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Polymer Chemistry

Electronic Supporting Information for

Grafting of functional methacrylate polymer brushes by photoinduced SET-LRP

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Atomic force microscopy (AFM) of the self-assembled monolayer (SAM) of initiator on silicon

AFM was used to study the topography of the surface. The SAM of initiator is homogeneous and the mean square roughness values R_q are (0.7 ± 0.1) nm and (1.14 ± 0.23) nm for Si substrate and SAM, respectively.

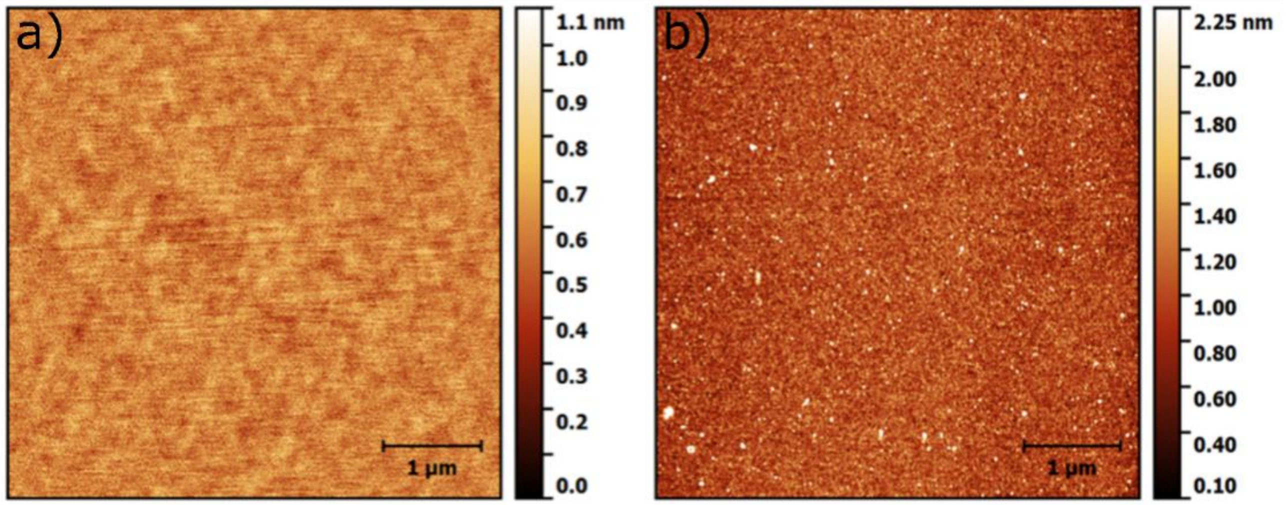


Figure SF1. Topographic images of (a) bare silicon and (b) SAM of initiator obtained in tapping mode in air at room temperature.

Additional X-ray photoelectron spectroscopy (XPS) characterization of the self-assembled monolayer (SAM) of initiator on silicon

The Br 3d envelope could be deconvoluted with one spin-orbit splitting doublet having its contributions at 70.2 eV (Br $3d_{5/2}$) and 71.2 eV (Br $3d_{3/2}$).

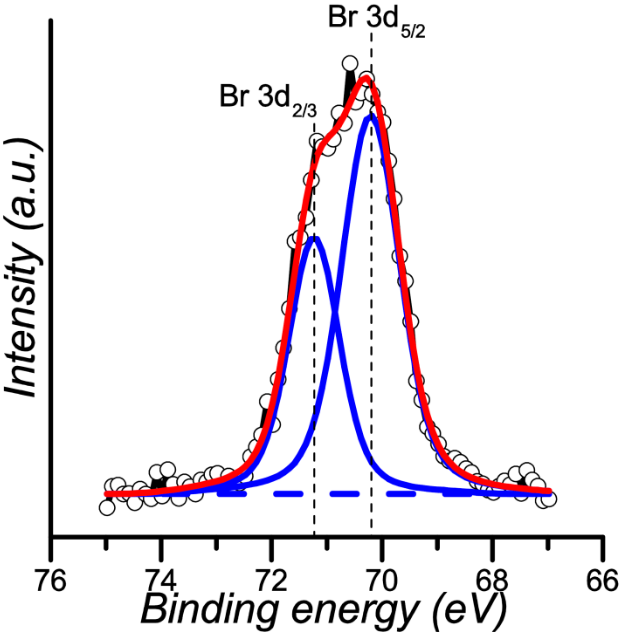


Figure SF2. High resolution Br 3d XPS spectra of initiator molecules.

