Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Multi-Functionalization of Helical Block Copoly(α-peptide)s by Orthogonal Chemistry

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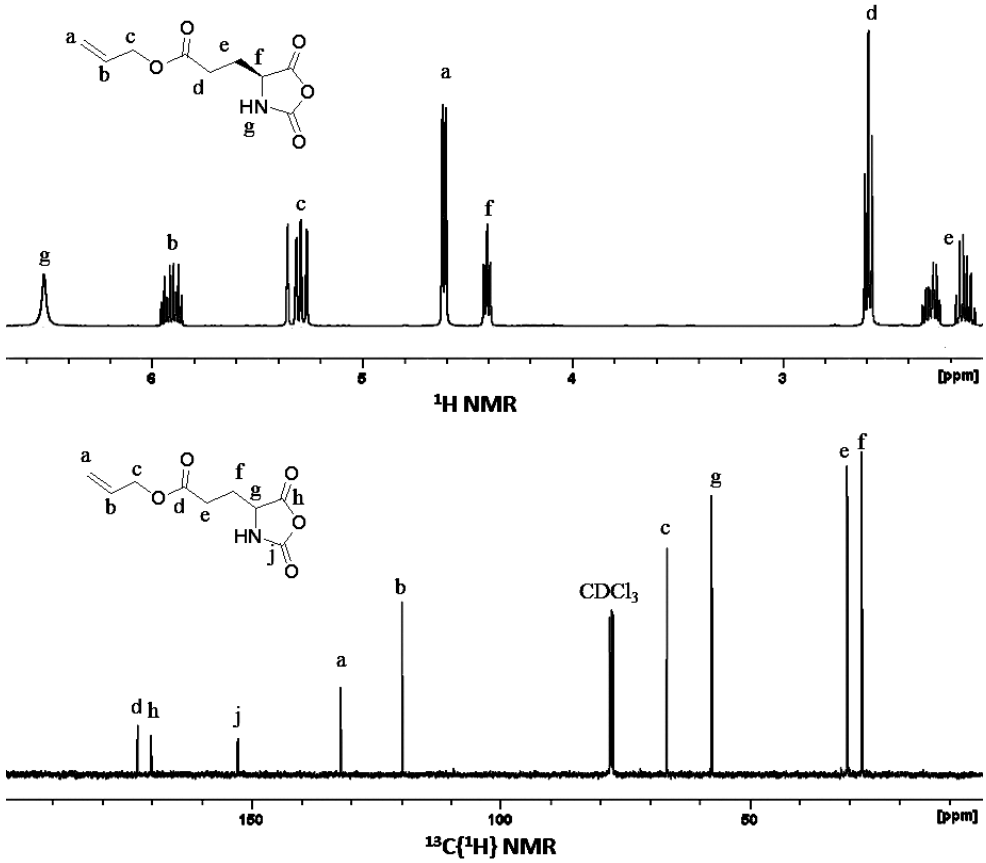

Figure S1. (A) ^{1}H and (B) $^{13}C\{^{1}H\}$ NMR spectra of γ-allyl-L-glutamic acid based *N*-carboxylanhydrides (AL-NCA) **3** in $CDCl_3$.

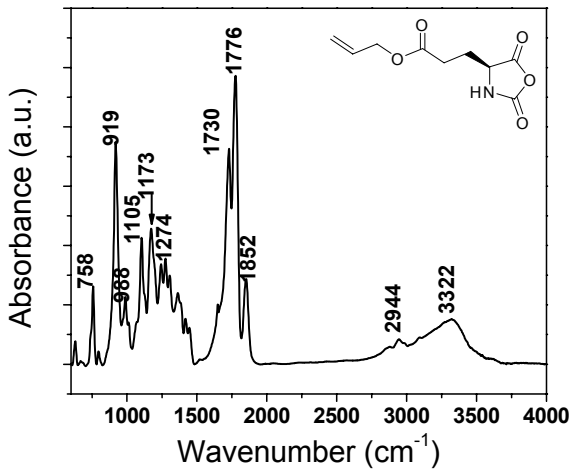

Figure S2. FTIR spectrum of neat γ-allyl-L-glutamic acid based *N*-carboxylanhydrides (AL-NCA) **3**.

