Electronic Supplementary Information

Controlled growth of protein resistant PHEMA brushes via S-RAFT polymerization

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Figure S1.¹H NMR spectrum of 4-(3-(triethoxysilyl)propylcarbamoyl)-2-cyanobutan-2-yl benzodithioate (**CTA-1**) recorded in CDCl₃ at 25 °C.



Figure S2. Tapping mode AFM images of functionalized silicon wafer substrates with: (*a*) CTA-1; (*b*) living PHEMA brushes (d = 54.2 nm); (*c*) chain extended PHEMA brushes (d = 73 nm). Chain extension was performed on a PHEMA functionalized substrate with initial d = 40.5 nm (not shown). Thicknesses were measured by ellipsometry.



Figure S3. Semi-logarithmic plots of monomer conversion (¹H NMR) versus time for RAFT polymerization of HEMA in solution for different ratios of sacrificial chain transfer agent [CTA-2]/[AIBN]: 0/1 for **B1** (black squares); 1/1 for **B2** (red circles); 2/1 for **B3** (blue triangle); 3/1 for **B4** (green inverted triangle). Experimental conditions: 80 °C, 1735 Eq. HEMA, 1,4-dioxane/water 80/20 v/v. Entries **B1-B4** are listed in Table 1, main document.



Figure S4. M_n values (**B2**: red circles, **B3**: blue triangles, **B4**: inverted green triangles) and polydispersity indices (open circles) versus monomer conversion (¹H NMR) for RAFT polymerization of HEMA in solution for different ratios of sacrificial [CTA-2]/[AIBN]: (*a*) 1/1 for **B2**; (*b*) 2/1 for **B3**; (*c*) 3/1 for **B4**. Experimental conditions: 80 °C, 1735 eq. HEMA, 1,4-dioxane/water 80/20 v/v. Entries **B2-B4** are listed in Table 1, main document.



Figure S5. Semi-logarithmic plots of monomer conversion (¹H NMR) versus time for RAFT polymerization of HEMA in solution using three volume ratios of 1,4-dioxane/water: 80/20 for **B2** (red circles); 50/50 for **B5** (purple diamonds); 20/80 for **B6** (grey diamonds). Experimental conditions: 80 °C, [HEMA]/[CTA-2]/[AIBN] = 1735/1/1. Entries **B2**, **B5** and **B6** are listed in Table 1, main document.



Figure S6. M_n values (**B5**: purple diamonds, **B6**: green diamonds) and polydispersity indices (open circles) versus monomer conversion (¹H NMR) for RAFT polymerization of HEMA in solution using three different volume ratios of 1,4-dioxane/water: (*a*) 50/50 for **B5**; (*b*) 20/80 for **B6**. Experimental conditions: 80 °C, [HEMA]/[CTA-2]/[AIBN] = 1735/1/1. Entries **B5** and **B6** are listed in Table 1, main document.