Polymer Chemistry

Electronic Supporting Information for

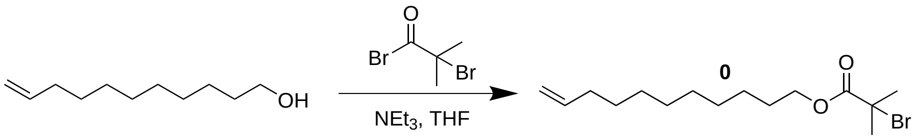
Synthesis of Non-Fouling Poly[*N*-(2-hydroxypropyl)methacrylamide] Brushes by Photoinduced SET-LRP

Mariia Vorobii,[a] Andres de los Santos Pereira,[a] Ognen Pop-Georgievski,[a] Nina Yu. Kostina,[a] Cesar Rodriguez-Emmenegger,[a,b,]* and Virgil Percec[b,]*

[a] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovsky sq. 2, 162 06 Prague, Czech Republic.*
E-mail: rodriguez@imc.cas.cz

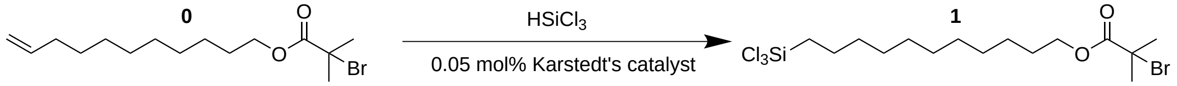
[b] *Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA.*
E-mail: percec@sas.upenn.edu

Synthesis of silane initiator



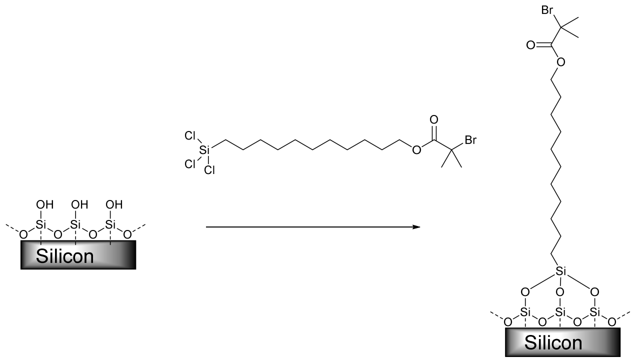
Supporting Scheme SS1. Synthesis of undec-10-en-1-yl 2-bromo-2-methylpropanoate **0**.

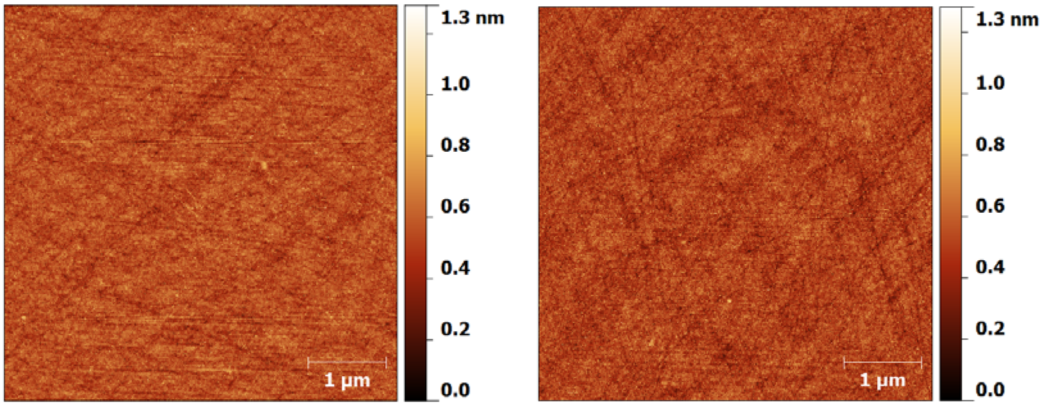
Synthesis of undec-10-en-1-yl 2-bromo-2-methylpropanoate (0). To a solution of undec-10-en-1-ol (15 mL, 75 mmol) and triethylamine (13.5 mL, 90 mmol) in dry THF (75 mL) was added dropwise a solution of α-bromoisobutyryl bromide (10.7 mL, 84.8 mmol) in dry THF (30 mL) at 0 °C. The reaction mixture stirred overnight at ambient temperature. Hexane (150 mL) was subsequently added to the mixture and it was washed twice with 2 N HCl, twice with brine, and water, and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by vacuum distillation. ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 1.21-1.43 (m, 12H), 1.61-1.73 (m, 2H), 1.93 (s, 6H), 2.03 (q, 2H, ^3J = 7.2 Hz), 4.16 (t, 2H, ^3J = 6.6 Hz), 4.87-5.04 (m, 2H), 5.72-5.9 (m, 1H).