Photoinduced SET-LRP of methacrylate monomers

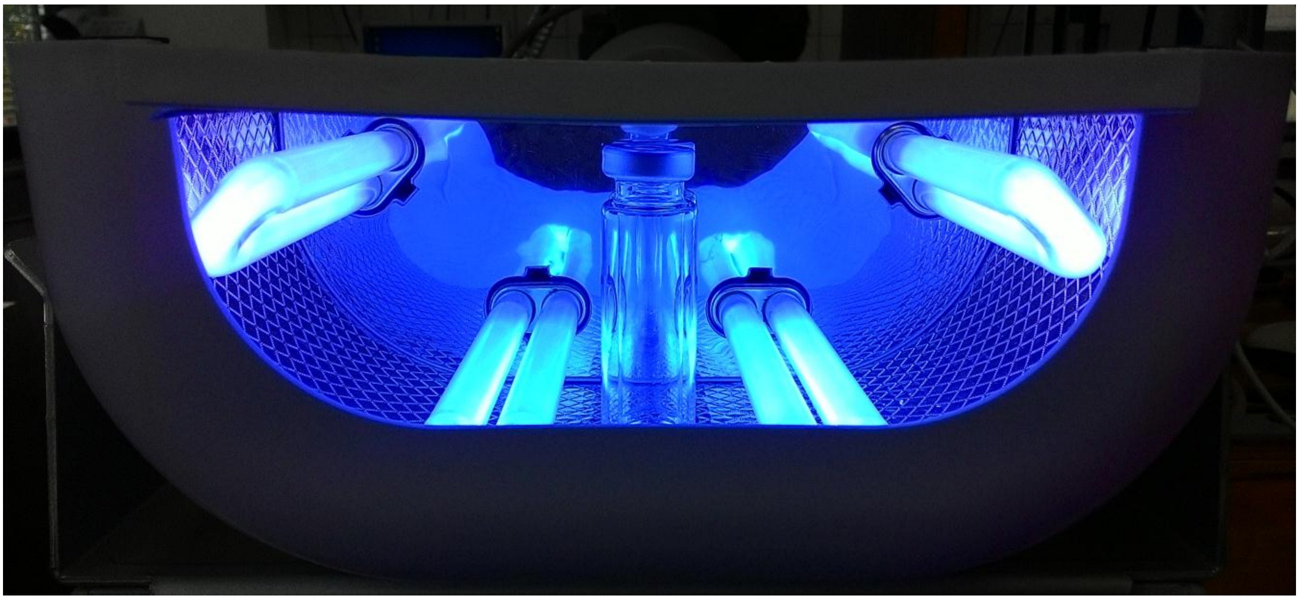
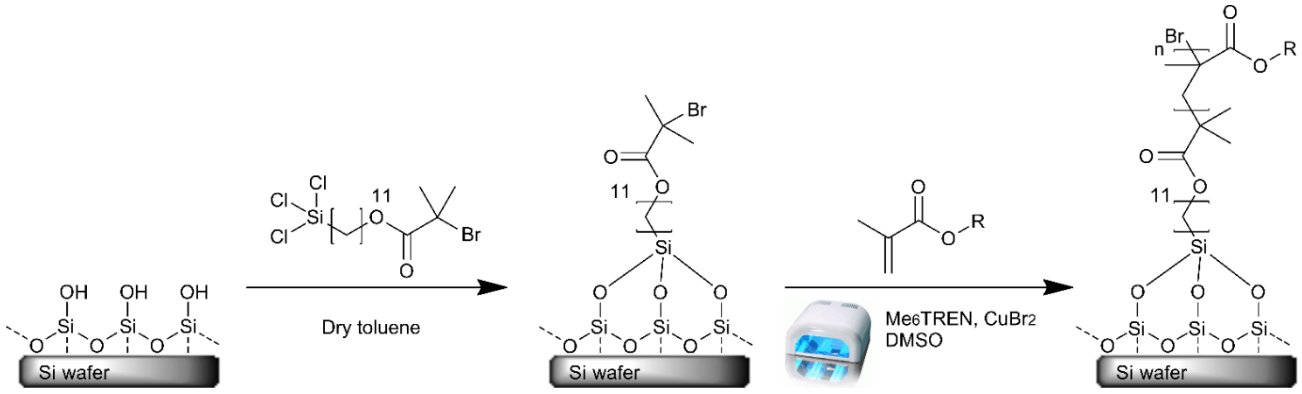


Figure SF3. Setup for surface-initiated photoinduced SET-LRP.



