-methylpropanoate

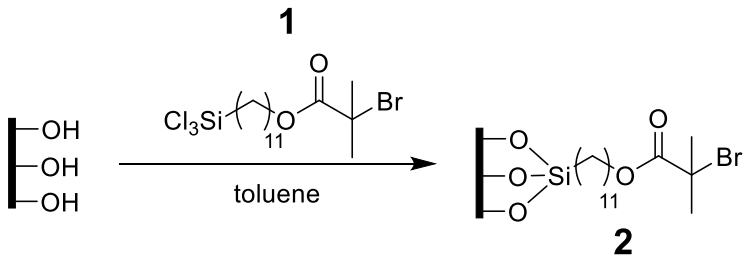
The product was synthesized according to literature.[3]

2.2 11-(trichlorosilyl)undecyl 2-bromo-2-methylpropanoate (1)

The product was synthesized according to literature.[3]

2.3 Grafting of Initiator

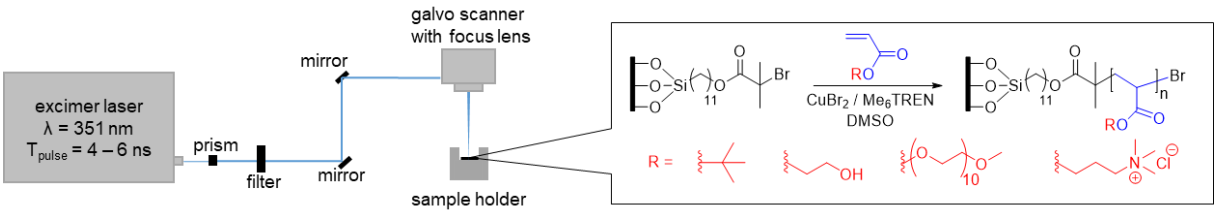
Silicon wafers were placed in a 1 to 1 solution of H_2SO_4 and H_2O_2. After 15 min, the wafers were taken out, rinsed with H_2O and placed in 1M HCl for another 15 min. Then the wafers were again taken out, rinsed with H_2O and placed in a 1 to 1 solution of NH_3 (25%) and H_2O_2 for 15 min. The substrates were rinsed with H_2O and blown dry with nitrogen. Whenever H_2O_2 was used, samples were only handled with PTFE tweezers.



Scheme S1. Silanization with **1** to give the initiator-armed substrate **2**.

A freshly prepared solution of 5 mg·mL^{-1} **1** in dry toluene was added to the freshly activated silicon substrates inside the glove box (**Scheme S1**). Subsequently, the Petri dish was covered with another Petri dish and the reaction was allowed to proceed for 3 h at ambient temperature. Then, the substrates were removed from the Petri dish, shaken in dry toluene to remove the silane, and then placed in a Petri dish filled with dry toluene before they were removed from the glove box. Subsequently, the substrates were rinsed with toluene (p.a.) and tetrahydrofuran (p.a.), followed quickly by EtOH (abs.) and MilliQ water. The substrates were blown dry with nitrogen and placed in a storage container. **N.B.** It is important that the substrates do not dry between the rinsing steps.

2.4 Laser-Induced Copper-Mediated Radical Polymerization of Polyacrylate Brushes



Scheme S2. (left) General set-up used for 2D laser lithography. A XeF excimer laser (λ = 351 nm, 4 – 6 ns pulses, 1.5 mJ per pulse) was combined with a software-controlled galvo scanner. Laser light was first sent through a prism to obtain a rectangular beam of 6 × 8 mm² before it passed a reflective filter to reduce its intensity by factor 100. Eventually, the light was guided into the galvo scanner where it was redirect onto a silicon substrate that was placed in an airtight chamber under nitrogen atmosphere.

0.23 mg $CuBr_2$ and 3.5 mL DMSO were mixed in a glass vial equipped with a stirring bar. Subsequently, 1.7 µL Me_6TREN was added and the vial was wrapped in aluminum foil. Then the mixture was purged with nitrogen for 30 min. Simultaneously, pure, inhibitor-free monomer was purged with nitrogen for 30 min. Afterwards, 10.3 mmol monomer was added to the DMSO solution. The new mixture was stirred for 10 min in the dark.