Supporting Scheme SS2. Hydrosilylation of **0**, yielding **1**.

Synthesis of 11-(trichlorosilyl)undecyl 2-bromo-2-methylpropanoate (1). To an Ar-filled dry flask containing 10-undecen-1-yl-2-bromo-2-methylpropionate (***0***) (8.15 g, 25.5 mmol) and trichlorosilane (25.3 mL, 251 mmol) was added Karstedt's catalyst in xylene (1.24 mL; Pt ~2 %; 0.05 mol%) and the mixture stirred overnight under argon. The mixture was rapidly passed through a plug of silica to remove the catalyst and remaining trichlorosilane was removed under reduced pressure. The product **1** was purified by Kugelrohr distillation at 190 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.21-1.47 (m, 16H), 1.51-1.74 (m, 4H), 1.93 (s, 6H), 4.16 (t, 2H, ^3J = 7 Hz).





Supporting Figure SF1. Topographic images of bare silicon (left) and SAM of initiator (right) obtained in tapping mode in air at room temperature. Analysis of roughness reveals R_q of 0.87 ± 0.26 nm and 1.22 ± 0.23 nm for Si and SAM, respectively.

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

Atomic force microscopy was utilized to probe the surface topography. The SAM of initiator resulted in a homogeneous film with an R_q of 1.22 ± 0.23 nm, close to the one observed for bare silicon.

Photo-induced SET-LRP of HPMA

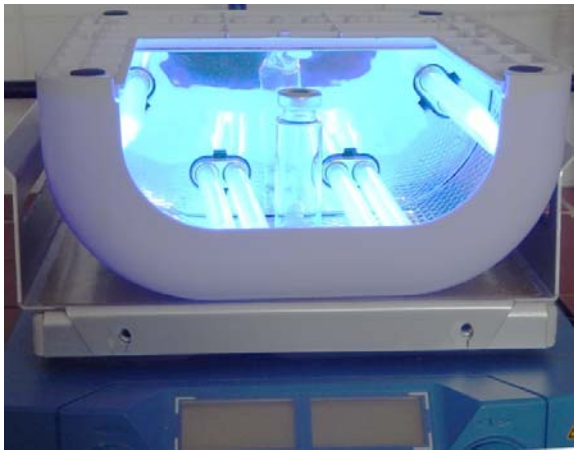
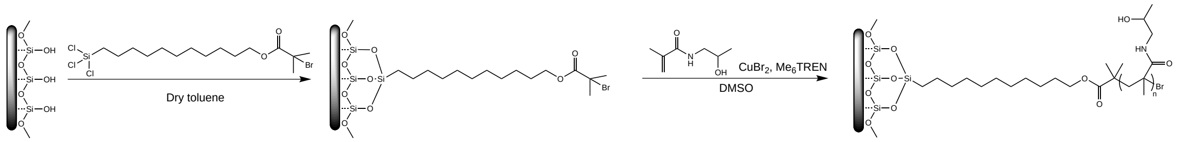
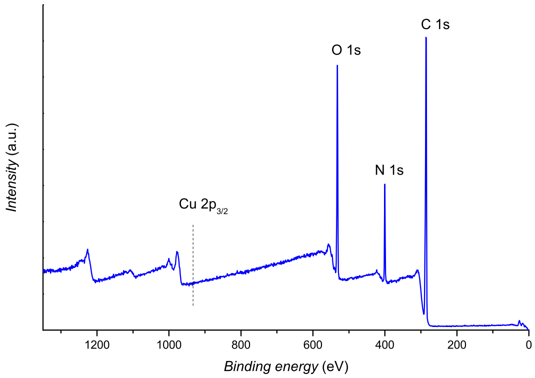


