Supporting information:

## How Controlled and Versatile is N-Carboxy Anhydride (NCA) Polymerization at 0 °C? Effect of Temperature on Homo-, Block- and Graft (Co)Polymerization

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Figure 1: MALDI-ToF-MS spectra of PBLG (left), PBLA (center) and PBLS (right) from reaction at 10 °C.



Figure 2: PBLS MALDI-ToF-MS full spectrum from reaction at 0 °C



Figure 3: PBLS MALDI-TOF-MS full spectrum from reaction at 60 °C



Figure 4: MADLI-ToF-MS spectra of PBLS<sub>10</sub>-co-PBLG<sub>30</sub> (top: measured; bottom: simulated), entry 1, **Table 3** 



Figure 5: MALDI-ToF-MS spectra of PBLS<sub>20</sub>-co-PBLG<sub>20</sub> (measured/simulated), entry 2, **Table 3.** 



Figure 6: MALDI-ToF-MS spectra of PBLS<sub>30</sub>-co-PBLG<sub>10</sub> (top: measured; bottom: simulated), entry 3, **Table 3**.



Figure 7: MALDI-ToF-MS spectra of PBLG<sub>20</sub>-co-PAla<sub>20</sub> (top: measured; bottom simulated), entry 4, **Table 3**.





Figure 8: MALDI-ToF-MS spectra of PBLG<sub>20</sub>-b-PBLS<sub>20</sub> (top: measured; bottom: simulated), entry 4, **Table 4.** 



Figure 9: MALDI-ToF-MS spectra of PBLG<sub>20</sub>-b-PAla<sub>20</sub> (top: measured; bottom: simulated), entry 10, **Table 4.** 



Figure 10: PBLG<sub>20</sub>-co-PAla<sub>20</sub> (<sup>13</sup>C-NMR measured in TFA, 500Mhz) entry 4, Table 3.



Figure 11: PBLG<sub>20</sub>-b-Pala<sub>20</sub> (<sup>13</sup>C-NMR measured in TFA, 500 Mhz) entry 9, Table 4.



Figure 12: PBLG<sub>20</sub>-co-PBLS<sub>20</sub> (<sup>13</sup>C-NMR measured in TFA, 500 Mhz), entry 2, **Table 3**.



Figure 13: PBLG<sub>20</sub>-b-PBLS<sub>20</sub> (<sup>13</sup>C-NMR measured in TFA, 500 Mhz), entry 4, Table 4.



Figure 14: MALDI-ToF-MS spectrum of P(BLG-co-(Lys-g-PBLG)), entry 2, Table 5.



Figure 15: Polymer structures corresponding to Figure 14



Figure 15. HFIP-SEC of block copolymerization of P(BLG-b-BLS) (dotted line) from a PBLG macroinitiator obtained at 20 °C (solid line).



Figure 16: HFIP-SEC of block copolymerization of P(BLG-b-BLS) (dotted line) from a PBLG macroinitiator obtained at 60 °C (solid line).