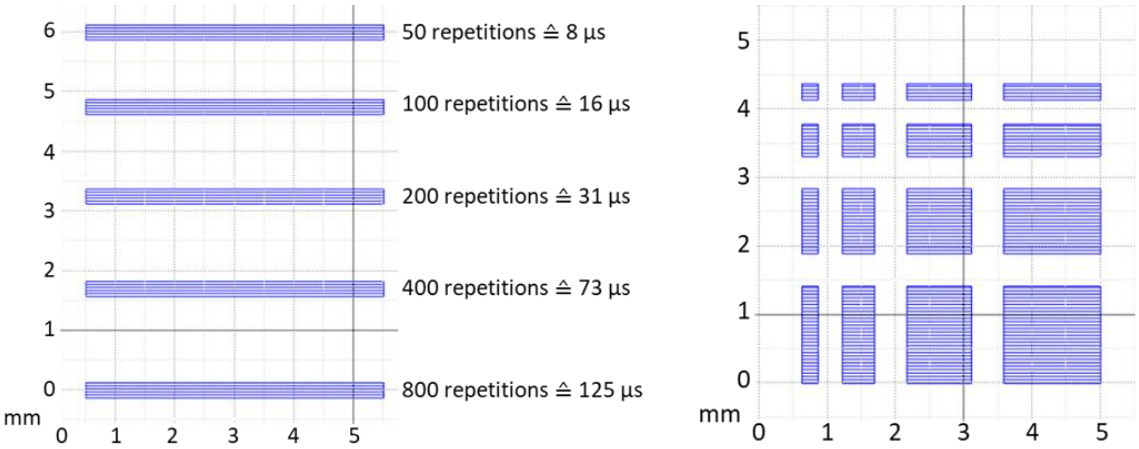
A silanized silicon substrate was placed in the PTFE-insert of a custom-made reaction chamber. The chamber was airtight and equipped with a quartz glass window (**Fig. S1**).

Fig. S1. Laser lithography chamber made from stainless steel with a PTFE insert and a quartz glass window.

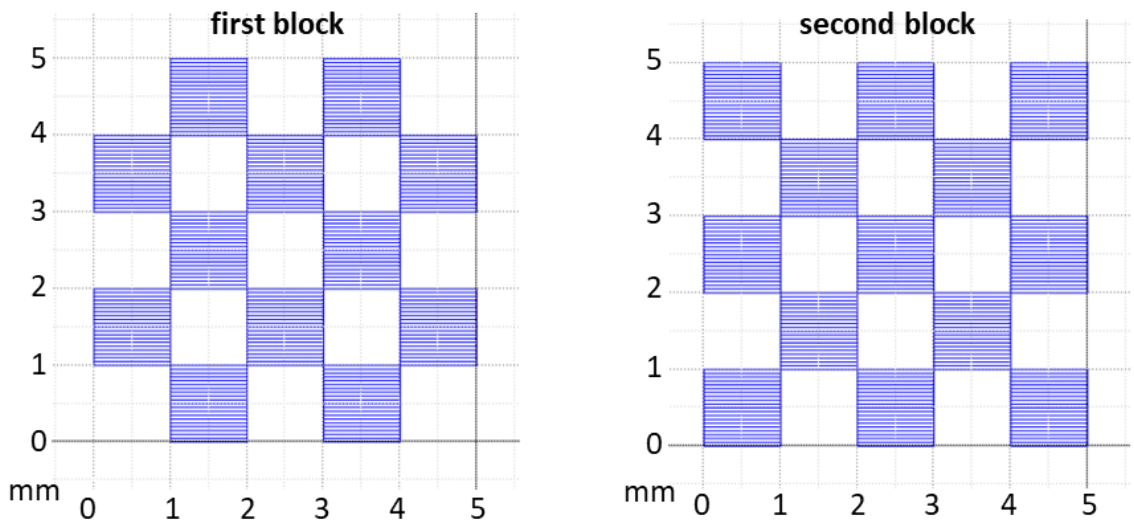
The reaction chamber filled with the substrate was purged with nitrogen for 30 min. Purging for shorter periods did not lead to reproducible results or led to no polymer grafting at all. Then the windows was covered with aluminum foil and 0.7 mL of the prepared monomer solution was added rapidly. A volume of 0.7 mL was determined to be just sufficient to fully cover the substrate. Subsequently, the sample was subjected to laser-induced copper-mediated radical polymerization at 351 nm. A pulsed XeF excimer laser (ATLEX 1000-I, ATL Lasertechnik GmbH) and a galvo scanner (SCANcube III, Scanlab GmbH) were employed.