Figure SF1. Typical setup for the surface-initiated photoinduced SET-LRP of HPMA

Additional characterization of poly(HPMA)



Supporting Scheme SS2. Photoinduced SET-LRP of HPMA



Supporting Figure SF3. Survey spectrum of 30 nm-thick poly(HPMA) brushes. No residual Cu was present on the surfaces.

Inspection of the survey spectrum clearly shows that no Cu remains on the surface (Supporting Figure SF3). The lack of cytotoxic Cu is an important advantage of this polymerization for its application to the generation of surfaces interfacing not only with biological fluids but also with cells and tissues.

Supporting Table ST1. Dynamic water contact angles

Surface	θ_{Adv} (°)	θ_{Rec} (°)
Silicon wafer	0*	0*
Initiator	82	72
Poly (HPMA)	35	9

*: The water drop completely spreads on the freshly cleaned silicon wafer chips.

Control experiments

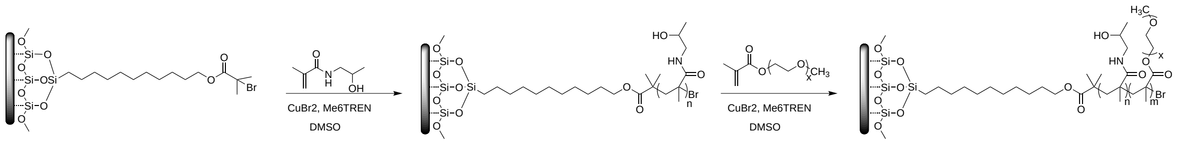
Control experiments were carried out with the procedure described in the Methods section of the manuscript for pure DMSO and 80 ppb of Cu including the following modifications: (i) without irradiation, (ii) without initiator SAM on the surface, and (iii) without catalyst.

(i) *Without irradiation.* The polymerization solution was prepared in the same way as described above for a typical polymerization and transferred to the vials containing the surfaces coated with a SAM of initiator. The samples were kept for 1 h and 2 h without irradiation. The observed increase in thickness was in the range of the error of the measured thickness and does not increase with the time the initiator coated surfaces are in contact with the polymerization solution.

(ii) Irradiation of substrate lacking the SAM of initiator. The degassed polymerization solution was transferred to crimped vials containing silicon wafer (lacking the SAM of the silane initiator). The three surfaces were subjected to 1 h irradiation. No thickness increase was detected.

(iii) No catalyst added. The polymerization solution was prepared without adding $CuBr_2$ and Me_6TREN. After irradiating the surfaces immersed in this polymerization solution for a period of 1 h no increase in the thickness was visible.

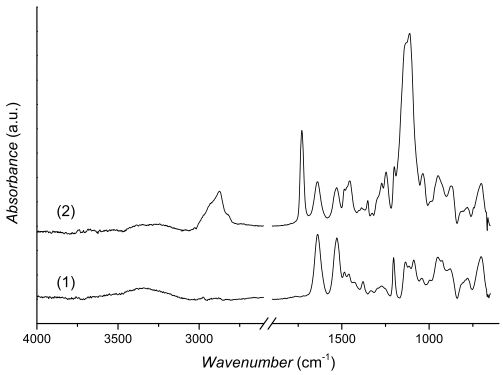
Additional assessment of the livingness of photo-triggered SET-LRP of HPMA



Supporting Scheme SS3. Preparation of a diblock copolymer brush of HPMA and MeOEGMA