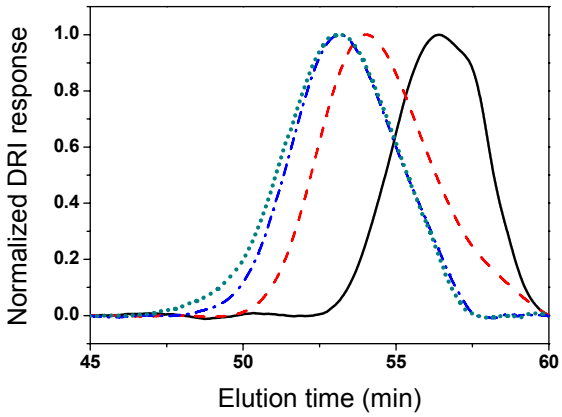

Figure S3. SEC chromatographs of PALG prepared from polymerizations with different monomer to initiator ratios: $[\mathbf{3}]_0:[^{n}BuNH_2]_0$ = 20 (—), 40 (– – –), 80 (–·–) and 160 (·····).

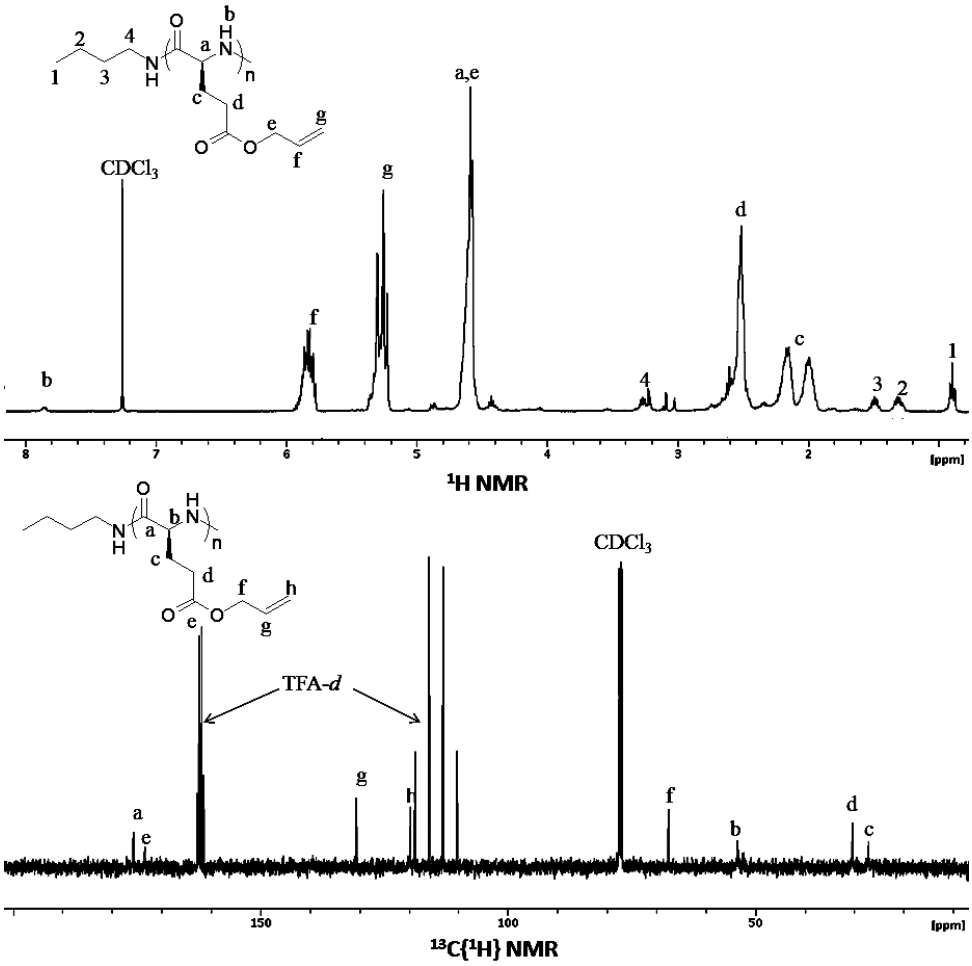

Figure S4. (A) ^{1}H and (B) $^{13}C\{^{1}H\}$ NMR spectra of PALG **4** in $CDCl_3/CF_3CO_2D$ (v:v=85:15).