Scheme SS1. Synthesis of methacrylate polymer brushes by photoinduced SET-LRP.

Table ST1. Theoretical and measured ratios between the contributions within the C 1s spectrum of polymer brushes prepared by SET-LRP from initiator molecules anchored on Si substrate.

Layer	Determined chemical species	Theoretical ratio	Measured ratio
Initiator	$\underline{C}$—Si : ($\underline{C}$—C, C—H) : ($\underline{C}$—O—(C=O), Br—$\underline{C}$—(C=O)—O) : O—$\underline{C}$=O	1 : 13 : 2 : 1	1.1: 10.2 : 1.2 : 2.0 : 1.0
2-(Dimethylamino)ethyl methacrylate (DMAEMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—N : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	2 : 1 : 3 : 1 : 1	2.8 : 0.9 : 3.5 : 1.0 : 1.0
2-Hydoxyethyl methacrylate (HEMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—H : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	2 : 1 : 1 : 1 : 1	3.7 : 0.9 : 0.9 : 0.9 : 1.0
2-Hydroxypropyl methacrylate (HPM))	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—H : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	3 : 1 : 1 : 1 : 1	3.9 : 0.9 : 1.2 : 0.9 : 1.0
Oligo(ethylene glycol) methyl ether methacrylate (MeOEGMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—C : O—$\underline{C}$=O	2 : 1 : 9(—11) : 1	2.4 : 1.0 : 11.0 : 1.0
***t*-Butyl methacrylate (*t*BMA)**	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	5 : 1 : 1 : 1	5.0 : 0.9 : 1.0 : 1.0
***n*-Butyl methacrylate (*n*BMA)**	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	5 : 1 : 1 : 1	5.7 : 1.0 : 1.1 : 1.0
Methyl methacrylate (MMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	2 : 1 : 1 : 1	2.2 : 1.0 : 0.9 : 1.0
2-Ethylhexyl methacrylate (EHMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	9 : 1 : 1 : 1	10.2 : 1.4 : 1.2 : 1.0
Isobornyl methacrylate (IBMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	12 : 1 : 1 : 1	11.8 : 1.0 : 1.0 : 1.0
Solketal methacrylate (SMA)	($\underline{C}$—C, $\underline{C}$—H) : $\underline{C*}$—C(=O)—O : $\underline{C}$—O—C: $\underline{C}$—O—(C=O) : O—$\underline{C}$=O	4 : 1 : 3 : 1 : 1	4.1 : 0.9 : 1.9 : 0.9 : 1.0

