Supporting Information to

Fibrillar gels via the self-assembly of poly(L-glutamate)-based statistical copolymers

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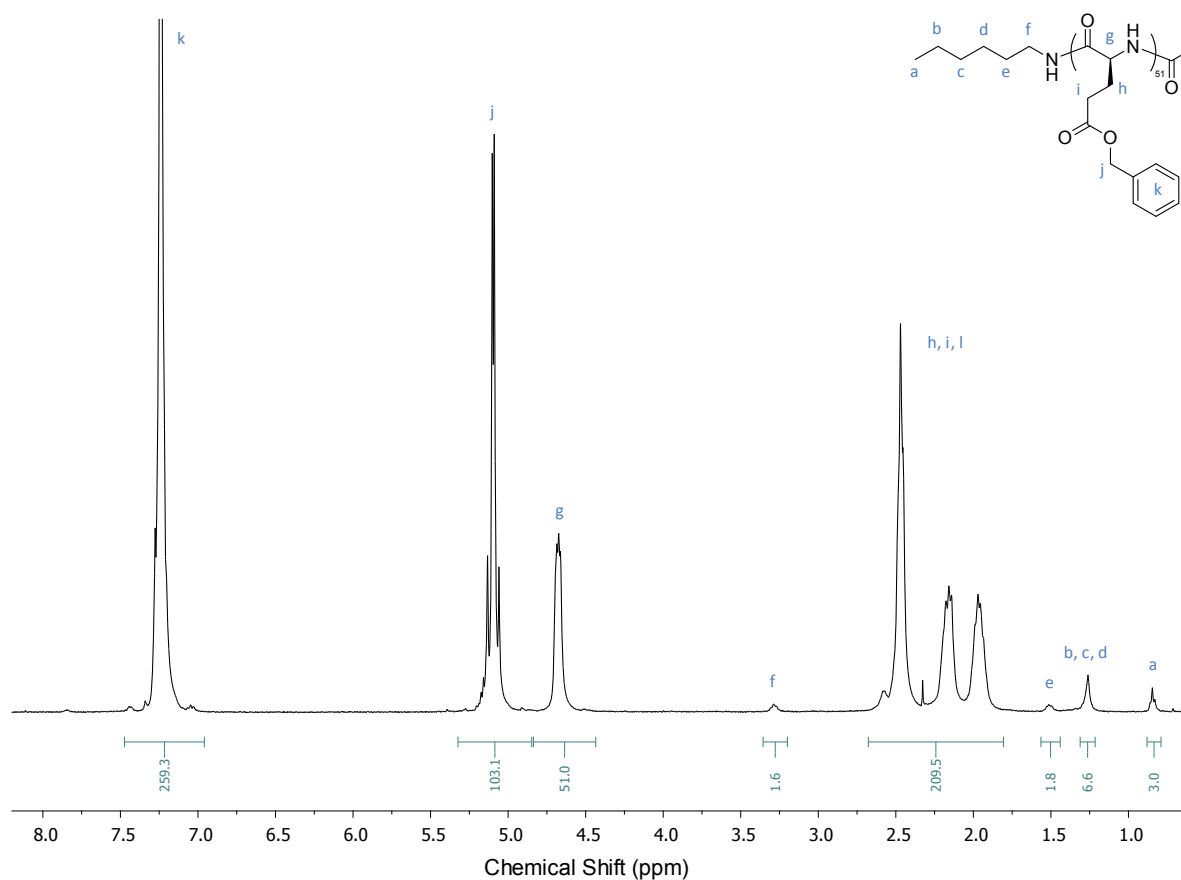
Research Campus Golm, 14424 Potsdam, Germany.

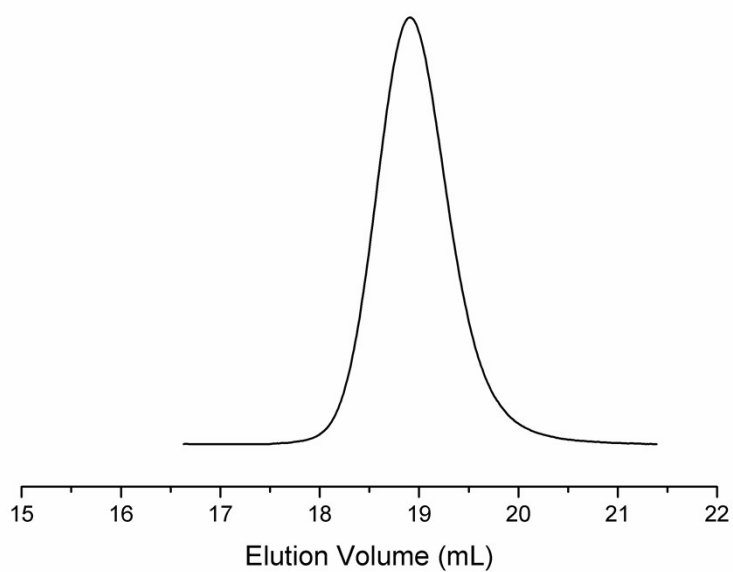*[3] University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Straße 24-25,*

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Homopolymer PBⷮLG₅₁

¹H-NMR, 400 MHz, CF₃COOD, δ (ppm) 7.26-7.24 (br, 255H), 5.60-5.13 (br, 102H), 4.69-4.66 (br, 51H), 3.29 (br, 2H), 2.58-1.94 (br, 593H), 1.53-1.50 (br, 2H), 1.36-1.34 (br, 6H), 0.86-0.83 (br, 3H).
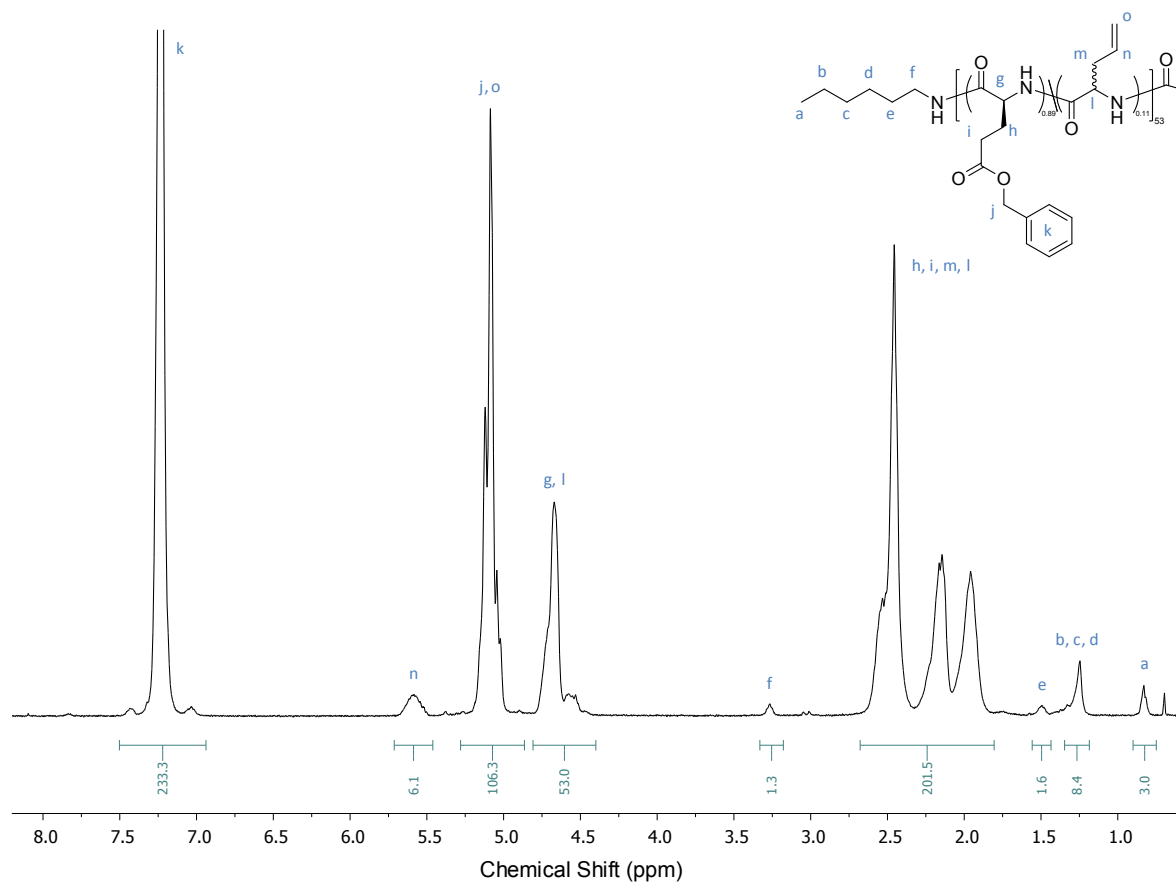