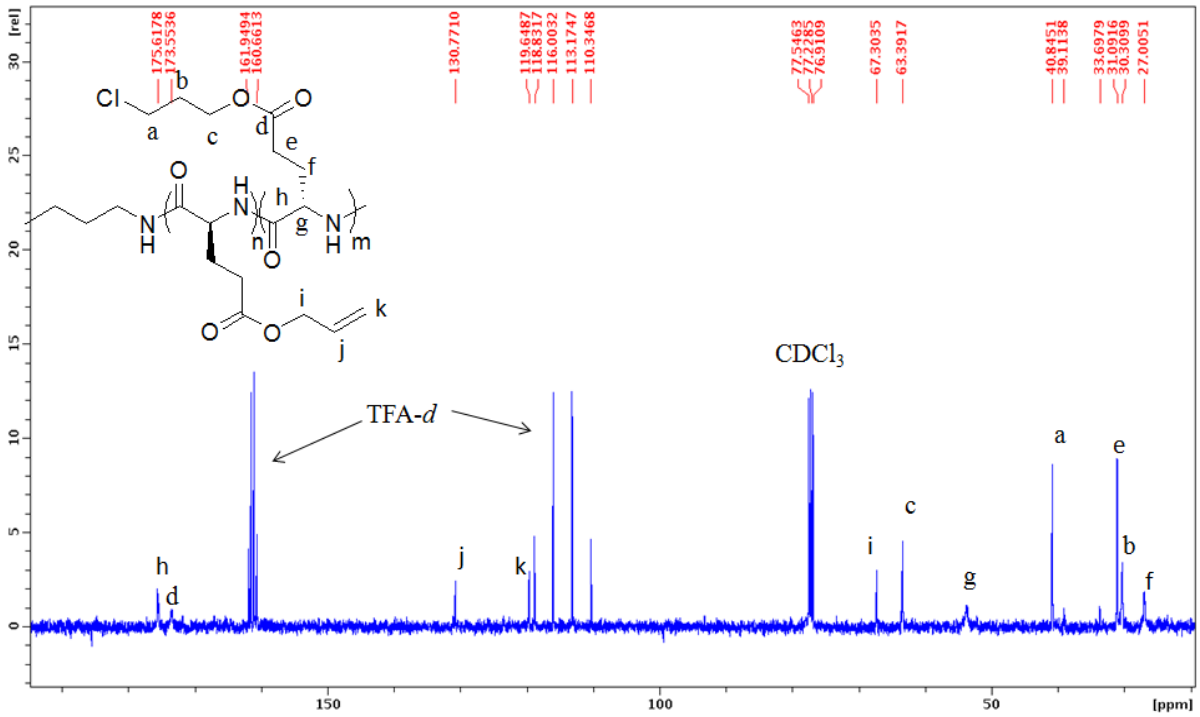

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of PALG-*b*-PCPLG **6** in $CDCl_3/CF_3CO_2D$ (v:v=85:15).

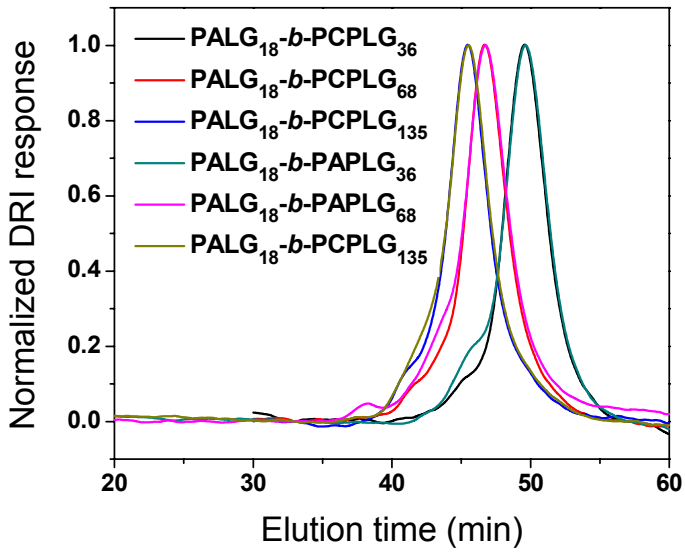

Figure S6. SEC chromatographs of $PALG_{18}$-*b*-$PCPLG_n$ (n= 36, 68, 135) having variable PCPLG block length and corresponding $PALG_{18}$-*b*-$PAPLG_n$ (n= 36, 68, 135) derived from NaN_3 substitution.