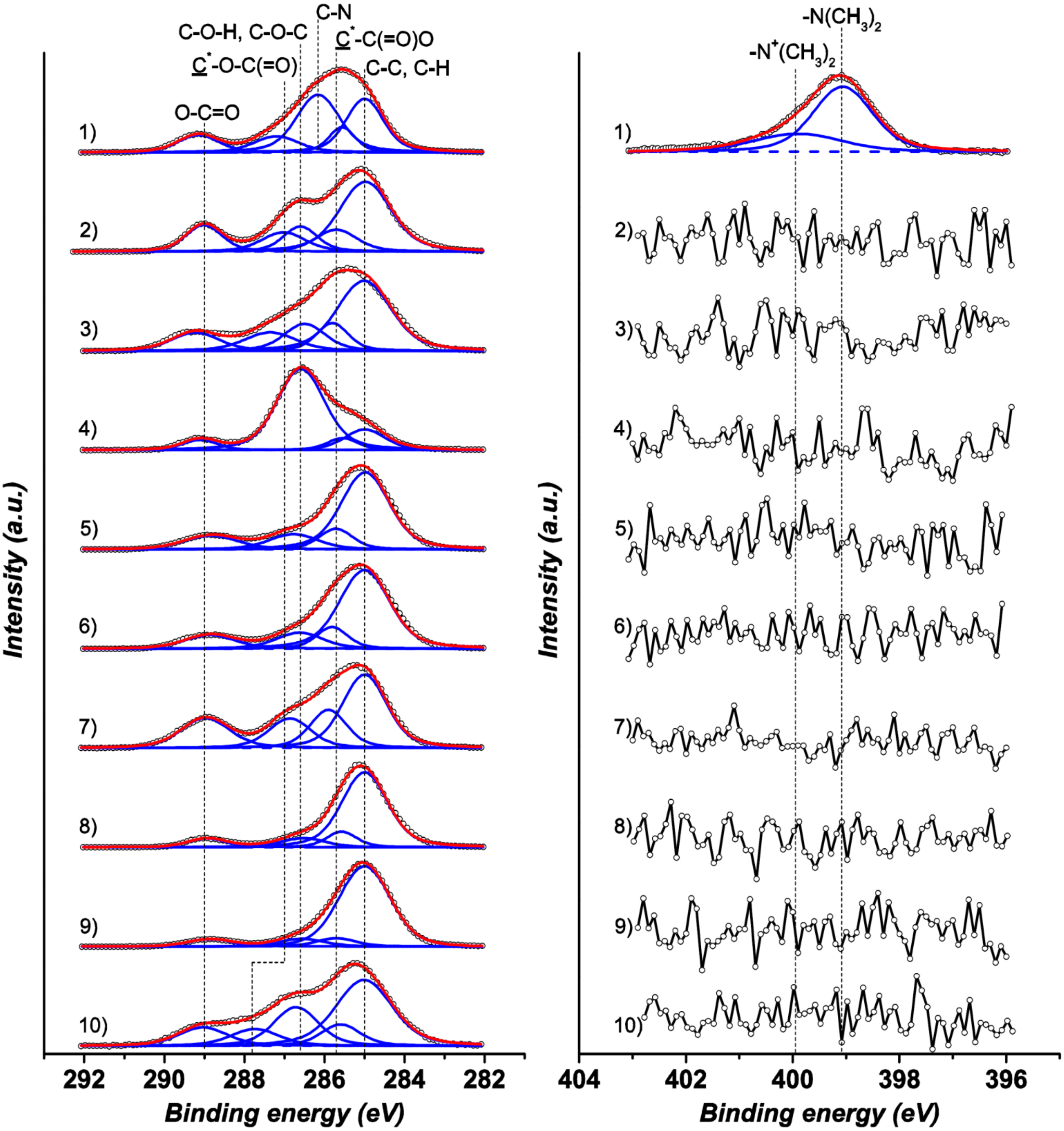


Figure SF4. High resolution C 1s and N 1s XPS spectra of DMAEMA (1), HEMA (2), HPM (3), MeOEGMA (4), *t*BMA (5), *n*BMA (6), MMA (7), EHMA (8), IBMA (9) and SMA (10) grown from the surface immobilized initiator by SET-LRP.