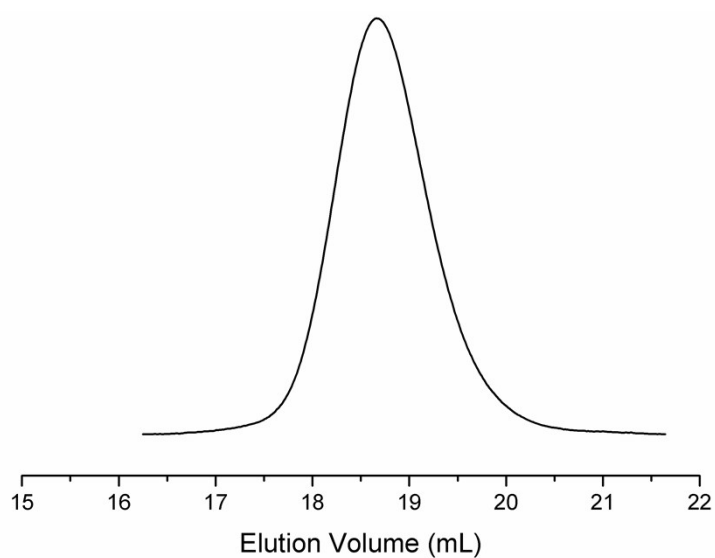**Figure S1a.** ¹H-NMR spectrum (400 MHz) of PBⷮLG₅₁ in CF₃COOD.

Figure S1b. SEC RI trace of PBⷮLG₅₁ in NMP.

Statistical Copolymer P(BLG$_{0.89}$-*co*-DLAG$_{0.11}$)$_{53}$

^{1}H-NMR, 400 MHz, CF$_3$COOD, δ (ppm) 7.25-7.23 (br, 235H), 5.59 (br, 6H), 5.16-5.02 (br, 106H), 4.71-4.53 (br, 53H), 3.27 (br, 2H), 2.53-1.94 (br, 203H), 1.51-1.48 (br, 2H), 1.33-1.25 (br, 6H), 0.85-0.82 (br, 3H).
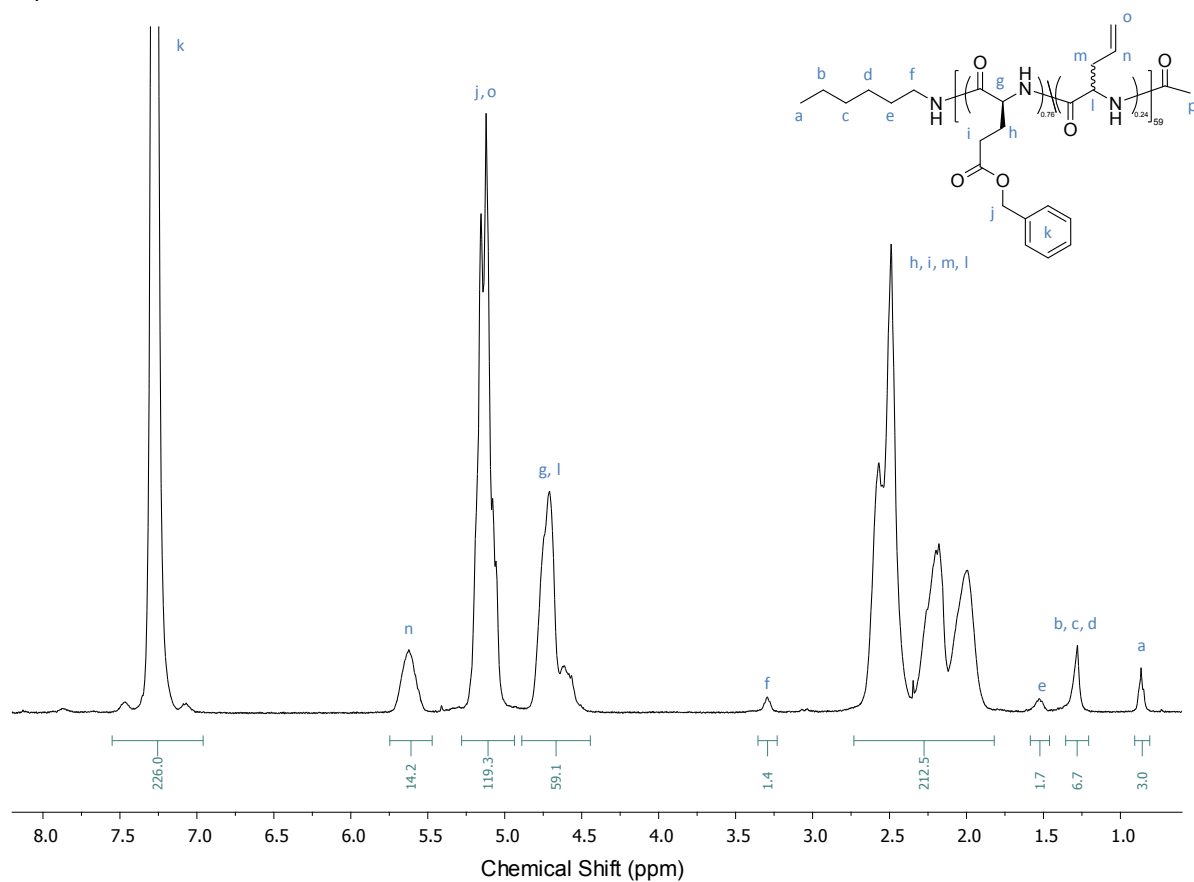