The excimer laser featured a 6 × 4 mm² laser beam (FWHM values) with divergences of 2 and 1 mrad respectively, which results in M² of around 54 and 18. A prism doubles the 4 mm size shortly after leaving the laser. At a distance to lens (56 mm focal length) of around 65 cm with a wavelength of 351 nm, the minimal theoretical spot size ranges around 185 × 96 µm². Pulse energy was set to 1.5 mJ per pulse of around 4 – 6 ns. The frequency was set to 500 Hz. The laser energy was reduced by factor 100 by a reflective filter. LaserDESK Software (Scanlab GmbH) was used for control of laser and galvo scanner and to design all target structures, which were filled with straight lines with 0.05 mm line spacing. Homopolymers were grafted in simple rectangles and the diblock copolymer a 4 × 4 mm² rectangle in the middle of an 8 × 8 mm² rectangle. Other employed structures are depicted in **Scheme S3** and **Scheme S4**.

After completion of the writing process, the substrate was further kept in the dark while the reaction chamber was opened. A few milliliters of a good solvent for the monomer was added before the chamber was opened. Afterwards, the substrate was exhaustively rinsed with toluene, tetrahydrofuran, absolute ethanol and water. For [2-acryloyloxy)ethyl]trimethylammonium chloride, absolute ethanol and water were employed for washing before the full sequence from toluene to water was used.



Scheme S3. (left) Structure used to assess film thickness evolution. Each bar was 0.25 mm in width and filled with 6 lines of 0.05 mm line spacing (right) structure used to assess resolution. The smallest structures was 0.236 × 0.236 mm². All structures were written 50 times.



Scheme S4. Checkerboard patterns. The first block was written 100 times and the second block 200 times.

3. Supporting Results

3.1 Profilometry

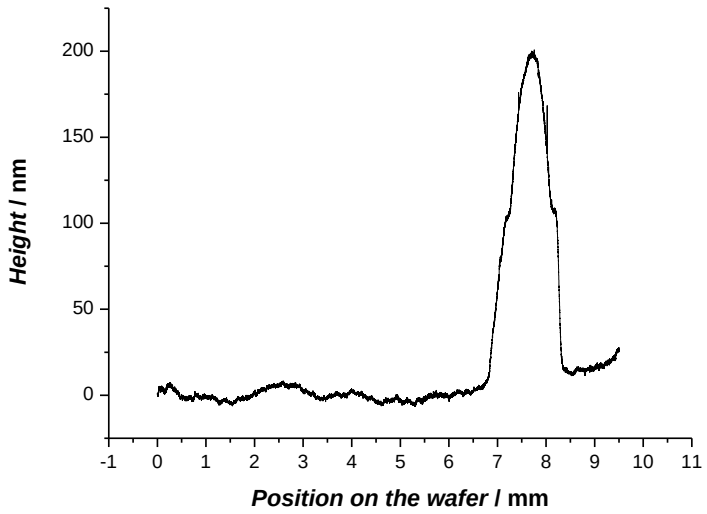


Fig. S2. Grafting of PtBA. Film thickness (from profilometry) obtained after 563 µs exposure to laser light.

