## SUPPORTING INFORMATION

## Controlled Ring-Opening Polymerization of *N*-(3-*tert*-Butoxy-3-oxopropyl) Glycine Derived *N*-Carboxyanhydrides towards Well-defined Peptoid-based Polyacids

Bailee N. Barrett,<sup>†</sup> Garrett L. Sternhagen<sup>†</sup> and Donghui Zhang\*

Department of Chemistry and Macromolecular Studies Group, Louisiana State University, Baton Rouge, Louisiana 70803, United States

\*Corresponding to: <u>dhzhang@lsu.edu</u>

<sup>†</sup> These authors contributed equally to the work



**Figure S1**. <sup>1</sup>H (top) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (bottom) of 2-((3-*tert*-butoxy-3-oxopropyl)amino) acetic acid (**1**, Scheme 1) in CDCl<sub>3</sub>.



**Figure S2**. <sup>1</sup>H (top) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (bottom) of 2-(N-(*tert*-butoxycarbonyl)-N-(3-*tert*-butoxy-3-oxopropyl) amino) acetic acid (**3**, Scheme 1) in CDCl<sub>3</sub>.



**Figure S3**. <sup>1</sup>H (top) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (bottom) of *N*-(3-*tert*-butoxy-3-oxopropyl) glycine derived *N*-carboxyanhydride (<sup>t</sup>BuO<sub>2</sub>Pr-NCA, Scheme 1) in CDCl<sub>3</sub>.



**Figure S4**. <sup>1</sup>H (top) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (bottom) of poly(N-(3-tert-butoxy-3-oxopropyl) glycine) polymer in DMSO-d<sub>6</sub>.



**Figure S5**. <sup>1</sup>H (top) and <sup>13</sup>C{<sup>1</sup>H} NMR spectra (bottom) of poly(N-2-(carboxyethyl) glycine) polymer in DMSO-d<sub>6</sub>.



**Figure S6**. Plots of the SEC-DRI chromatograms for the butylamine-initiated ROPs of  ${}^{t}BuO_{2}Pr$ -NCA in toluene at room temperature with different initial monomer-to-initiator ratios ([M]<sub>0</sub>:[I]<sub>0</sub>=25:1 – 200:1, Entry 6-9, Table 1).



**Figure S7**. A representative SEC-MALS-DRI chromatogram of poly(N-(3-tert-butoxy-3-oxopropyl) glycine) polymers obtained from the butylamine-initiated ROPs of <sup>t</sup>BuO<sub>2</sub>Pr-NCA ( $[M]_0 = 0.5 \text{ M}, [M]_0:[I]_0 = 100:1$ , in toluene, r.t.), showing the DRI (blue curve) and RALS response (black curve).



**Figure S8**. ESI-MS spectrum of oligomers obtained by benzylamine-initiated ROP of  $EtO_2Et-NCA$  in toluene at room temperature and the structural assignment of the molecular ions and corresponding calculated m/z values. Competitive termination by transamidation relative to chain propagation resulted in the formation of only low molecular weight oligomeric species shown here.



**Figure S9**. <sup>1</sup>H NMR spectra of poly(N-(3-tert-butoxy-3-oxopropyl) glycine) polymer precursor (top) and resulting poly(N-(2-carboxyethyl) glycine) (bottom) obtained after TFA treatment, in DMSO-d<sub>6</sub>.



**Figure S10**. DLS correlograms (black curve) and intensity-weighted decay time distribution of poly(N-(2-carboxyethyl) glycine) (blue curve) in aqueous solution at two different pH (= 2.35 (A) and 11.8 (B)). DLS correlograms were fitted by MEM method (red curve) to determine the  $R_h$  values.