SUPPORTING INFORMATION

Structure-pDNA complexation and structure-cytotoxicity relationships of PEGylated, cationic aminoethyl-based polyacrylates with tunable topologies

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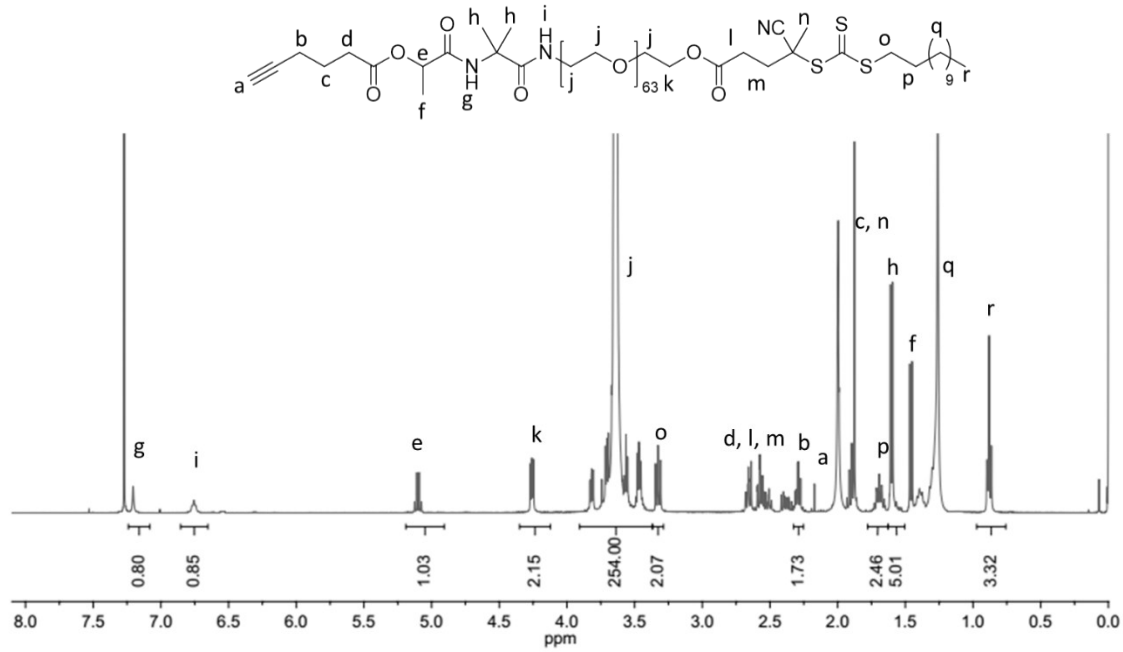

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the α-alkynyl,ω-dodecyltrithiocarbonate-PEG obtained by esterification of the α-alkynyl,ω-hydroxyl-PEG with CDP using DCC and DMAP.