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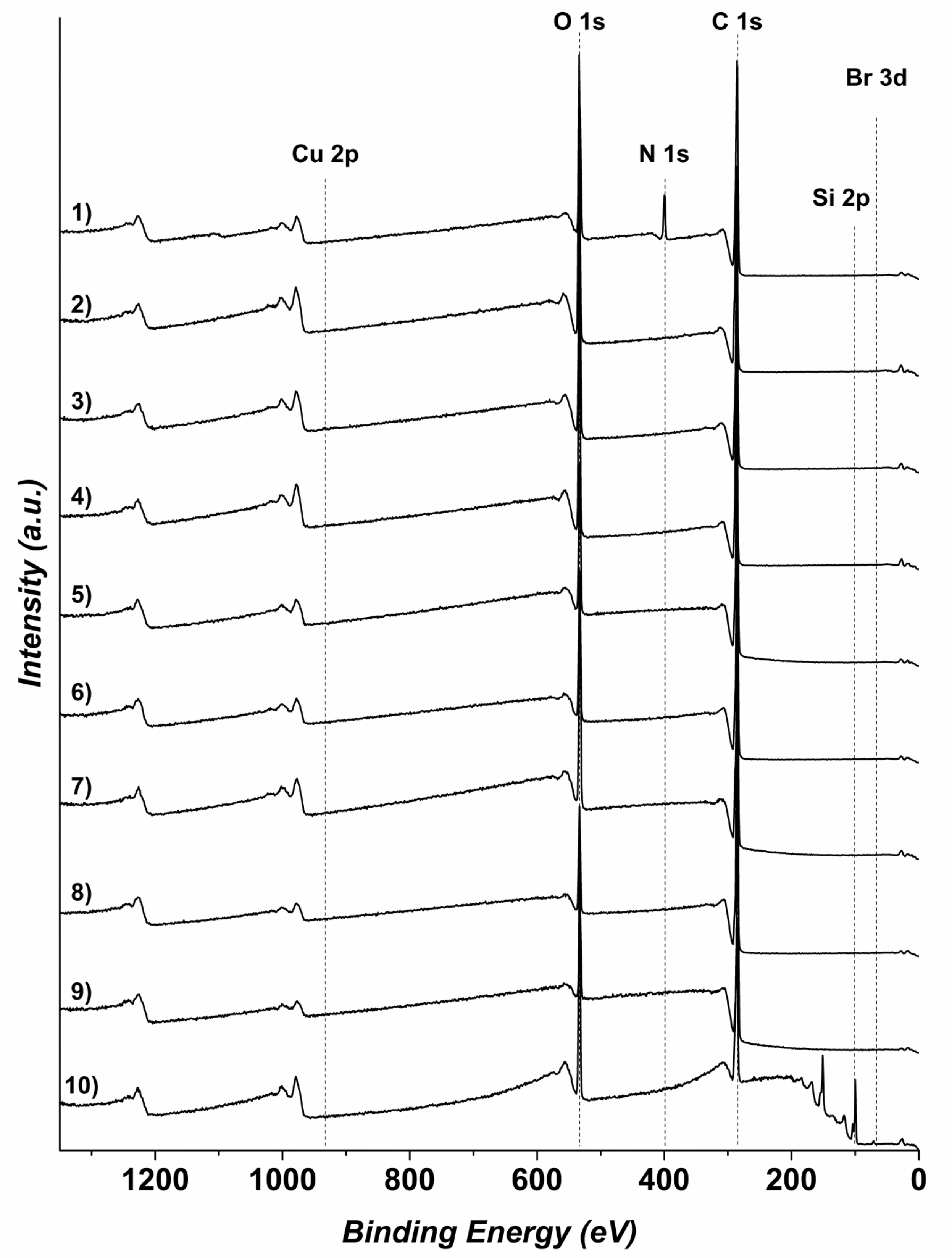


Figure SF5. XPS survey spectra of DMAEMA (1), HEMA (2), HPM (3), MeOEGMA (4), *t*BMA (5), *n*BMA (6), MMA (7), EHMA (8), IBMA (9) and SMA (10) grown from the surface immobilized initiator by SET-LRP. No signals arising from residual Cu are visible (expected at 933 eV).

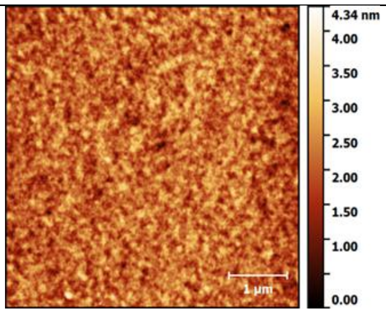
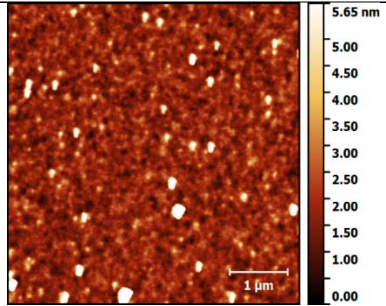
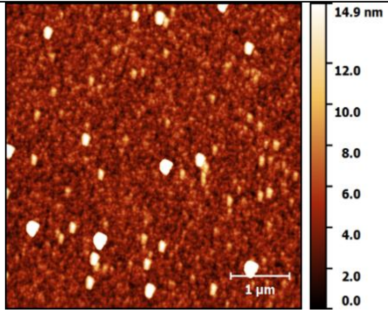
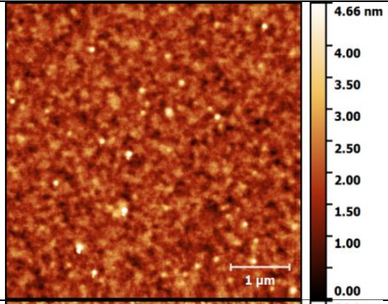
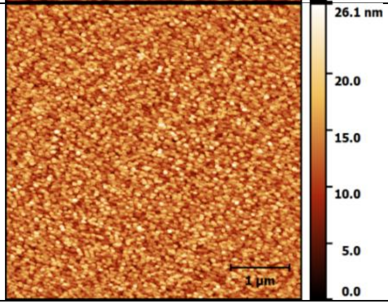
Table ST2. Dynamic water contact angle.