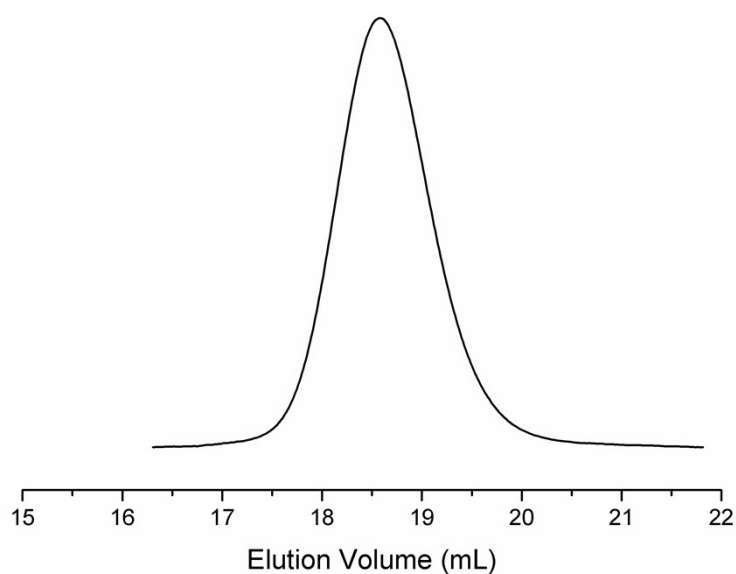**Figure S2a.** ^{1}H-NMR spectrum (400 MHz) of P(BLG$_{0.89}$-*co*-DLAG$_{0.11}$)$_{53}$ in CF$_3$COOD.

Figure S2b. SEC RI trace of P(BLG$_{0.89}$-*co*-DLA$_{0.11}$)$_{53}$ in NMP.

Statistical Copolymer P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$

^{1}H-NMR, 400 MHz, CF$_3$COOD, δ (ppm) 7.28-7.26 (br, 225H), 5.62 (br, 14H), 5.19-5.06 (br, 118H), 4.74-4.57 (br, 59H), 3.29 (br, 2H), 2.57-1.98 (br, 211H), 1.54-1.51 (br, 2H), 1.36-1.28 (br, 6H), 0.88-0.85 (br, 3H).
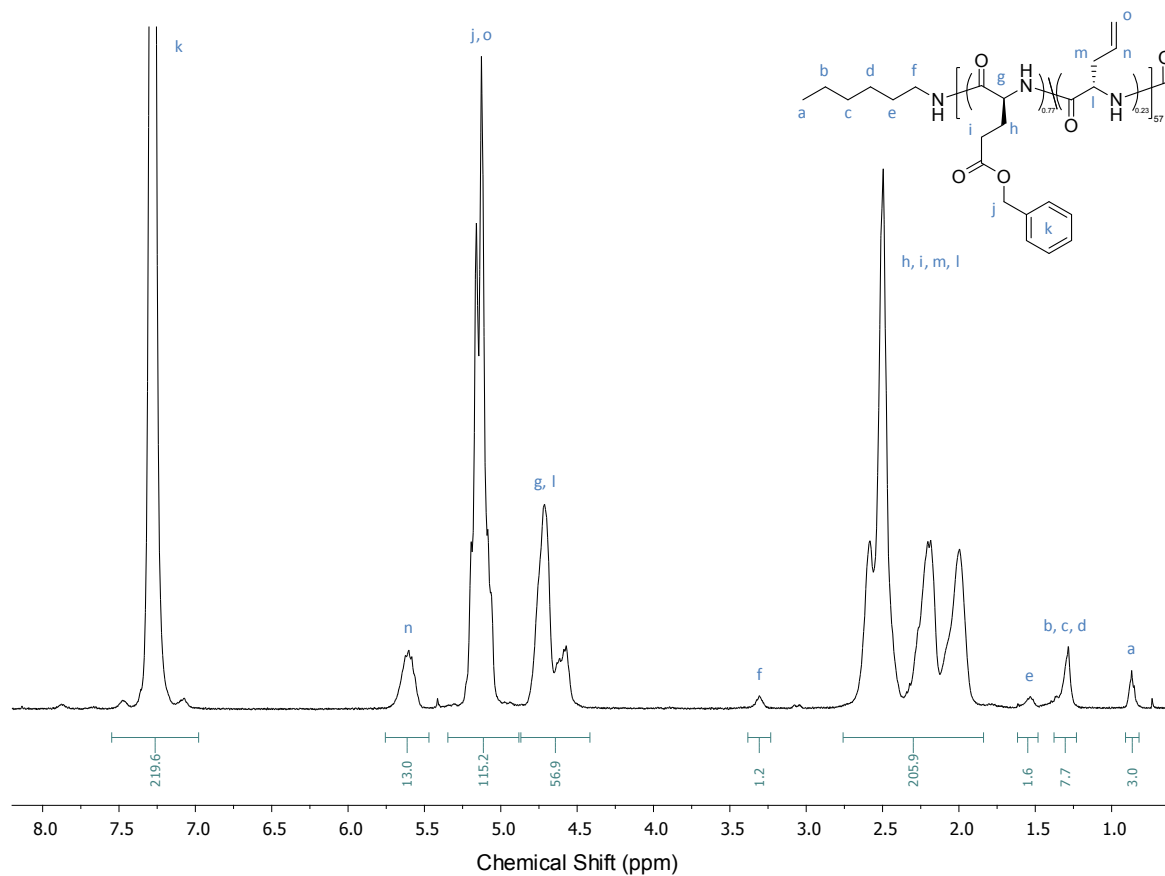

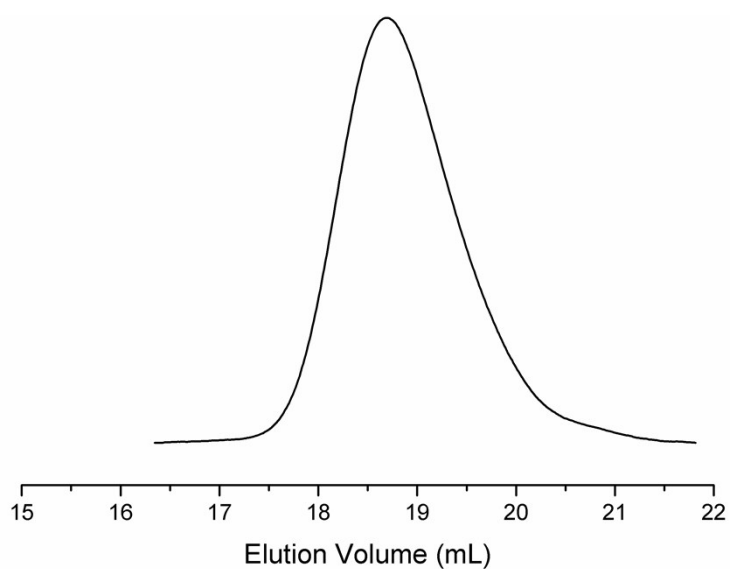**Figure S3a.** ^{1}H-NMR spectrum (400 MHz) of P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$ in CF$_3$COOD.

