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Supporting Information

Copolymers of ϵ -caprolactone and ϵ -caprolactam via polyesterification: Towards

sequence-controlled poly(ester amide)s

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DMSO- d_6 :CD₃OD = 7:1 at 37 °C.



Fig. S1 ¹H NMR spectrum of **P6** in TFEA/CDCl₃ = 4/1.



Fig. S2 ¹³C NMR spectrum of **P6** in TFEA/CDCl₃ = 4/1.



Fig. S3 ¹H NMR spectrum of monomer 2 in CDCl₃.



Fig. S4 ¹³C NMR spectrum of monomer 2 in CDCl₃.



Fig. S5 Kinetic analysis for the synthesis of P0 in $CDCl_3$ based on ¹H NMR spectra. Proton signals corresponding to end groups and cyclic oligomers are designated.



Fig. S6 Kinetic analysis for the synthesis of P5 in DMSO-d₆ based on ¹H NMR spectra. Proton

signals corresponding to end groups and cyclic oligomers are designated.



Fig. S7 ESI-MS spectrum of P0 supernatant.



Fig. S8 ESI-MS spectrum of P5 supernatant.



Fig. S9 ¹³C NMR spectra of **P0-P5** in DMSO- d_6 (characteristic peaks shown only).



Fig. S10 GPC traces of PO-P3.



Fig. S11 GPC traces of kinetic analysis for the synthesis of P0.



Fig. S12 IR spectra of PO-P6.



Fig. S13 TGA curves of PO-P6.



Fig. S14 DSC thermograms of PO-P6.



Fig. S15 Contact angle images for droplets of water on P0-P6 surfaces.



Fig. S16 ¹H NMR spectra of **P0** with NaOD (3 equiv.) monitored during the degradation process in DMSO- d_6 :D₂O = 20:1 at 37 °C.



Fig. S17 ¹H NMR spectra of **P1** with NaOD (3 equiv.) monitored during the degradation process in DMSO- d_6 :D₂O = 20:1 at 37 °C.



Fig. S18 ¹H NMR spectra of **P2** with NaOD (3 equiv.) monitored during the degradation process in DMSO- d_6 :D₂O = 20:1 at 37 °C.



Fig. S19 ¹H NMR spectra of **P3** with NaOD (3 equiv.) monitored during the degradation process in DMSO- d_6 :D₂O = 20:1 at 37 °C.



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Fig. S22 ¹H NMR spectra of **P0** with TBD (5 equiv.) monitored during the degradation process in DMSO- d_6 :CD₃OD = 7:1 at 37 °C.



Fig. S23 ¹H NMR spectra of **P5** with TBD (5 equiv.) monitored during the degradation process in DMSO- d_6 :CD₃OD = 7:1 at 37 °C.