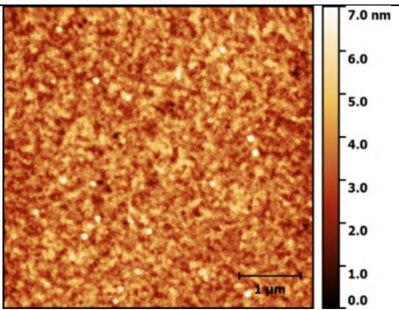
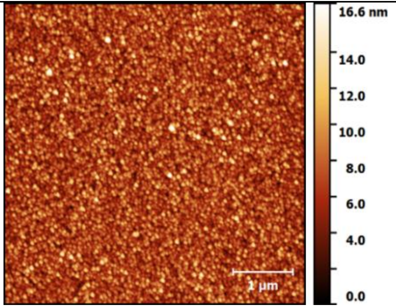
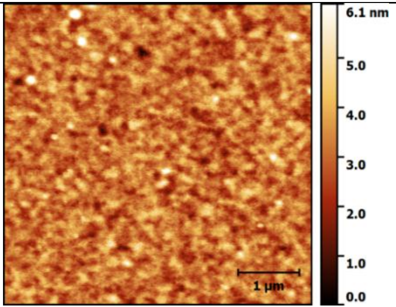
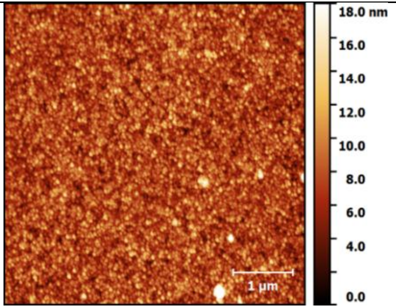
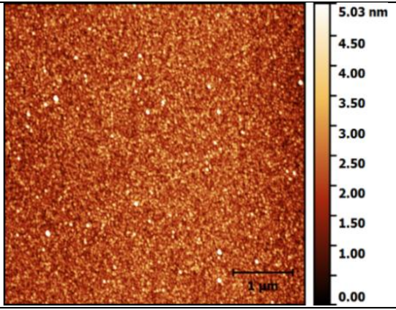
	Sample	θadv	θrec
1	**Silicon wafer (plasma cleaned)**	0*	0*
2	**Initiator**	83	77
3	**Poly(DMAEMA)**	72	25
4	**Poly(HEMA)**	47	18
5	**Poly(HPM)**	36	15
6	**Poly(MeOEGMA)**	58	29
7	**Poly(*t*BMA)**	100	64
8	**Poly(*n*BMA)**	86	76
9	**Poly(MMA)**	78	46
10	**Poly(EHMA)**	89	88
11	**Poly(IBMA)**	72	60
12	**Poly(SMA)**	104	63

*: The water drop completely spreads on freshly air-plasma-activated silicon chips.

AFM of the obtained polymer brushes on silicon

Table ST3. Topographic images and roughness reveals of prepared polymer brushes obtained in tapping mode in air at room temperature.