Figure S3b. SEC RI trace of P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$ in NMP.

Statistical Copolymer P(BLG$_{0.77}$-*co*-LAG$_{0.23}$)$_{57}$

^{1}H-NMR, 400 MHz, CF$_3$COOD, δ (ppm) 7.29-7.27 (br, 220H), 5.60 (br, 13H), 5.19-5.06 (br, 114H), 4.74-4.57 (br, 57H), 3.30 (br, 2H), 2.59-1.99 (br, 205H), 1.55-1.51 (br, 2H), 1.37-1.28 (br, 6H), 0.88-0.85 (br, 3H).
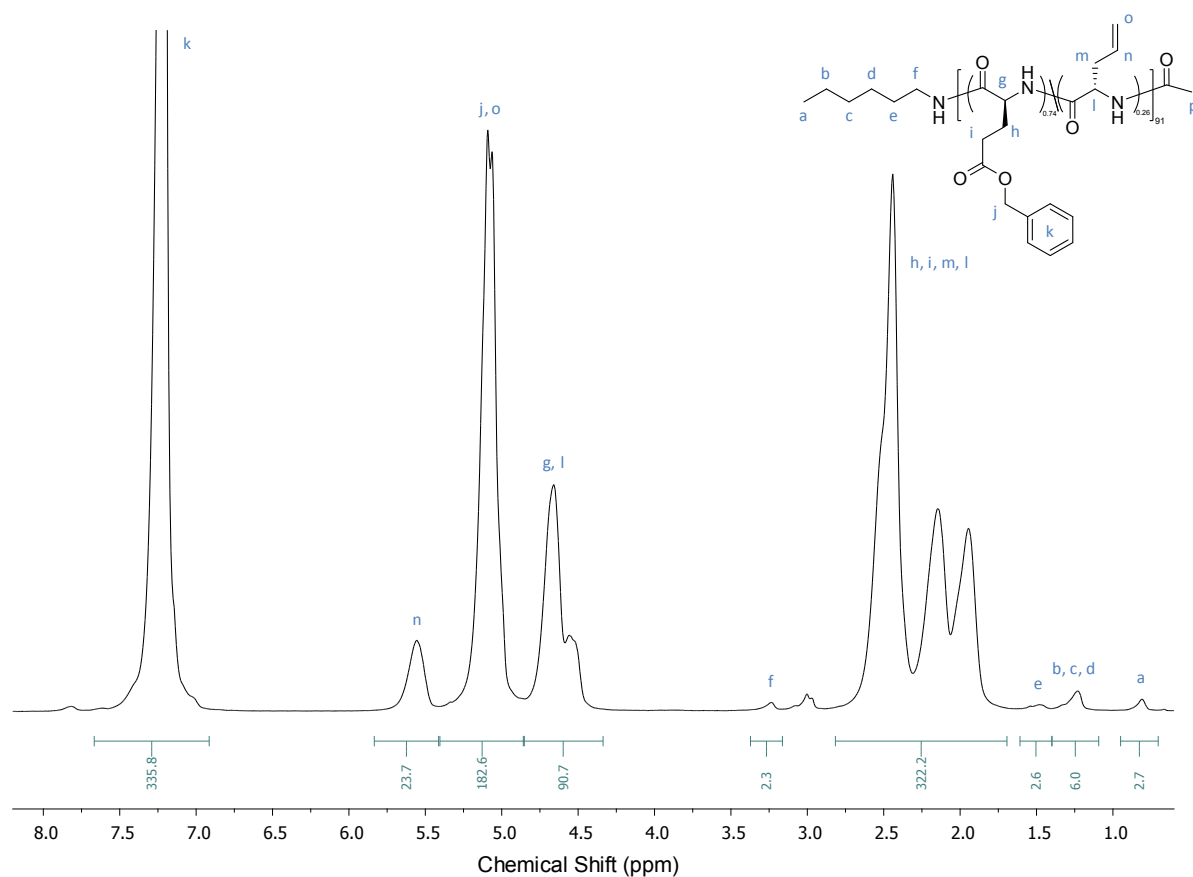

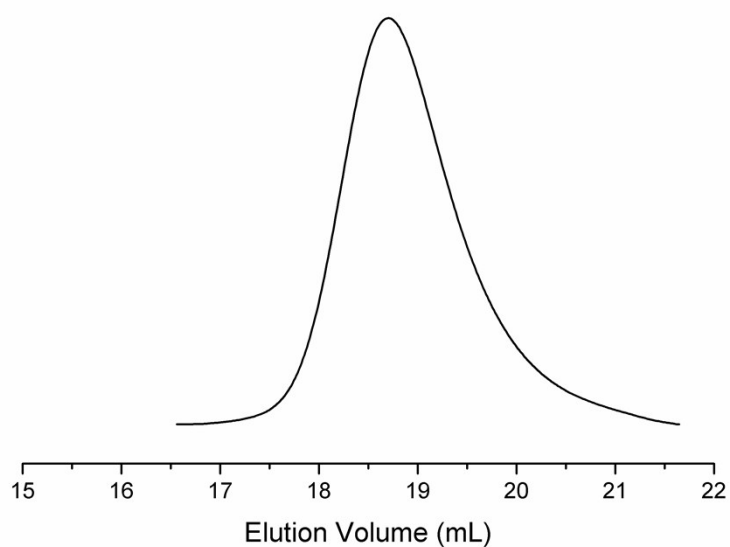**Figure S4a.** ^{1}H-NMR spectrum (400 MHz) of P(BLG$_{0.77}$-*co*-LAG$_{0.23}$)$_{57}$ in CF$_3$COOD.

Figure S4b. SEC RI trace of P(BLG$_{0.77}$-*co*-LAG$_{0.23}$)$_{57}$ in NMP.

Statistical Copolymer P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{91}$

