

## Supporting Information

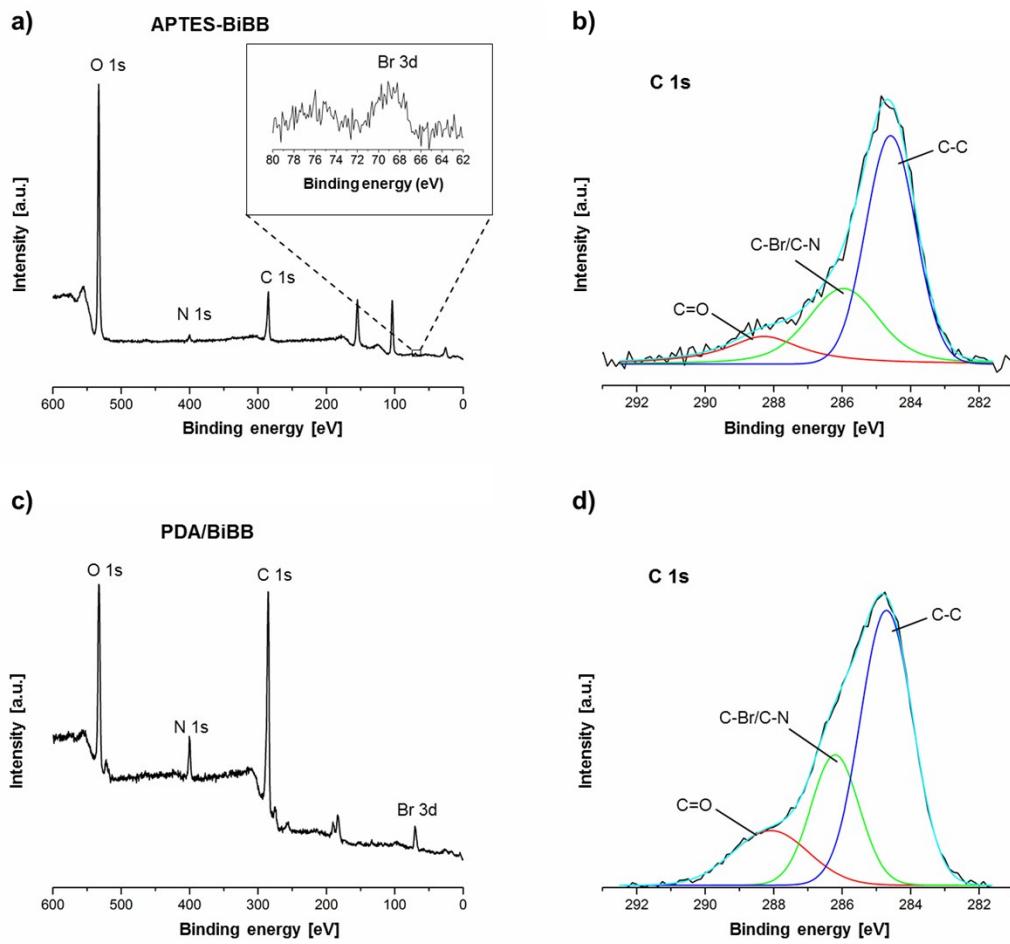
### **Substrate-Independent Cu(0)-Mediated Controlled Radical Polymerization: Grafting of Block Copolymer Brushes from Poly(dopamine) Modified Surfaces**

Daniel Hafner, Rainer Jordan\*

#### **X-ray photoelectron spectroscopy (XPS)**

For the detection of surface-bound initiator X-ray photoelectron spectroscopy was performed on both APTES-BiBB and PDA/BiBB. Besides the expected peaks of oxygen, nitrogen and carbon on both samples a weak Br 3d signal is detected on APTES-BiBB at a binding energy of 69.0 eV.<sup>47</sup> The low intensity can be explained with a gradual loss of bromine during the measurements due to the continuous exposure of energy. Additionally, three carbon species can be distinguished and assigned to C-C, C-N/C-Br and C=O at a binding energy of 284.6 eV, 286.0 eV and 288.3 eV, respectively.<sup>47,9</sup> Similarly, a peak originating from Br appears at 70 eV for PDA/BiBB.<sup>47,9</sup> Furthermore, the signals of C-C, C-N/C-Br and C=O can also be found at 284.7 eV, 286.2 eV and 288.1 eV, respectively.

All in all, XPS clearly proves the binding of bromine initiator to both APTES and PDA modified SiO<sub>2</sub>. The ellipsometrically determined thickness of APTES-BiBB and PDA/BiBB was ~ 2 nm and 25-35 nm, respectively.



**Figure S1:** XPS spectra of initiator modified  $\text{SiO}_2$ : APTES-BiBB (a) and its core-level spectrum (b). PDA/BiBB (c) and its core-level spectrum (d).

## SI-CuCRP on different substrates

**Table S1:** Results of SI-CuCRP of HEMA on different PDA/BiBB modified substrates. Ligand: PMDETA, solvent:  $\text{H}_2\text{O}$ .

Substrate	$t_R$ [min]	$\theta_s$ , pure [°]	$\theta_s$ , PDA [°]	$\theta_s$ , PDA/BiBB [°]	$\theta_s$ , PHEMA [°]
$\text{SiO}_2$	15	< 10	36	68	51
Au	15	75	29	71	51

Cu	30	90	38	72	57
Al/Al <sub>2</sub> O <sub>3</sub>	20	98	32	72	54
PTFE	30	112	42	74	58

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## FT-IR of PHEMA

**Table S2:** Assignment for the spectral bands of PHEMA.

Frequency [cm <sup>-1</sup> ]	Assignment
3680 – 3050	v (O-H)
2946	v <sub>as</sub> (CH <sub>2</sub> , CH <sub>3</sub> )
2884	v <sub>s</sub> (CH <sub>2</sub> , CH <sub>3</sub> )
1726 – 1720	v (C=O)
1487 – 1451	δ (CH <sub>2</sub> )
1389 – 1365	δ <sub>twist, rock</sub> (CH <sub>2</sub> )
1276 – 1248	δ (OH)
1159	v (C-O)
1080	v (C-O-C)
749	v (-C-O-)

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