3.2 XPS

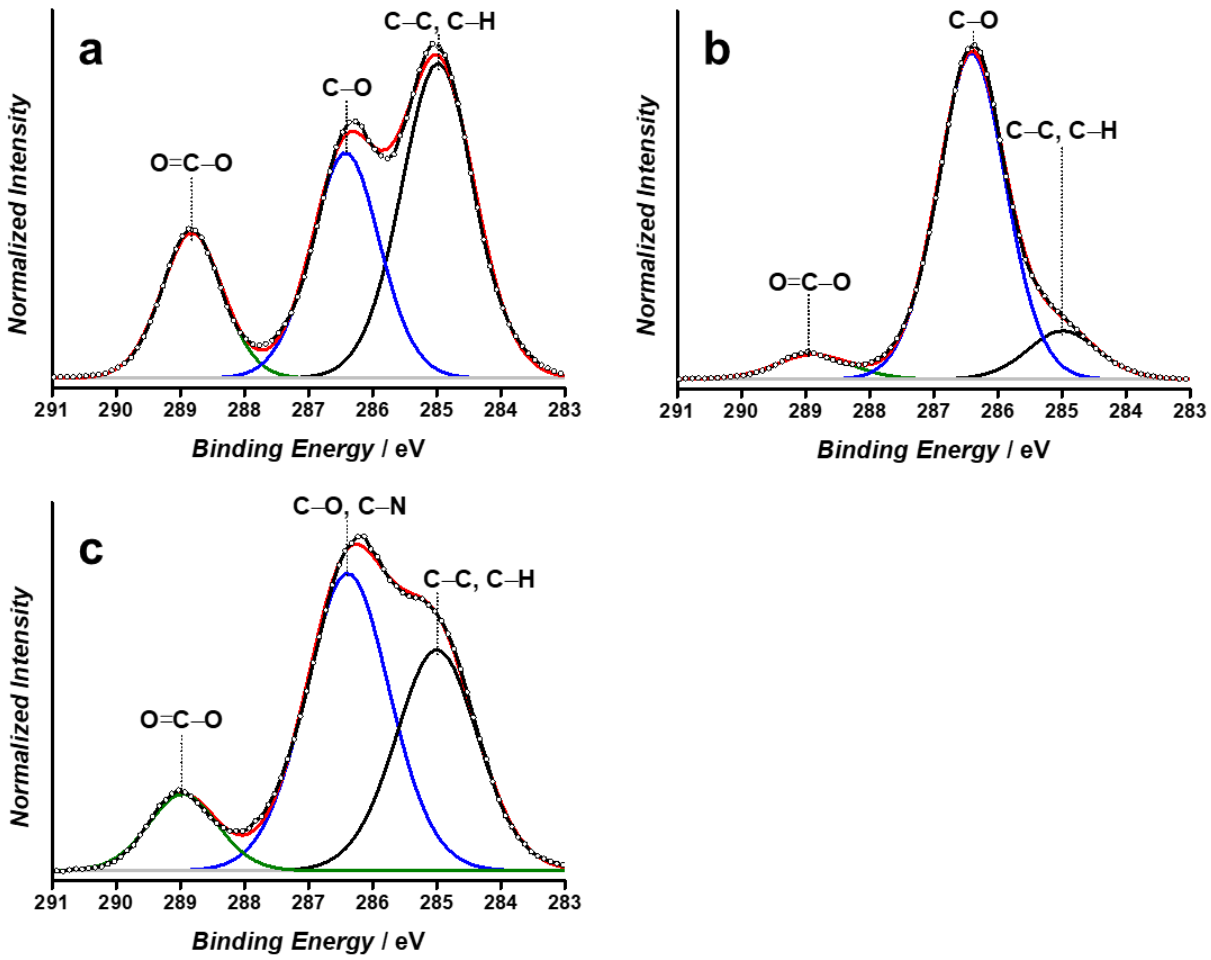


Fig. S3. C 1s XPS spectra of (a) PHEA, (b) POEGA, (c) PAETMAC.

Three different peaks corresponding to O=C–O (288.9 eV), C–O, C–N (~286.6 eV), and C–C, C–H (285.0 eV) were fitted.[3] (C–O, C–N)/O=C-O ratios were calculated for all polymers and are in good to excellent agreement with the expected values. There were little deviations from the theoretical C–C, C–H contributions in the case of PHEA and PAETMAC, however, these were also found for photoCMP grafting with standard UV light[3] and stem in all likelihood from a small surface contamination. Besides the observed shift of the C–O peak (286.8 eV) towards smaller binding energy (286.4 eV) corresponding to the additional presence of C–N groups, PAETMAC also showed the expected positively charged nitrogen and chlorine signals.