^{1}H-NMR, 400 MHz, CF$_3$COOD, δ (ppm) 7.22 (br, 335H), 5.56 (br, 24H), 5.15-5.02 (br, 182H), 4.73-4.52 (br, 91H), 3.23 (br, 2H), 2.55-1.94 (br, 319H), 1.54-1.48 (br, 2H), 1.33-1.23 (br, 6H), 0.81 (br, 3H).
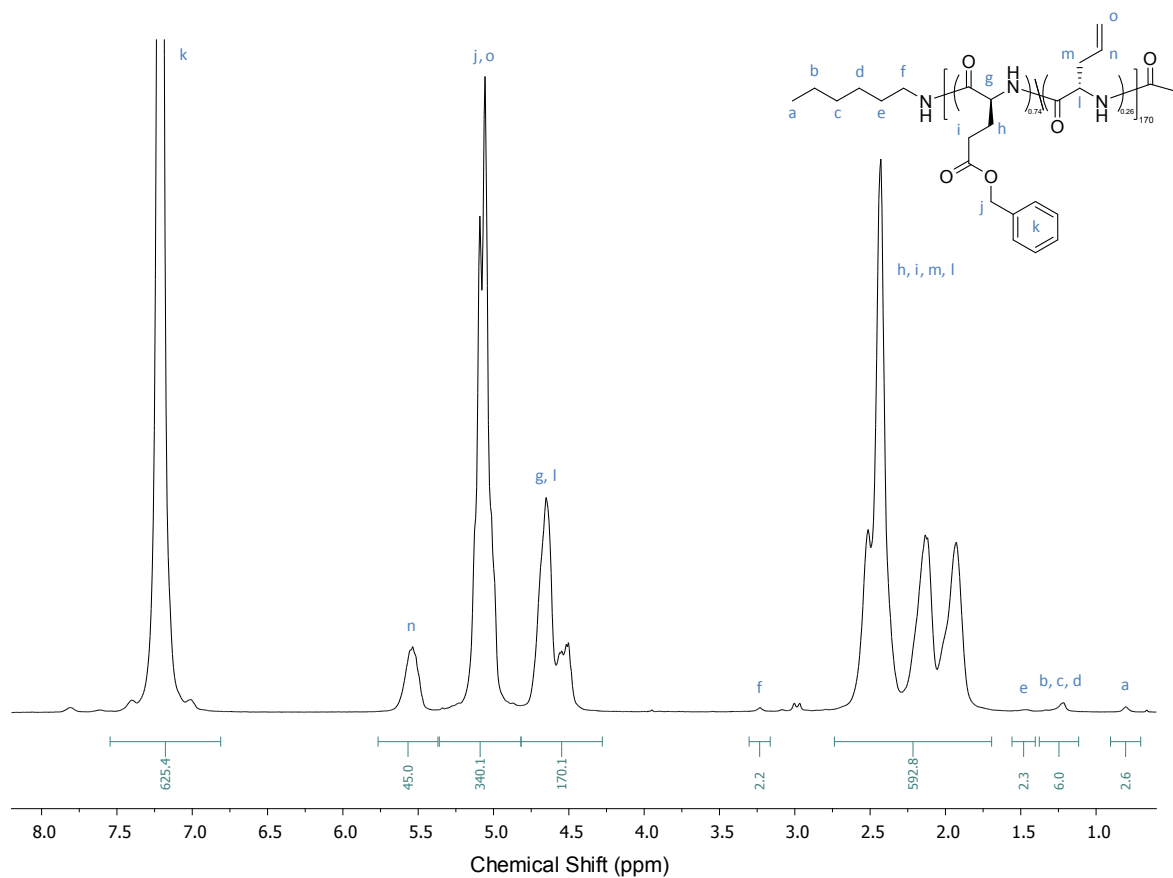

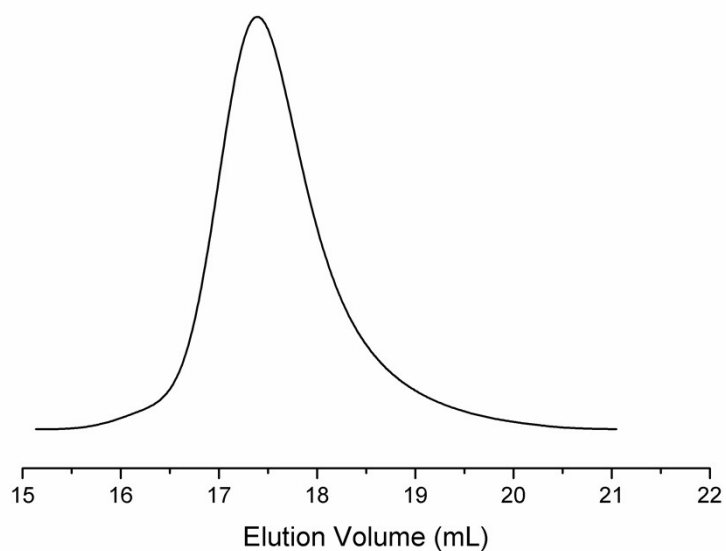**Figure S5a.** ^{1}H-NMR spectrum (400 MHz) of P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{91}$ in CF$_3$COOD.

Figure S5b. SEC RI trace of P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{91}$ in NMP.

Statistical Copolymer P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{170}$

^{1}H-NMR, 400 MHz, CF$_3$COOD, δ (ppm) 7.20 (br, 625H), 5.54 (br, 45H), 5.14-5.00 (br, 340H), 4.70-4.50 (br, 170H), 3.23 (br, 2H), 2.51-1.93 (br, 593H), 1.53-1.47 (br, 2H), 1.34-1.22 (br, 6H), 0.80 (br, 3H).
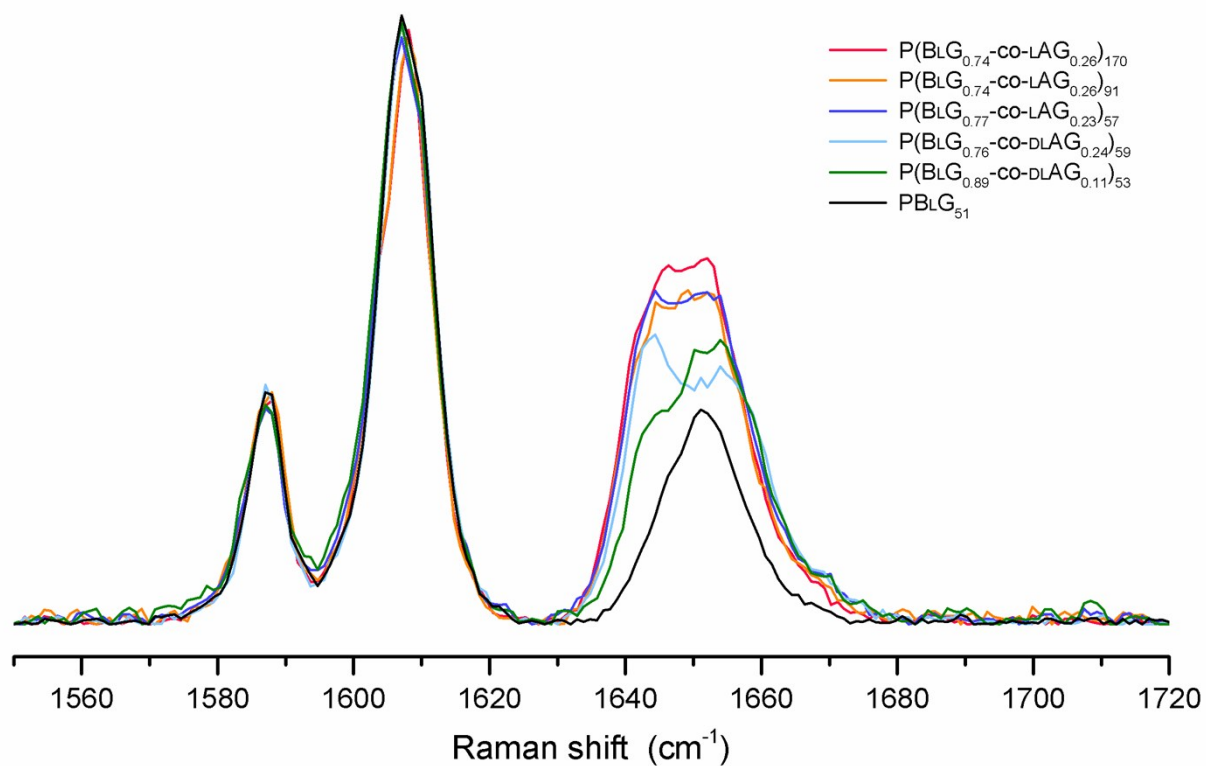

Figure S6a. ^{1}H-NMR spectrum (400 MHz) of P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{170}$ in CF$_3$COOD.