	Surface	Thickness, nm	AFM image	Roughness
1	**Poly(DMAEMA)**	42.5±1.1		1.75±0.36
2	**Poly(HEMA)**	40.9±0.2		1.50±0.35
3	**Poly(HPM)**	33.6±1.1		2.90±0.26
4	**Poly(MeOEGMA)**	26.8±1.8		1.20±0.26
5	**Poly(*t*BMA)**	21.6±0.7		3.65±0.1

6	**Poly(*n*BMA)**	31.7±0.1		1.00±0.23
7	**Poly(MMA)**	30.4		2.3±0.28
8	**Poly(EHMA)**	28.6±1.4		1.70±0.15
9	**Poly(IBMA)**	35.2±0.2		0.66±0.01
10	**Poly(SMA)**	4.4±0.03		2.35±0.26

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Blank experiment

Blank experiments were carried out starting from the polymerization conditions for DMAEMA in pure dimethyl sulfoxide (DMSO), using 7.7 ppm of copper according to the general procedure. Specific components of the polymerization system were individually excluded to establish their importance. The thickness obtained (if any are compared with the "normal" polymerization condition for 30 min polymerization, thickness = 95 nm). The following conditions were assessed:

1) No irradiation.

The polymerization mixture was prepared in DMSO according to the general procedure and kept overnight in the fridge. After degassing the solution was injected into degassed reactors containing silicon substrates functionalized with initiator SAM. The reactors were kept in the dark at room temperature for 30 min. After removing the substrates from the reactors, rinsing and drying them by blowing with nitrogen a negligible increase of thickness was observed by ellipsometry.

2) No SAM of initiator.

The polymerization procedure was carried out according to the general protocol, but substituting the initiator-functionalized substrates for freshly activated silicon wafer samples, lacking the SAM of the silane initiator. The surfaces were subjected to 30 min of irradiation and no increase in thickness was observed by ellipsometry.

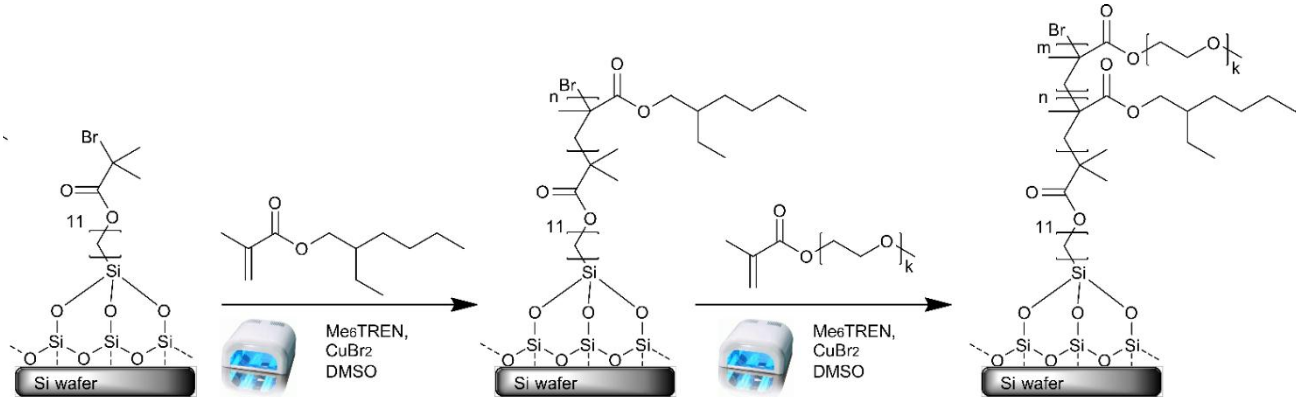
3) No catalyst.

The polymerization solution was prepared lacking of $CuBr_2$ and Me_6TREN, degassed for 30 min, and injected to previously degassed vials containing silicon wafers modified with initiator SAM. After 30 min of incubation in the polymerization solution the samples were removed from the reactors, rinsed copiously with solvent and dried by blowing nitrogen. A thickness increase of 4 nm was measured by ellipsometry.

4) No catalyst and no irradiation.

To analyse the ability of monomer to self-polymerize, a mixture of DMSO and DMAEMA was prepared, degassed for 30 min and injected to degassed vials containing initiator SAM-coated silicon chips. The samples were kept in the dark for 30 min. The substrates were subsequently removed from the vials, rinsed with solvent and dried by blowing with nitrogen. No increase in thickness was observed by ellipsometry.