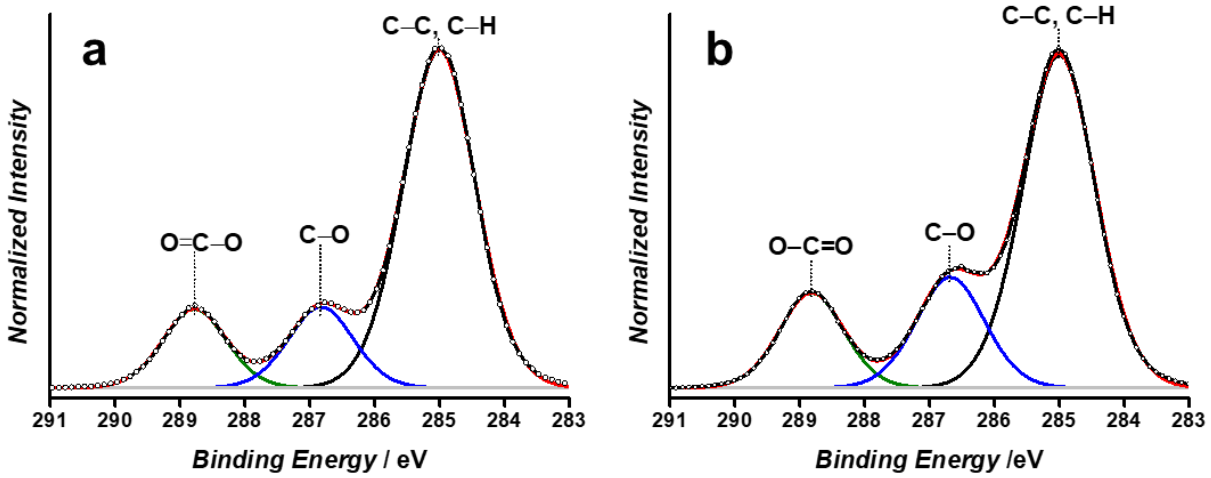


Fig. S4. C 1s XPS spectra of (a) PtBA, (b) PtBA-*b*-PHEA.