Figure S6b. SEC RI trace of P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{170}$ in NMP.
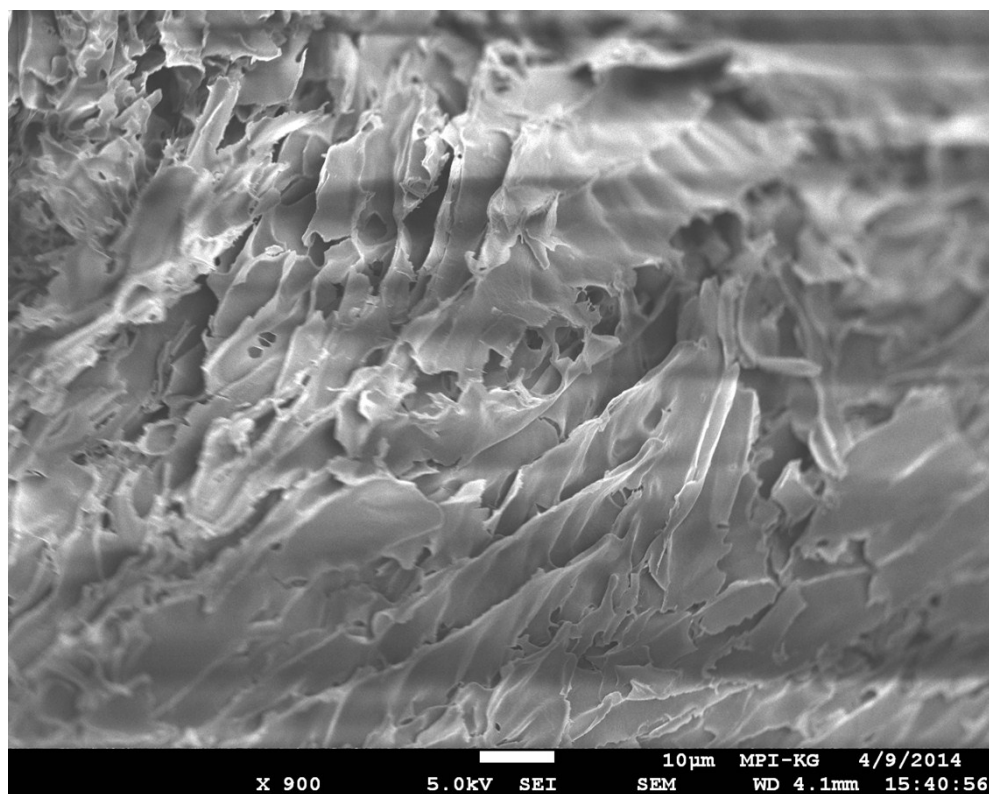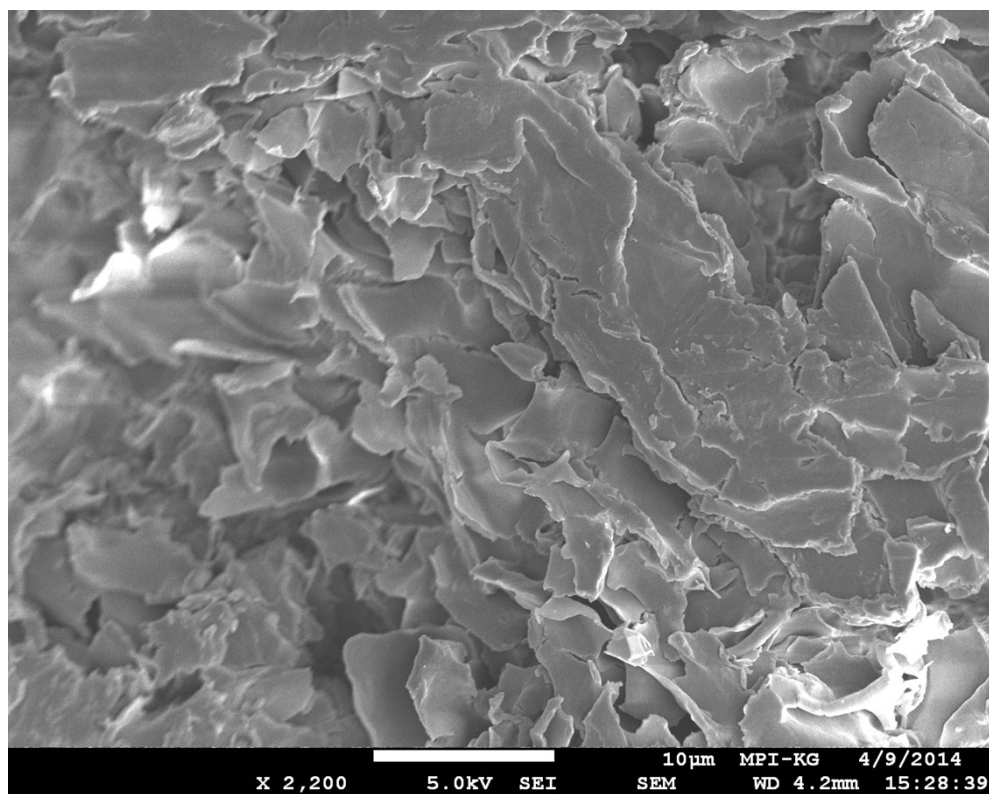
Raman Spectroscopy