Diblock copolymer brush of poly(EHMA-*b*-MeOEGMA)



Scheme SS2. Synthesis of diblok polymer brushes by photoinduced SET-LRP. Conditions firs block [EHMA] = 1.68 M, [$CuBr_2$] = 166 μM, [Me6TREN] = 995 μM in DMSO/toluene (1:2), conditions second block [MeOEGMA] = 1.68 M, [$CuBr_2$] = 166 μM, [Me6TREN] = 995 μM in DMSO.

XPS depth profiling of diblock copolymer

The top region displays clear predominance of C—O—C contributions. At a depth of 50 nm, the ratio (C—O—C, C—O—(C=O)):(C—C, C—H) strongly decreases from values of 3.5–4.0 until to a stable ratio of about 0.5, indicating enrichment of the bottom region with the poly(EHMA) block. Concomitantly, the (C—C, C—H):(O—C=O) ratio increases from about 1.5 to 9.0, further proving the dominance of the contributions characteristic for the EHMA monomer units. The C*—C(=O)—O : O—C=O ratios remains close to 1.0 throughout the whole depth profile.

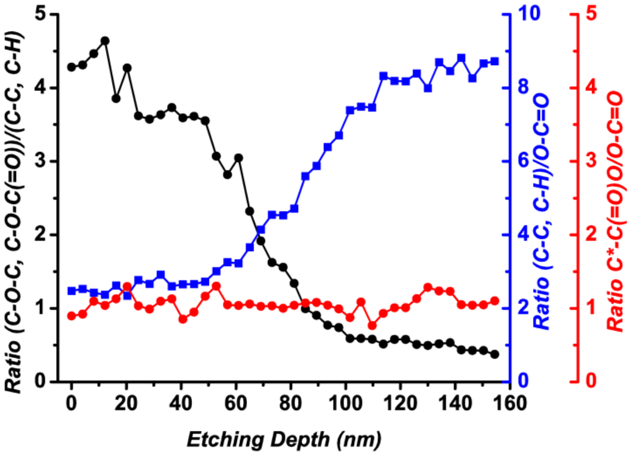


Figure SF6. Evolution of the (C—O—C, C—O—(C=O)):(C—C, C—H), (C—C, C—H):(O—C=O) and C*—C(=O)—O : O—C=O ratios of the contributions within the C 1s XPS spectrum over etch depth.

Measurement of protein fouling by surface plasmon resonance (SPR)

Surface plasmon resonance was employed to measure the fouling from solutions of human serum albumin (HSA 5 $mg\cdot mL^{-1}$) and fibrinogen (Fbg, 1 $mg\cdot mL^{-1}$) in phosphate-buffered saline (PBS, pH 7.4), as well as from undiluted human blood plasma (BP) and fetal bovine serum (FBS). Table ST4 presents results of fouling measured on surfaces prepared with SET-LRP and previously published results for comparison.

Table ST4. Protein fouling as determined by SPR

	Surface	**Fouling ($ng\cdot cm^{-2}$)**			
		FBS	**HSA**	**BP**	**Fbg**
1	**Poly(MeOEGMA) (thickness 12 nm)**	4.35	0	28.6	0
2	**Poly(MeOEGMA) (thickness 28 nm)**	1.95	0	16.2	0
3	**Poly(MeOEGMA) (thickness 51 nm)**	2.5	0	16.3	0
4	**Poly(MEOEGMA) by ATRP[1] (thickness 30 nm)**	0[2]	0	22.5	0
5	**SAM of OEG6[3]**	26	0	71	3.6
6	**Gold[3]**	261[2]	126	307	321

Entries 4 – 6 correspond to the references mentioned on the table and are given for comparison purpose.

Notes and references

1. C. Rodriguez-Emmenegger, E. Brynda, T. Riedel, M. Houska, V. Subr, A. B. Alles, E. Hasan, J. E. Gautrot and W. T. Huck, *Macromol. Rapid Commun.*, 2011, **32**, 952-957.
2. C. Rodriguez-Emmenegger, E. Hasan, O. Pop-Georgievski, M. Houska, E. Brynda and A. B. Alles, *Macromol. Biosci.*, 2012, **12**, 525-532.
3. C. Rodriguez-Emmenegger, M. Houska, A. B. Alles and E. Brynda, *Macromol. Biosci.*, 2012, **12**, 1413-1422.