3.3 Grazing Angle ATR-FTIR

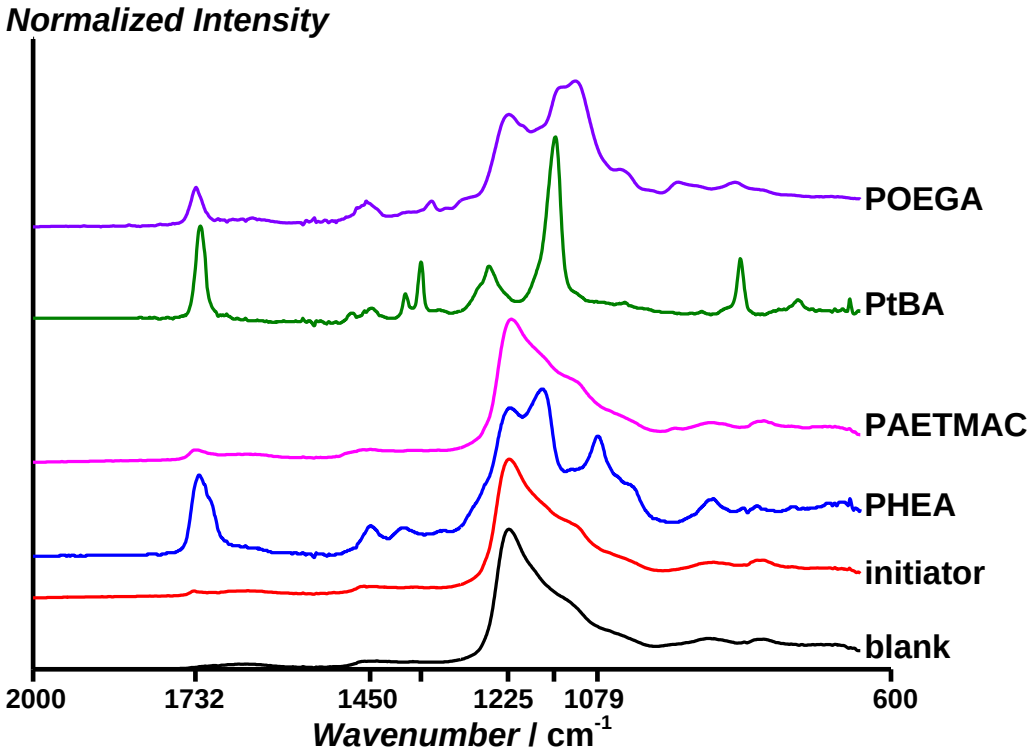


Fig. S5. Grazing Angle ATR-FTIR of a blank silicon sample (**black**), the grafted initiator (**red**), poly(2-hydroxyethyl acrylate) (PHEA; **blue**), poly(acryloyloxyethyl trimethylammonium chloride) (PAETMAC; **magenta**), poly(*t*-butyl acrylate) (PtBA; **olive**) and poly(oligo(ethylene glycol) methyl ether acrylate) (POEGAM; **violet**).

At around 1732 cm^{-1}, the C=O stretching vibration was found for all samples except the blank. Further peaks were found at 1450 cm^{-1} for CH_2 scissoring especially for PHEA, PtBA and POEGA. The symmetric bending vibration of CH_3 was observed at 1367 cm^{-1} for PtBA. The SiO_2 background peak remained visible for all but the PtBA sample at 1225 cm^{-1}. A peak at 1160 cm^{-1} indicates asymmetric C-O-C stretching and at 1079 cm^{-1} the C–OH stretch vibration of a saturated alcohol was observed.

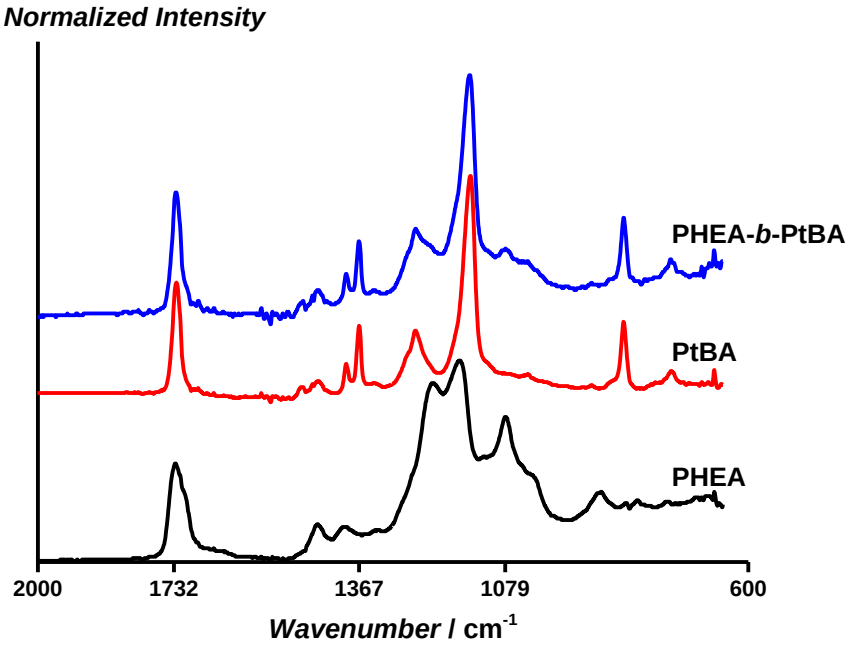


Fig. S6. Grazing angle attenuated total reflection Fourier-transform (GAATR-FTIR) infrared spectra of PHEA (**black**), PtBA (**red**), and PHEA-*b*-PtBA (**blue**) on silicon substrate.

