Supporting Information

Surface-initiated Polymerization of Azidomethacrylates and Film Elaboration via Click Chemistry

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Figure S1-1. Reflectance FTIR spectra of gold substrates coated with poly(AZPMA) brushes grown for (a) 0.5 h (b) 4 h (c) 6 h and (d) 8 h from a monolayer of initiator.

Figure S1-2. Topographical AFM image (tapping mode) of a gold-coated Si wafer modified with a 250 nm poly(AZPMA) brush.

Figure S1-3. Evolution of the ellipsometric brush thickness with time for the homopolymerization of AzPMA and mEGMA from initiator monolayers on Au using CuBr/Me₄Cyclam/dnNbpy/DMF as the catalyst at 50 °C.

Figure S1-4. Reflectance FTIR spectra of gold substrates coated with poly(AzPMEA-co-mPEGMA) brushes (50/50 monomer ratio during polymerization) grown for polymerization times of (a) 5 min (b) 30 min (c) 1 h (d) 2 h and (e) 4 h.

Figure S1-5. Evolution of the ellipsometric thickness with polymerization time (50 °C) for polyAzPMA, poly(AzPMA-co-mPEGMA), and poly(mPEGMA) brushes grown from initiators on gold.

Figure S1-6. Reflectance FTIR spectra of polyAzPMA, poly(AzPMA-co-mPEGMA), and poly(mPEGMA) brushes grown from initiators on gold using different comonomer ratios.

Figure S1-7. Reflectance FTIR spectra of gold–supported ~200 nm-thick poly(AzPMA-co-PEGMA) (50/50 monomer ratio) brushes after reaction between the copolymer and a fluorescent dye for (a) 1 h (b) 30 min (c) 15 min (d) 5 min (e) 1 min (f) 0 min.

Figure S1-8. Conversion of the azide groups in ~200 ± 30 nm-thick poly(AzPMA), poly(AzPMA-co-mEGMA) and poly(AzPMA-co-mPEGMA) brushes during reaction with an alkyne-containing fluorescent dye.

Figure S1-9. Measurement of the molar extinction coefficient of the alkyne modified fluorescein dye.

Figure S1-10. UV-vis spectra of 200 ± 30 nm-thick poly(AzPMA), poly(AzPMA-co-mPEGMA), and poly(mPEGMA) brushes grown from ITO substrates and derivatized in a 5 min click reaction with an alkynylated fluorescein.

Figure S1-11. Reflectance FTIR spectra of poly(AzPMA-co-mPEGMA) brushes grown from gold substrates, before and after reaction with alkynylated mPEG 5000 in water.
Figure SI-1. Reflectance FTIR spectra of gold substrates coated with poly(AzPMA) brushes grown for (a) 0.5 h (b) 4 h (c) 6 h and (d) 8 h from a monolayer of initiator. A UV/O₃ cleaned gold slide served as a background.

Figure SI-2. Topographical AFM image (tapping mode) of a gold-coated Si wafer modified with a 250 nm poly(AzPMA) brush. The image is a 5 × 5 μm survey scan with a root mean square roughness of 1.9 nm, as calculated by the Nanoscope IV software.
Figure SI-3. Evolution of the ellipsometric brush thickness with time for the homopolymerization of AzPMA and mEGMA from initiator monolayers on Au using CuBr/Me₄Cyclam/dnNbp/DMF as the catalyst at 50 °C (× AzPMA, □ mEGMA) and CuCl/PMDETA/DMF at 50 °C (○ AzPMA, ◦ mEGMA). Each point represents the average of three independent polymerizations, and the error bars correspond to the standard deviation.

Figure SI-4. Reflectance FTIR spectra of gold substrates coated with poly(AzPMA-co-mPEGMA) brushes (50/50 monomer ratio during polymerization) grown for polymerization times of (a) 5 min (b) 30 min (c) 1 h (d) 2 h and (e) 4 h.
Figure SI-5. Evolution of the ellipsometric thickness with polymerization time (50 °C) for poly(AzPMA), poly(AzPMA-co-mPEGMA), and poly(mPEGMA) brushes grown from initiators on gold. Polymerizations occurred at various monomer ratios using the CuCl/PMDETA/DMF system. ◇ AzPMA/mPEGMA (100/0), △ AzPMA/mPEGMA (75/25), × AzPMA/mPEGMA (50/50), □ AzPMA/mPEGMA (25/75), ○ AzPMA/mPEGMA (0/100). Each point represents a different film.

Figure SI-6. Reflectance FTIR spectra of polyAzPMA, poly(AzPMA-co-mPEGMA), and poly(mPEGMA) brushes grown from initiators on gold using different comonomer ratios. (a) AzPMA/mPEGMA (100/0) (b) AzPMA/mPEGMA (75/25) (c) AzPMA/mPEGMA (50/50) (d) AzPMA/mPEGMA (25/75) (e) AzPMA/mPEGMA (0/100). The polymerization occurred at 50 °C with a CuCl/PMDETA/DMF catalyst.
Figure SI-7. Reflectance FTIR spectra of gold–supported ~200 nm-thick poly(AzPMA-co-mPEGMA) (50/50 monomer ratio) brushes after reaction between the copolymer and a fluorescent dye for (a) 1 h (b) 30 min (c) 15 min (d) 5 min (e) 1 min (f) 0 min.

Figure SI-8. Conversion of the azide groups in ~200 ± 30 nm-thick poly(AzPMA), poly(AZPMA-co-mEGMA) and poly(AzPMA-co-mPEGMA) brushes during reaction with alkyne-terminated fluorescein. Conversions were determined from the percent reduction in the azide peak area in reflectance FTIR spectra such as those in Figure SI-7. + AzPMA/mEGMA (100/0), × AzPMA/mEGMA (75/25), ○ AzPMA/mEGMA (50/50), □ AzPMA/mEGMA (25/75), ◊ (black) AzPMA/mPEGMA (75/25), △ AzPMA/mPEGMA (50/50), ◊ (red) AzPMA/mPEGMA (25/75). Each point represents a different film.
Figure SI-9. Measurement of the molar extinction coefficient of the alkyne-modified fluorescein dye.

Figure SI-10. UV-vis spectra of 200 ± 30 nm-thick polyAzPMA, poly(AzMPA-co-mPEGMA), and poly(mPEGMA) brushes grown from ITO substrates and derivatized in a 5 min click reaction with a alkynylated fluorescein. Blue line: AzPMA (25/75), magenta line: AzPMA/mPEGMA (50/50), black line: AzPMA/mPEGMA (75/25), red line: AzPMA/mPEGMA (100/0). The green line is the spectrum of AzPMA/mPEGMA (100/0) before the click reaction.
Figure SI-11. Reflectance FTIR spectra of poly(AzPMA-co-mPEGMA) brushes grown from gold substrates, before and after reaction with alkynylated mPEG 5000 in water. For each data set, the two spectra correspond to the initial brush (bottom) and the “clicked” brush (top). The initial film thicknesses were 50 ± 10 nm, and the click reaction was run for 12 hours at room temperature using a CuBr/bpy catalyst. (a) AzPMA/mPEGMA (100/0), (b) AzPMA/mPEGMA (75/25), (c) AzPMA/mPEGMA (50/50), (d) AzPMA/mPEGMA (25/75).