Figure S7. Amide I band for dry P(BLG$_x$-*co*-AG$_{1-x}$)$_n$ polymers after baseline correction and normalization.
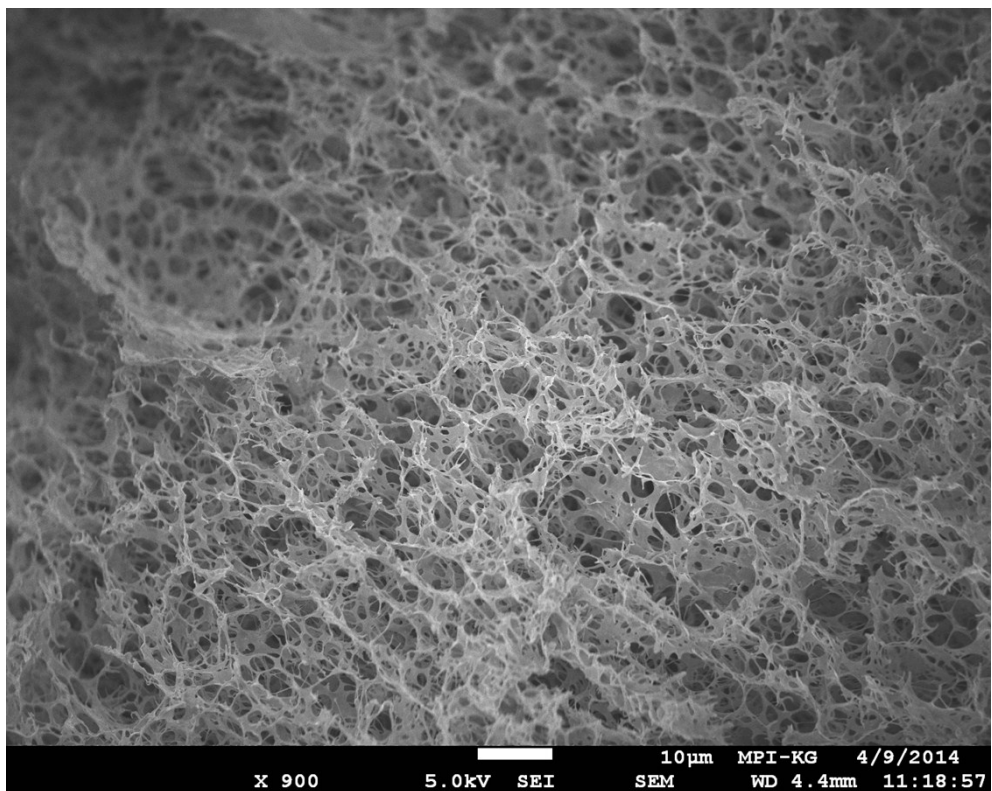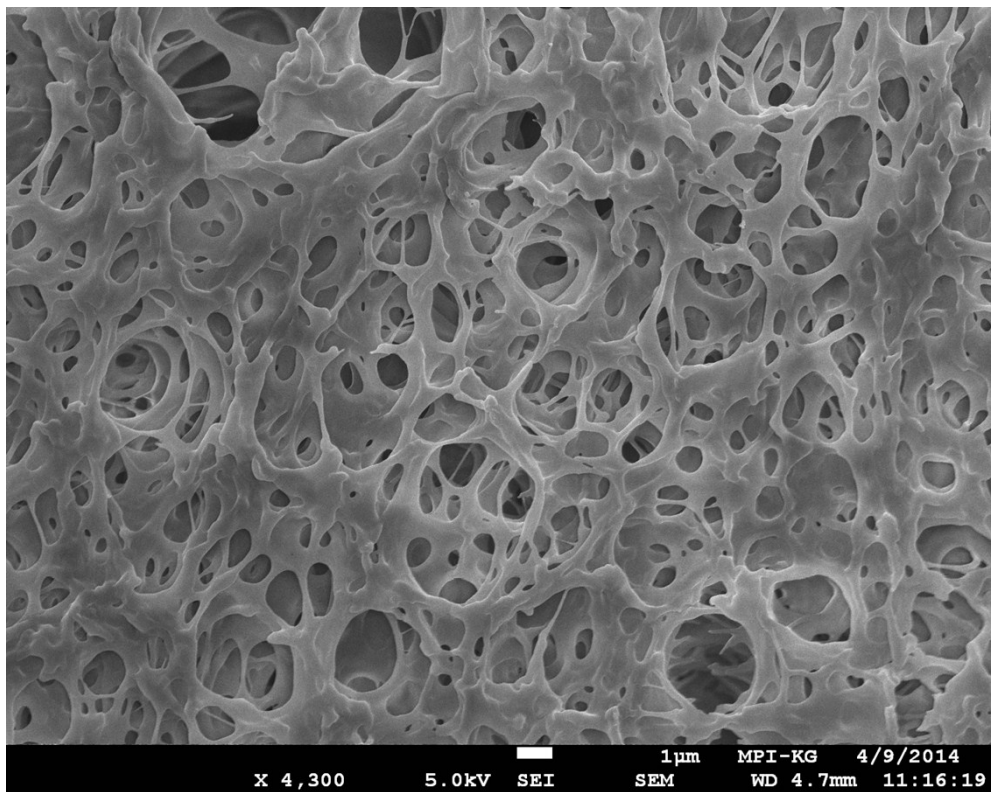
High Resolution Scanning Electron Microscopy (SEM)

Figure S8a. Freeze-dried P(BLG$_{0.89}$-*co*-DLAG$_{0.11}$)$_{53}$-dioxane solution (10 g·L^{-1}).

Figure S8b. Freeze-dried P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$-dioxane solution (10 g·L^{-1}).

Figure S8c. Dried crosslinked P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$-dioxane gel (10 g·L^{-1}).

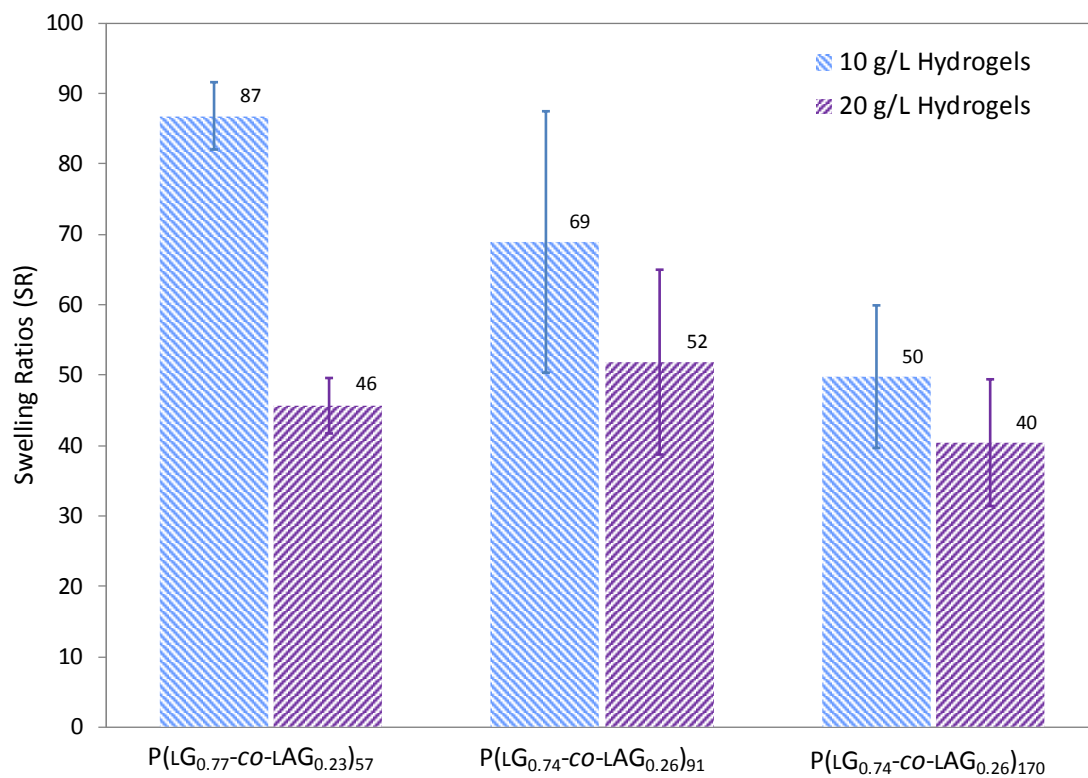**Figure S8d.** Dried crosslinked P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$-dioxane gel (10 g·L^{-1}).

