Esterification of poly(γ-glutamic acid) (γ-PGA) mediated by its tetrabutylammonium salt

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Electronic Supplementary Information

Molecular weight distribution (MWD)

Table S1 Molecular weight distribution (MWD) of γ-PGA (1), γ-PGA sodium salt (2) and γ-PGA tetrabutylammonium salt (3)

Sample	M_p Kg mol^{-1}	M_n Kg mol^{-1}	M_w Kg mol^{-1}	M_z Kg mol^{-1}	M_w/M_n	M_z/M_w	Rec. Mass %
1	13.4	12.7	16.1	20.9	1.3	1.3	84.1
2	22.6	20.6	28.3	39.8	1.4	1.4	92.1
3	47.9	12.6	31.6	47.0	2.5	1.5	96.0

Table S2 Molecular weight distribution (MWD) of poly(α-ethyl γ-glutamate) (4), poly(α-benzyl γ-glutamate) (5) and poly(α-*n*-butyl γ-glutamate) (6)

Sample	M_p Kg mol^{-1}	M_n Kg mol^{-1}	M_w Kg mol^{-1}	M_z Kg mol^{-1}	M_w/M_n	M_z/M_w	Rec. Mass %
4 A1	29.6	19.3	33.4	52.7	1.7	1.6	95.2
4 B1	15.3	12.0	30.0	73.2	2.5	2.4	15.6
4 A2	30.4	20.1	30.8	42.6	1.5	1.4	93.4
4 B2	23.3	10.9	21.8	34.8	2.0	1.6	11.6
5	45.2	19.2	39.5	61.7	2.1	1.6	22.4
6	23.1	14.0	20.8	28.5	1.5	1.4	50.6

Nuclear Magnetic Resonance (NMR)

Fig. S3 ^{1}H NMR of γ-PGA tetrabutylammonium salt (3) (400 MHz, DMSO-d_6)

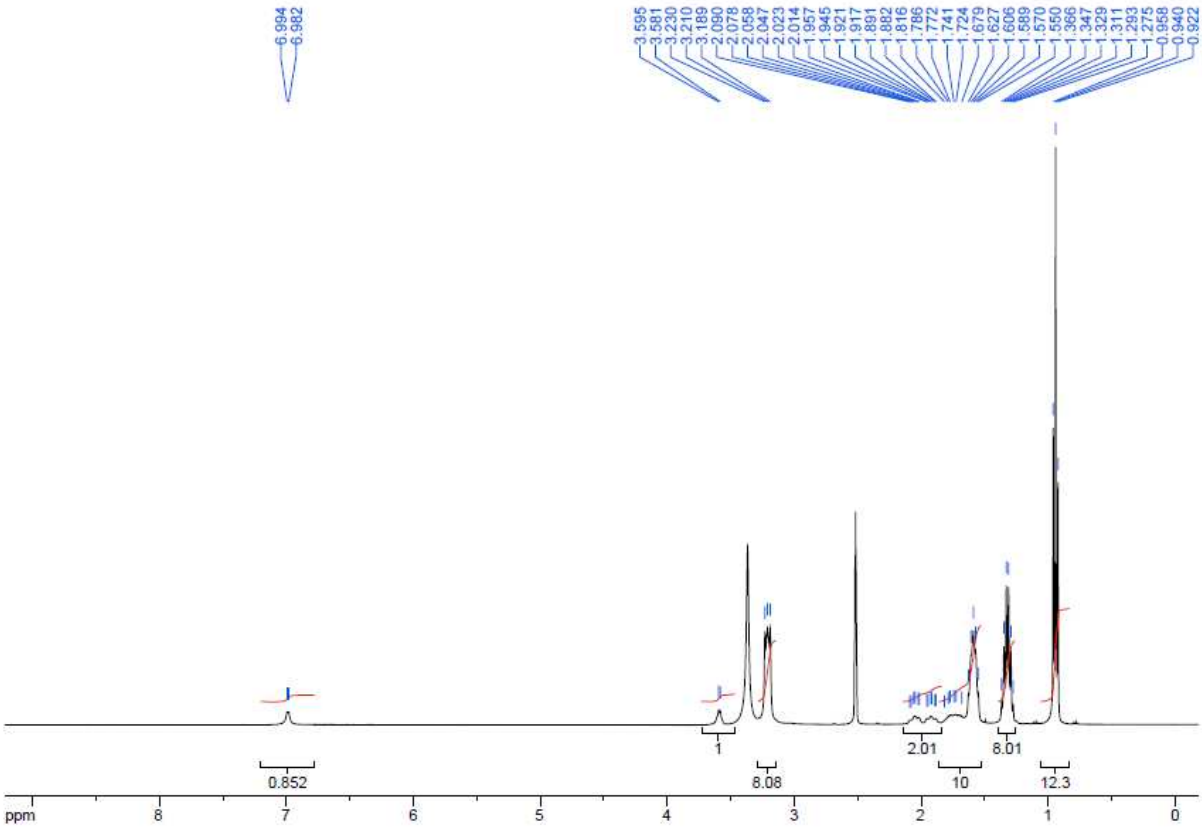
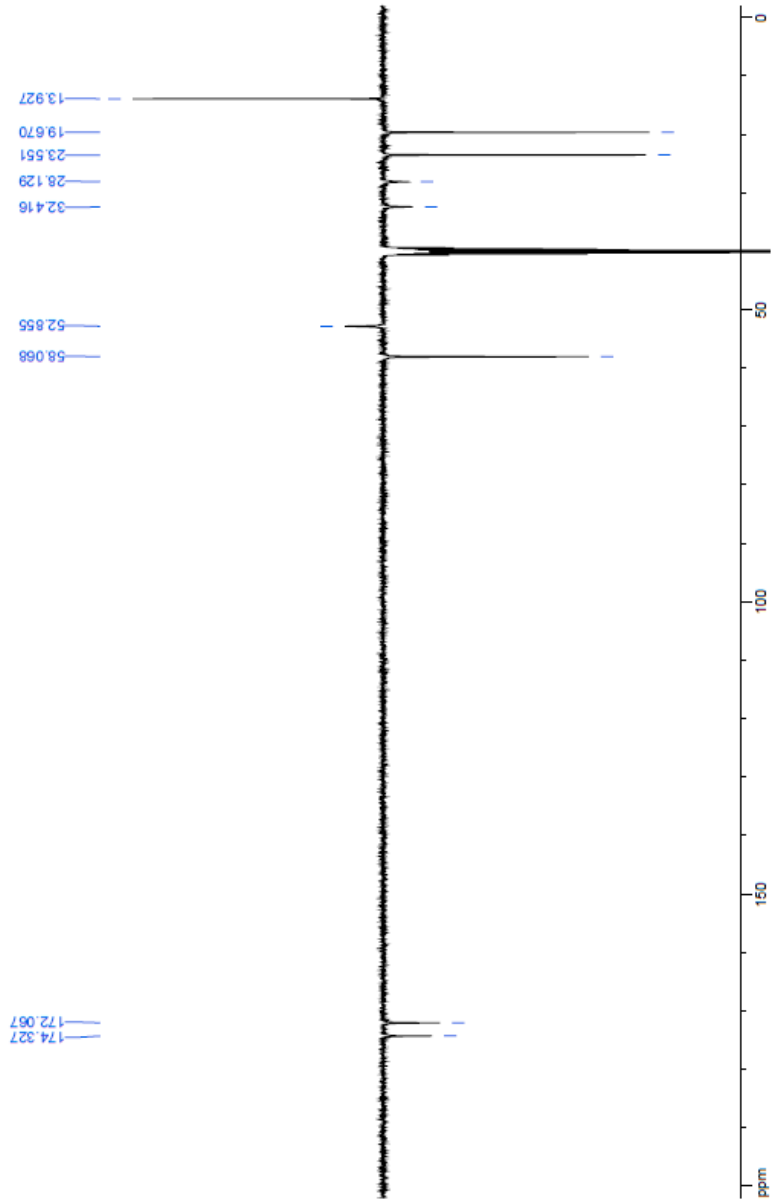