All three polymers show the expected C=O stretching vibration at 1732 cm^{-1} and the asymmetric C–O–C stretching at 1160 cm^{-1}. The spectrum of the diblock copolymer grafts show the symmetric CH_3 bending vibration at 1367 cm^{-1} very prominently in both PtBA and PHEA-*b*-PtBA. The C–O stretching vibration of the primary alcohol of PHEA was found at 1079 cm^{-1}, prominently in pure PHEA and little in the diblock copolymer. Also found in the PHEA spectrum was the SiO_2 background peak at 1225 cm^{-1} due to the low film thickness. The weak contribution of the C–O stretching vibration of the primary alcohol to the diblock copolymer's spectrum is associated with the relatively low surface area of only 25% that was functionalized. Moreover, it is known from literature that even for a fully functionalized substrate of 120 nm PHEA-*b*-PtBA as diblock (with only 47 nm PtBA as first block), the respective peak remained rather low.[3]

3.4 ToF-SIMS

Table S1. ToF-SIMS surface spectra of the initiator, all grafted polyacrylates and their diblock copolymer.

Sample	Characteristic fragments	
	Positive polarity	Negative polarity[*]
Initiator	[¥]	Br^- (m)
Poly(*t*-butyl acrylate)	$C_4H_9^+$ (vs)	$C_4H_9O^-$ (s)
Poly(2-hydroxyethyl acrylate)	$C_2H_5O^+$ (vs)	$C_2H_5O_2$- (vs) CH_3O^- (s)
Poly[oligo(ethylene glycol) methyl ether acrylate]	$C_2H_5O^+$ (vs)	$C_2H_3O^-$ (vs) $C_2H_5O_2^-$ (vs) CH_3O^- (s)
Poly{[2-(acryloyloxy)-ethyl]trimethylammonium chloride}	$C_3H_8N^+$ (vs) $C_5H_{12}N^+$ (s)	Cl^- (vs)
Poly(2-hydroxyethyl acrylate)-*b*-poly(*t*-butyl acrylate)	$C_4H_9^+$ (vs)	$C_2H_5O_2^-$ (m) $C_4H_9O^-$ (m)

vs = very strong, s = strong, m = medium

[*] All polymer sample showed intense signals for $C_3H_3O_2^-$.

[¥] only unspecific hydrocarbon fragments detected

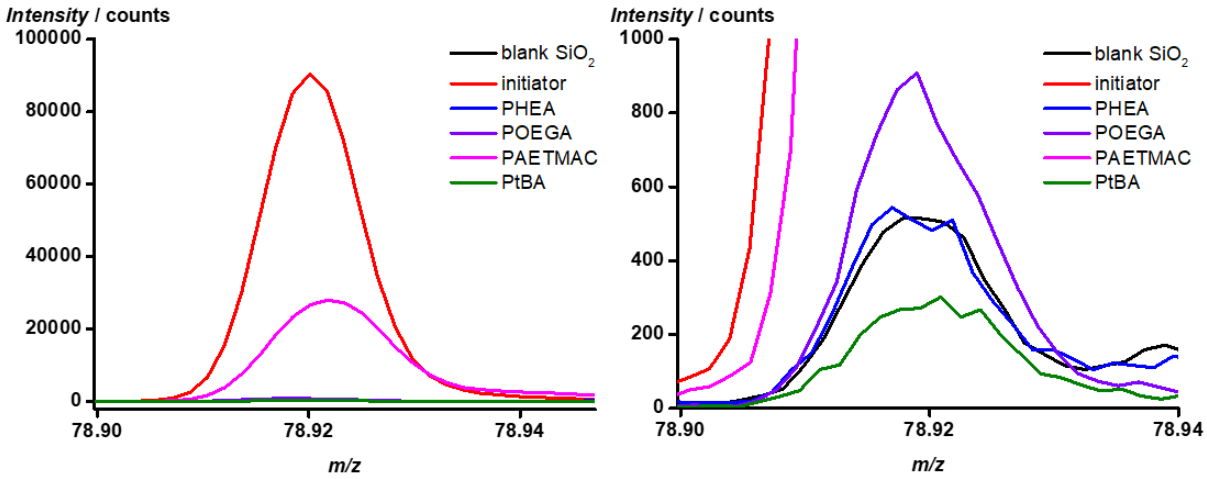


Fig. S7. Bromine intensity in static ToF-SIMS.

