Supporting Information for

Reactive Block Copolymers for Patterned Surface Immobilization with Sub-30 nm Spacing

Hatice Turgut, Nico Dingenouts, Vanessa Trouillet, Peter Krolla-Sidenstein, Hartmut Gliemann, Guillaume Delaittre*

Index

| Additional schemes | S2 |
|---|------------|
| Characterization of M1–3 and BCP 1–4 | S 3 |
| Additional AFM images | S8 |
| Photocrosslinking | S 9 |
| Synthesis and characterization of the alkyne-functionalized water-soluble polymer | S10 |
| References | S11 |

Additional schemes



Scheme S1. Synthetic route for MI1 and BCP1.



Scheme S2. Synthetic route for MI2 and BCP2.



Scheme S3. Synthetic route for MI3 and BCP3.



Figure S1. ¹H NMR spectra of samples taken during the synthesis of **MI2** at t_0 (top) and t_{end} (bottom), with indication of integrals used for conversion and comonomer composition calculations.



Figure S2. (A) Chemical route for the conversion of 4-chloromethylphenyl groups into 4azidomethylphenyl groups to obtain **BCP4** from **BCP3.** (B) Selected region of the ¹H NMR spectra of **BCP 3** (top) and **BCP4** (bottom) showing the shift of the methylene protons after chloride-to-azide transformation.



Figure S3. SEC traces of PI chain extension attempt from a PS-SG1: (A) with a target of 30% conversion at [isoprene]/[PS-SG1] = 1025; (B) with a target of 20% conversion at [isoprene]/[PS-SG1] = 1335. $(M_{n,SEC} (PS-SG1) = 23000 \text{ g mol}^{-1}).$



Figure S4. (A) Representative repeating unit distribution for a PI block synthesized in the current study. (B) ¹H NMR peak assignments for the ethylenic protons present in the PI block of PS-*b*-PI derivatives.



Figure S5. ¹H NMR spectrum of **BCP1**, **BCP2**, **BCP3**, and **BCP4** showing similar integral values for styrene and isoprene repeating units.

Example of volume fraction calculation for **BCP3**: According to ¹H NMR data, for 1u styrene, there exist 1.25/0.8 = 1.5625u isoprene and 0.04 CMS (u is an arbitrary number)





Figure S6. ¹⁹F NMR spectrum of BCP2.

| Table S1. | Macromolecular | characteristics of | the macroinitiators | s and block co | polymers i | reported in |
|-----------|----------------|--------------------|---------------------|----------------|------------|-------------|
| the curre | nt study. | | | | | |

| Macroinitiators | | | | | Block copolymers | | | |
|-----------------|--|------|-----------------|------|--|----------------|--|------------------|
| Name | M _{n,SEC} ^a g mol ^{−1} | Đª | %F [♭] | Name | M _{n,SEC} ^a g mol ^{−1} | Đ ^a | M _{n,NMR} ^b g mol ^{−1} | fps :f pi |
| MI1 | 22.3 | 1.10 | - | BCP1 | 57.7 | 1.36 | 44.5 | 0.46:0.54 |
| MI2 | 25.3 | 1.10 | 4.0 | BCP2 | 61.9 | 1.32 | 47.3 | 0.50:0.50 |
| MI3 | 25.5 | 1.11 | 4.8 | BCP3 | 61.8 | 1.36 | 49.4 | 0.47:0.53 |
| | | | | BCP4 | 63.5 | 1.33 | 49.4 | 0.47:0.53 |

Additional AFM images



Figure S7. (Top row) AFM phase images of (A) a 33 nm-thick film of **BCP1** spin-coated from a 0.3 wt% solution in toluene; (B) 29 nm thick film of **BCP1** spin-coated from a 0.3 wt% solution in toluene, and (C) 7 nm thick film of **BCP1** spin-coated from a 0.2 wt% solution in toluene. (Bottom row) Schematic representations of (D) PI wetting the surface in the case of thick films demonstrated on images A-B (E) BCP perpendicular orientation on Si wafer in the case of ultrathin films demonstrated on image C. *Scale bar 200 nm*.



Figure S8. AFM *height* images of (A) a **BCP4** film, (B) the **CuAAC** sample, and (C) the **control** sample. *Scale bar 300 nm*.

Photocrosslinking

The thin films produced in the current study were initially thought to be employed for functionalization in aqueous media. However, the CuAAC investigation revealed that surface morphological alterations could occur in water. Consequently, stabilization of the nanostructures seemed to be required. Covalent crosslinking is typically applied to permanently fix block copolymer films.^{1–3} Particularly, systems bearing azides are amenable to crosslinking upon light or thermal treatment.^{4–6} Hence, a **BCP4**-coated Si wafer was irradiated with UV light for 15 min (see Experimental Section for details). Interestingly, if the structures are crosslinked, they must be stable not only in aqueous medium but also in any organic solvents. After irradiation, the film was indeed subjected to thorough and multiple washings with acetone, DCM, and toluene, before a final incubation in DMSO for 30 min. The AFM phase and height images of this sample are depicted in Figure S9. Undoubtedly, an irradiation time of 15 min was sufficient to guarantee the integrity of the structures.



Figure S9. AFM phase (left) and height (right) images of a photocrosslinked ultra-thin **BCP4** film after multiple washings and incubation with organic solvents.

Synthesis and characterization of the alkyne-functionalized water-soluble polymer



Scheme S4. Synthetic route for ≡-PDMAAm.



Figure S10. ¹H NMR spectra of TMS-=-PDMAAm (top) and =-PDMAAm (bottom).



Figure S11. SEC traces of TMS-≡-PDMAAm (black full line) and its deprotected counterpart ≡-PDMAAm (orange dotted line).

References

- (1) Rudolph, T.; Schacher, F. H. *Eur. Polym. J.* **2016**, *80*, 317–331.
- (2) Leiston-Belanger, J. M.; Russell, T. P.; Drockenmuller, E.; Hawker, C. J. *Macromolecules* **2005**, *38* (18), 7676–7683.
- (3) Tietz, K.; Finkhäuser, S.; Samwer, K.; Vana, P. *Macromol. Chem. Phys.* **2014**, *215* (16), 1563–1572.
- (4) Park, J.; Lee, C.; Jung, J.; Kang, H.; Kim, K.-H.; Ma, B.; Kim, B. J. Adv. Funct. Mater. 2014, 24 (48), 7588–7596.
- Bang, J.; Bae, J.; Löwenhielm, P.; Spiessberger, C.; Given-Beck, S. A.; Russell, T. P.; Hawker, C.
 J. Adv. Mater. 2007, 19 (24), 4552–4557.
- Jung, H.; Hwang, D.; Kim, E.; Kim, B.-J.; Lee, W. B.; Poelma, J. E.; Kim, J.; Hawker, C. J.; Huh, J.;
 Ryu, D. Y.; Bang, J. ACS Nano 2011, 5 (8), 6164–6173.