Fig. S4 ^{13}C NMR of γ-PGA tetrabutylammonium salt (3) (100 MHz, DMSO-d_6)



^{1}H NMR of poly(α-ethyl γ-glutamate) (4)

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.18 (t, J=7.2 Hz, 3H, -OCH$_2$*CH$_3$*), 1.70-1.81 (m, 1H, -*CH$_2$*CH$_2$CO-), 1.89-2.01 (m, 1H, -*CH$_2$*CH$_2$CO-), 2.16-2.26 (m, 2H, -CH$_2$*CH$_2$*CO-), 4.02-4.12 (m, 2H, -O*CH$_2$*CH$_3$), 4.15-4.23 (broad m, 1H, -*CH*COO), 8.24 (d, J=7.4 Hz,1H, -CO*NH*).
Signal area *ratio* of the side-chain OCH$_2$ to the main-chain CH was:
- 1.43 in the case of 4A1, corresponding to 72% functionalization degree;
- 2.0 in the case of 4A2, corresponding to 100% functionalization degree;
- 0.45 in the case of 4B1, corresponding to 22% functionalization degree;
- 2.0 in the case of 4B2, corresponding to 100% functionalization degree.

Additional signals in the intervals 4.2-4.3 ppm and 8.2-8.3 ppm, corresponding to *CH*COO and CO*NH* of the underivatized polymer were observed in 4A1 and 4B1.

^{1}H NMR of poly(α-benzyl γ-glutamate) (5)

^{1}H NMR (400 MHz, DMSO-d_6) δ 1.75-1.86 (broad m, 1H, -*CH$_2$*CH$_2$CO-), 1.95-2.05 (broad m, 1H, -*CH$_2$*CH$_2$CO-), 2.23 (br t, 2H, J=7.6 Hz, -CH$_2$*CH$_2$*CO-), 4.27-4.33 (broad m, 1H, -*CH*COO), 5.10 (s, 2H, O*CH$_2$*C$_6$H$_5$), 7.32-7.34 (m, 5H, -C$_6$*H$_5$*), 8.19 (d, J=7.2 Hz,1H, -CO*NH*).
Signal area *ratio* of the side-chain OCH$_2$ to the main-chain CH was 2, corresponding to 100% functionalization degree.

^{1}H NMR of poly(α-*n*-butyl γ-glutamate) (6)

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.87 (t, J=7.2 Hz, 3H, -OCH$_2$CH$_2$CH$_2$*CH$_3$*), 1.26-1.38 (m, 2H, -OCH$_2$CH$_2$*CH$_2$*CH$_3$), 1.48-1.60 (m, 8H, -OCH$_2$*CH$_2$*CH$_2$CH$_3$), 1.69-1.83 (broad m, 1H, -*CH$_2$*CH$_2$CO-), 1.90-2.04 (broad m, 1H, -*CH$_2$*CH$_2$CO-), 2.16-2.26 (broad m, 2H, -CH$_2$*CH$_2$*CO-), 3.96-4.10 (m, 2H, -O*CH$_2$*CH$_2$CH$_2$CH$_3$), 4.14-4.26 (broad m, 1H, -*CH*COO), 8.24 (d, J=6.9 Hz,1H, -CO*NH*).
Signal area *ratio* of the side-chain OCH$_2$ to the main-chain CH was 1.99, corresponding to 99% functionalization degree.