3.5 XPS-Mapping

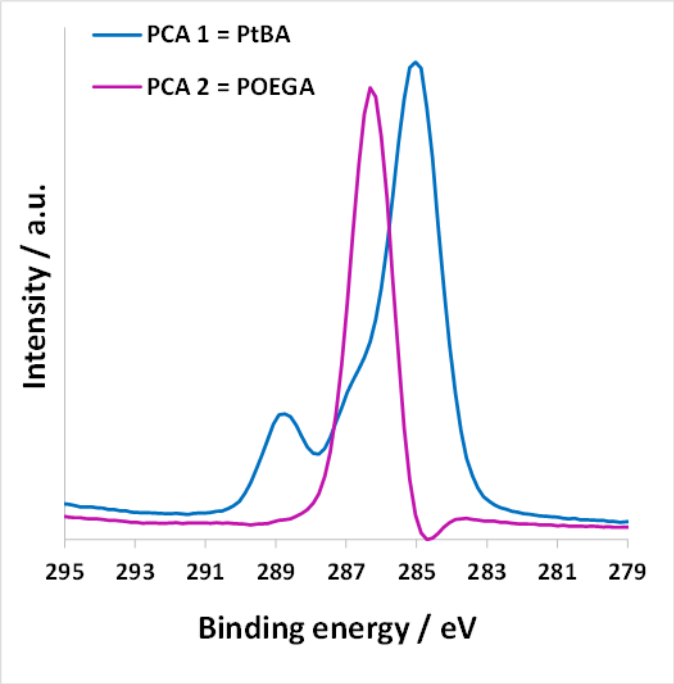


Fig. S8. Principal component analysis of all C 1s spectra from the 3 × 3 mm² area. The first component (PCA 1) can be attributed to PtBA, the second one (PCA 2) to POEGA since they are similar to the specific spectra expected for these both polymers.

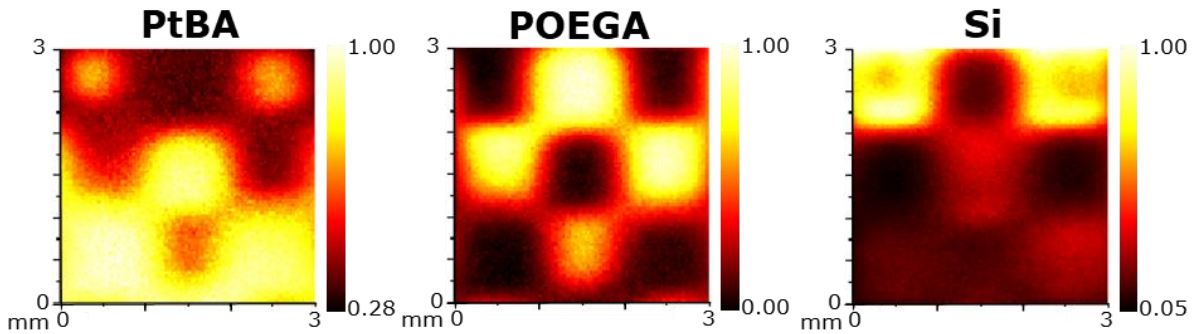


Fig. S9. XPS mapping of a checkerboard pattern of PtBA, POEGA, and silicon.

4. References

[1] K. L. Parry, A. G. Shard, R. D. Short, R. G. White, J. D. Whittle, A. Wright, *Surf. Interface Anal.* **2006**, *38*, 1497-1504.

[2] J. H. Scofield, *J. Electron Spectros. Relat. Phenomena* **1976**, *8*, 129-137.

[3] J. Laun, M. Vorobii, A. de los Santos Pereira, O. Pop-Georgievski, V. Trouillet, A. Welle, C. Barner-Kowollik, C. Rodriguez-Emmenegger, T. Junkers, *Macromol. Rapid Commun.* **2015**, *36*, 1681-1686.