Fourier Transform Infrared (FTIR) Spectroscopy

Figure S9a. FTIR spectra of freeze-dried hydrogel prepared from P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{91}$-dioxane (20 g·L^{-1}) gels deprotected following route A and B; different parts of the hydrogel (core and edge) were analyzed in order to check for effective deprotection.

Figure S9b. FTIR spectra of freeze-dried hydrogel prepared from P(BLG$_{0.74}$-*co*-LAG$_{0.26}$)$_{170}$-dioxane (20 g·L^{-1}) gels deprotected following route A and B; different parts of the hydrogel (core and edge) were analyzed in order to check for effective deprotection (normalization to Amide II signal).
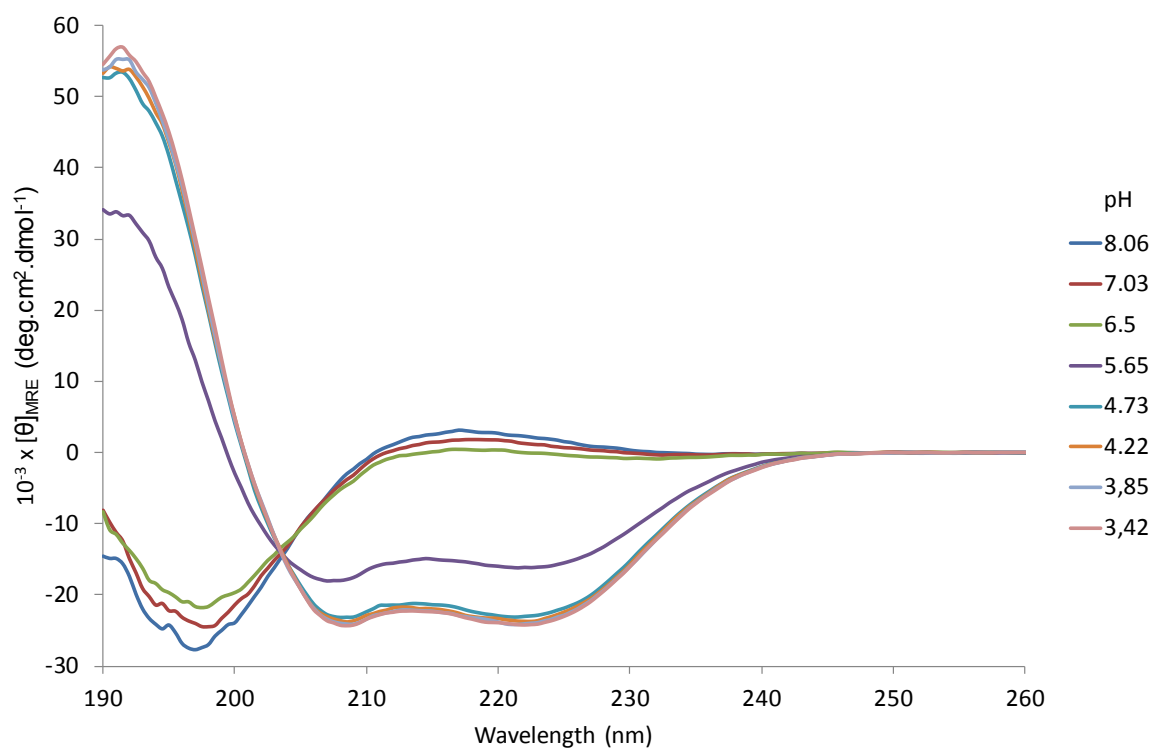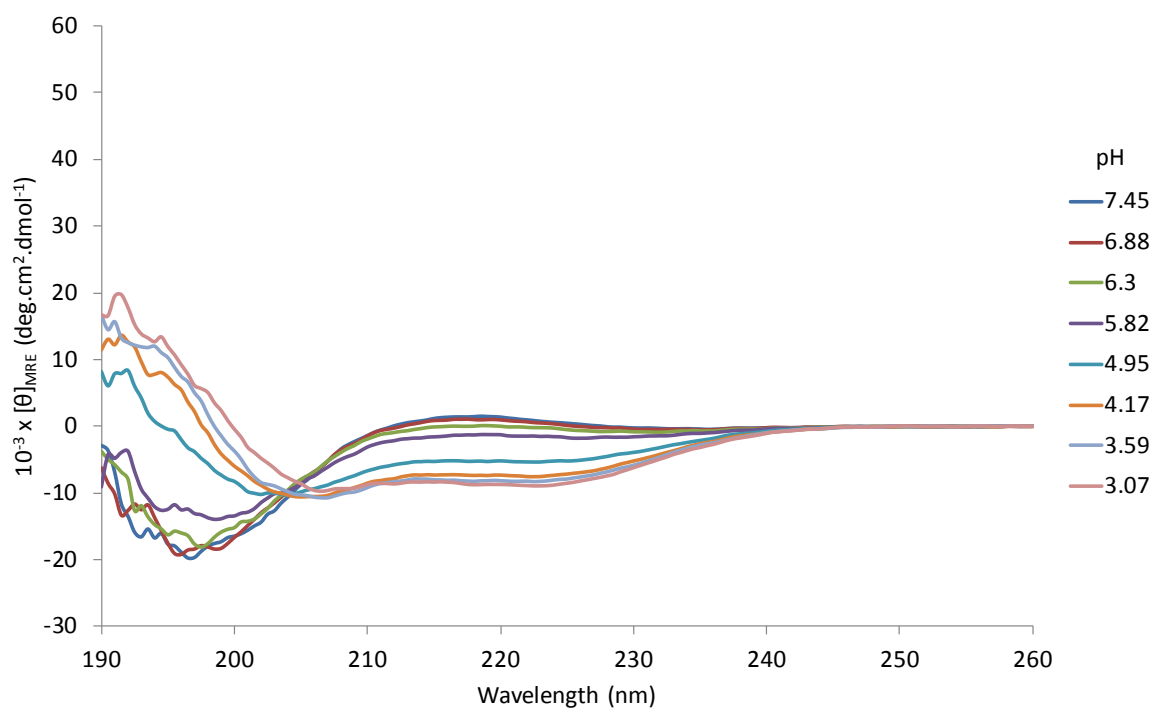
Figure S10. Average swelling ratios (SR) of 10 to 20 g·L^{-1} (i.e., 1 and 2% w/v) hydrogels; for each series, the average SR value was calculated from 3 to 5 measurements, and the error bar corresponds to the standard deviation of each series.

Circular Dichroism (CD) Spectroscopy

Figure S11a. CD spectra of PLG$_{51}$ (debenzylated PBLG$_{51}$) in water at different pH.

Figure S11b. CD spectra of P(LG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$ (debenzylated P(BLG$_{0.76}$-*co*-DLAG$_{0.24}$)$_{59}$) in water at different pH.