Supporting Information

Synthesis of Well-defined Carboxyl Poly(*ɛ*-caprolactone) by Finetuning the Protection Group

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Fig. S1 ¹HNMR and ¹³CNMR spectra of 2,6-(CH₃)BCL, 2,6-(H)BCL, 2,6-(NO₂)BCL in CDCl₃.



Fig. S2 HPLC analysis on isomer mixtures of 2,6-(CH₃)BCL, 2,6-(H)BCL and 2,6-(NO₂)BCL and

purified monomers of 1,2,3,4,5 and 6.

Table S1 The ratios of 2-BCL and 6-BCL with different substitutions by	HPLC analysis.
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Entry	R	2-BCL : 6-BCL
1	CH ₃	1:7
2	Н	1:5
3	NO ₂	1:6



Fig. S3 ¹HNMR and ¹³CNMR spectra of 2-(CH₃)BCL and 6-(CH₃)BCL in CDCl₃.



Fig. S4 1 HNMR and 13 CNMR spectra of 2-(H)BCL and 6-(H)BCL in CDCl₃.



Fig S5 ¹HNMR and ¹³CNMR spectra of 2-(NO₂)BCL and 6-(NO₂)BCL in CDCl₃.



Fig. S6 ¹HNMR spectra of P(CH₃)BCL, P(H)BCL and P(NO₂)BCL in CDCl₃.



Fig. S7 Size exclusion chromatogram of P(6-CH₃)BCL (black curve) and PCCL (blue curve) both

acquired in DMF.



Fig. S8 Size exclusion chromatogram of P(6-H)BCL (black curve) and PCCL (blue curve) both

acquired in DMF.



Fig. S9 Size exclusion chromatogram of P(6-NO₂)BCL (black curve) and PCCL (blue curve) both

acquired in DMF.



Fig. S10 FTIR spectra of P(CH₃)BCL₄₀ and PCCL₄₀-g-TEMPO.



Fig. S11 ¹HNMR spectrum of PCCL₄₀-g-TEMPO in CDCl₃.