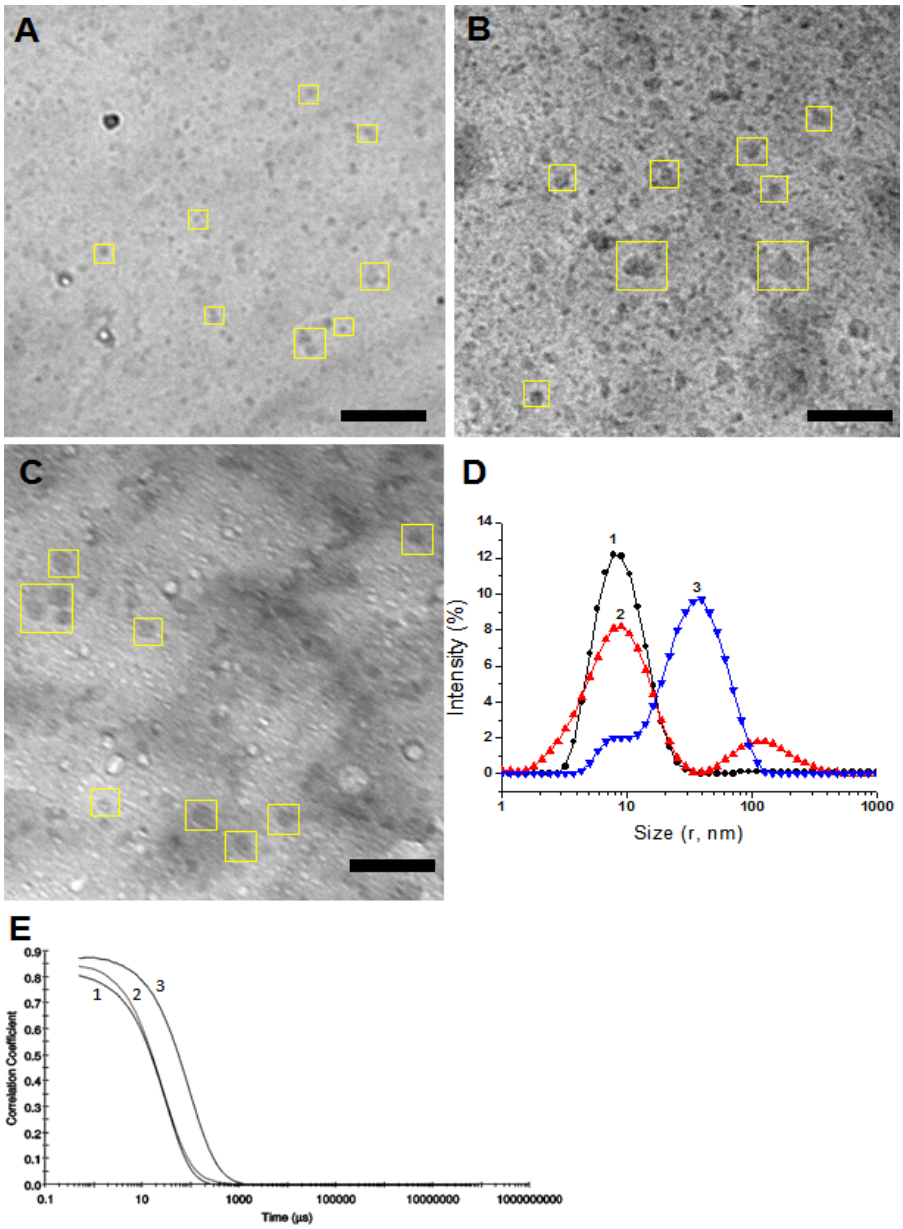

Figure S7. (A) CryoTEM images of $PALG_{18}$-*b*-($PPLG_{36}$-*g*-mannose), (B) $PALG_{18}$-*b*-($PPLG_{68}$-*g*-mannose) and (C) $PALG_{18}$-*b*-($PPLG_{135}$-*g*-mannose) in water (Scale bar: 100 nm); (D) DLS size distribution plot and (E) correlograms of $PALG_{18}$-*b*-($PPLG_{36}$-*g*-mannose) (1) (R_h=8.71±0.18 nm, PDI=0.253±0.039), $PALG_{18}$-*b*-($PPLG_{68}$-*g*-mannose) (2) (R_h=8.71±0.04 nm, PDI=0.432±0.041) and $PALG_{18}$-*b*-($PPLG_{135}$-*g*-mannose) (3) (R_h=25.81±0.19 nm, PDI=0.287±0.001) in water at 20 °C.

Table S1. pH and Temperature dependent CD analysis of $PALG_{18}$-*b*-($PPLG_{36}$-*g*-mannose) in water.

Entry	C ($mg \cdot mL^{-1}$)	Solvent	Temperature (^oC)	$[\theta]_{222}$	f_H (%)
1	0.2	H_2O, pH=2	20	-28, 208	80
2	0.2	H_2O, pH=4	20	-28, 338	80
3	0.2	H_2O, pH=7	20	-27, 364	78
4	0.2	H_2O, pH=10	20	-28, 908	82
5	0.2	H_2O, pH=12	20	-27, 869	79
6	0.2	H_2O, pH=13	20	-6, 802	19
7	0.17	H_2O, neutralized	20	-22, 885	65
8	0.2	H_2O, pH=7	5	-29, 049	82
9			20	-27, 364	78
10			40	-24, 859	71
11			60	-22, 089	63
12			80	-18, 613	53
13			Back to 60	-22, 024	63
14			Back to 40	-25, 836	73
15			Back to 20	-28, 327	80
16			Back to 5	-30, 362	86