Supporting Table ST3. Dynamic water contact angles of the block polymer brushes

Surface	Thickness (nm)	θ_{Adv} (°)	θ_{Rec} (°)
Poly (HPMA)	26.2 ± 2.3	35	9
Poly (HPMA-*b*-MeOEGMA)	116.1 ± 1.8	67	17



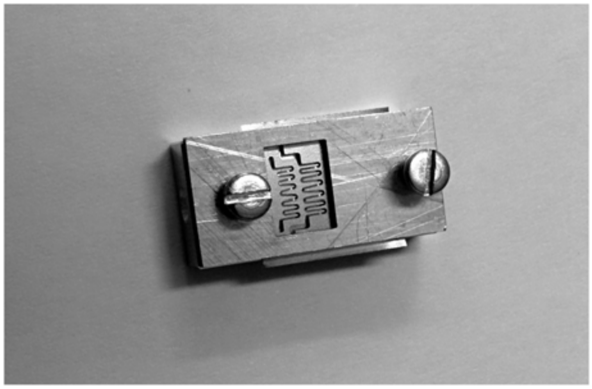
Supporting Figure SF4. Representative GAATR-FTIR spectra of the poly(HPMA) ((1), thickness 220 nm) and poly(HPMA-*b*-MeOEGMA) ((2), thickness 120 nm).

Diblock poly(HPMA-b-MeOEGMA).

FTIR-GAATR spectroscopy further confirms the attainment of the poly(HPMA-*b*-MeOEGMA) diblock structure. Supporting Figure SF4 shows the comparison of the spectra obtained for a pure poly(HPMA) brush and the diblock copolymer. In addition to the features already discussed for poly(HPMA), poly(HPMA-*b*-MeOEGMA) displays a characteristic band at 1730 cm^{-1} that can be assigned to the carbonyl ester group of the methacrylate polymer block. Moreover, the group of bands between 2820 cm^{-1} and 2990 cm^{-1} corresponds to the C—H vibrations of the oligo(ethylene glycol) side chains of the polymer. The most pronounced difference in the spectrum of poly(HPMA-*b*-MeOEGMA) is the appearance of the strong vibration at 1113 cm^{-1} arising from the C—O stretching of the ether groups present in the side chains.

Patterning of poly(HPMA) brushes

To achieve patterning, the irradiation areas were restricted by using a microengineered shadow mask (Supporting Figure SF5). The silicon wafer decorated with SAM of initiator was place in a holder and covered with the shadow mask featuring a zig-zag line pattern. The holder were placed in crimped vials and the polymerization proceeded in analogous fashion as described above (DMSO/water, 1:1, with 80 ppb Cu). After UV irradiation for 30 min the surfaces were carefully removed from the holders, rinsed copiously with DMSO, acetone, and water and dried under a nitrogen flow. The success of the confined polymerization was assessed by ellipsometry (mapping) and profilometry.



Supporting Figure SF5. Picture of the sample holder featuring the shadow mask used in this experiments.

Quantification of fouling by SPR

The fouling from human serum albumin (HSA, 5 mg·mL^{-1} in PBS), fibrinogen (Fbg, 1 mg·mL^{-1}), fetal bovine serum (FBS, undiluted) and human blood plasma (HBP, undiluted) were determined by surface plasmon resonance (SPR). The fouling on poly(HPMA) brushes prepared by photo-triggered SET-LRP are presented along with previously published values of fouling for comparison purposes.

Supporting Table ST4. Fouling from proteins determined by SPR

Surface	Fouling (pg·mm^{-2})			
	HSA	Fbg	FBS	HBP
Poly (HPMA)	0	0	0	18
Poly (HPMA) by ATRP[1]	0	0	0	0
Poly(HOEGMA)* (30 nm)[2]	0	0	0	197
SAM of OEG6[3]	0	36	260	710
Gold[3]	1260	3210	-	3070

*HOEGMA: Oligo(ethylene glycol) methacrylate

References

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3 C. Rodriguez-Emmenegger, M. Houska, A. B. Alles and E. Brynda, *Macromol. Biosci.*, 2012, **12**, 1413-1422.