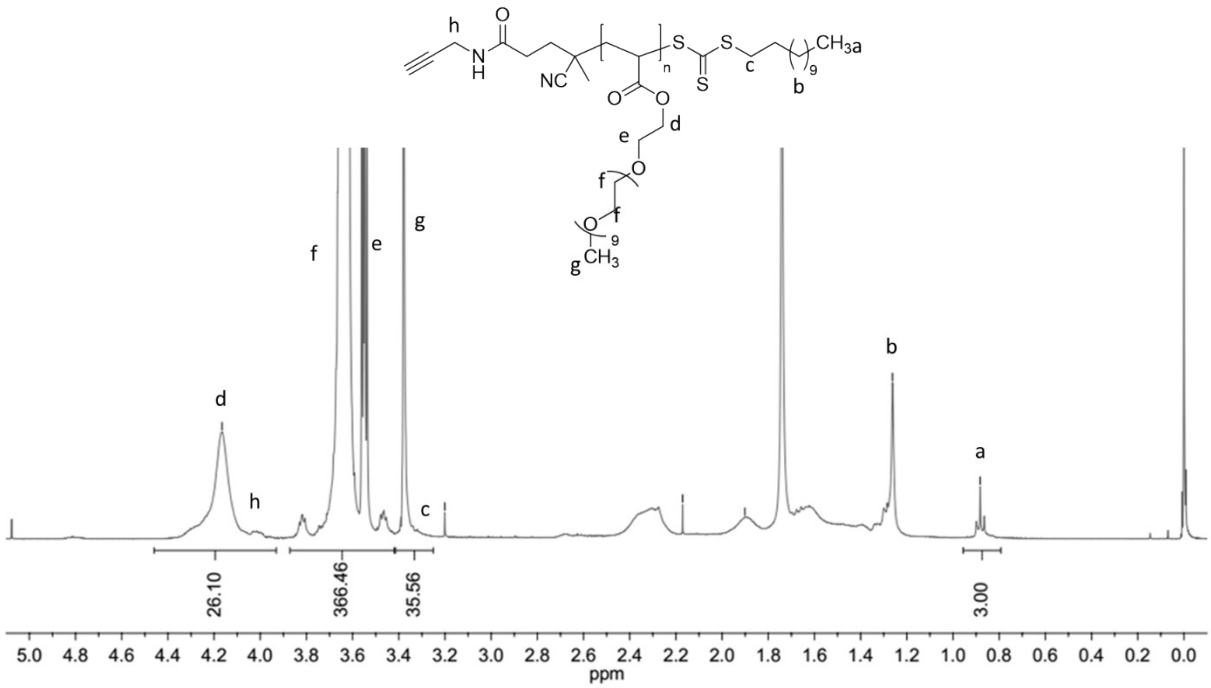

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of POEGA synthesized by RAFT polymerization of OEGA with ACVA and COPYDC ($[OEGA]_0/[COPYDC]_0/[ACVA]_0$ = 30/1/0.1) in DMF at 70 °C. $DP_{n,POEGA}$ = 12 was calculated by comparing the integration area values of the signal at 0.88 ppm corresponding to the methyl protons $S(CH_2)_{11}CH_3$ and of the signal at 4.17 ppm corresponding to the methylene protons $CH{\equiv}CCH_2NHC(=O)$ and $CH_2CH_2O(CH_2CH_2O)_8CH_3$.

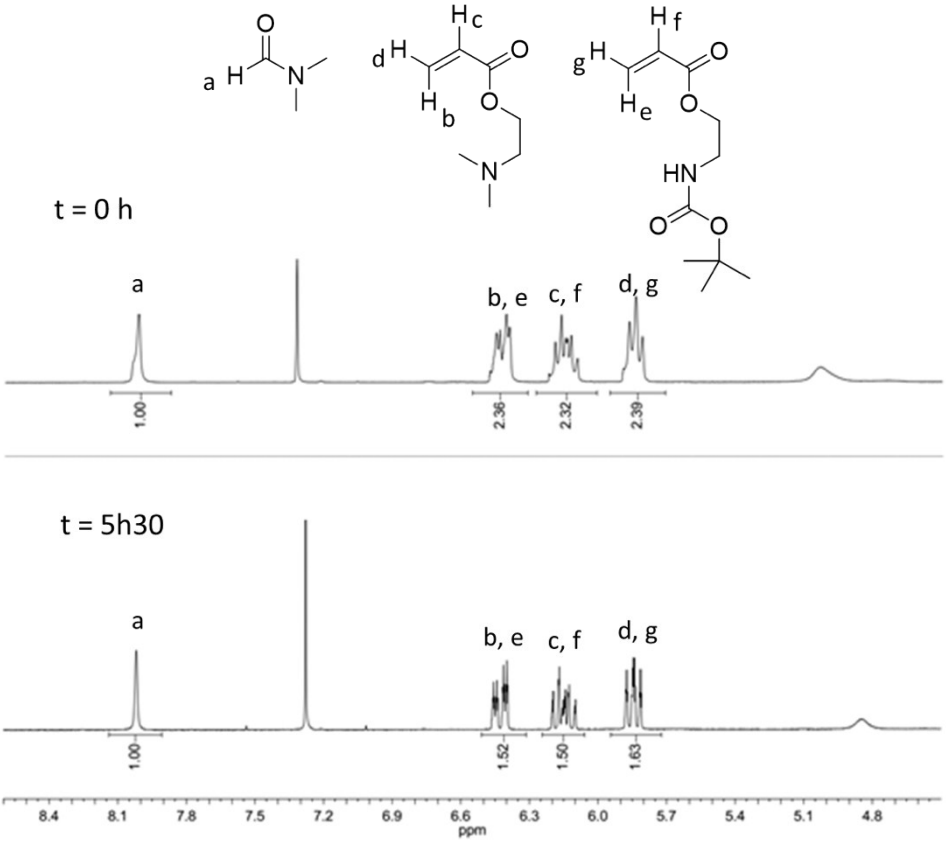

Figure S3. Overlaid of ^{1}H NMR spectra (400 MHz, $CDCl_3$) between 4.6 and 8.5 ppm of the crude mixture of RAFT copolymerization of DMAEA and *t*BocAEA using lPEG-CTA as the macromolecular chain transfer agent and ACVA as the initiator at 70°C in 1,4-dioxane and DMF using $[DMAEA]_0/[tBocAEA]_0/[lPEG\text{-}CTA]_0/[ACVA]_0$ = 50/50/1/0.2. Total of conversion of DMAEA and *t*BocAEA was determined to be 22% by comparing the integration areas of vinylic proton of DMAEA and *t*BocAEA at 5.81-6.46 ppm and with the integral area value of the CH of DMF at 8.02 ppm.

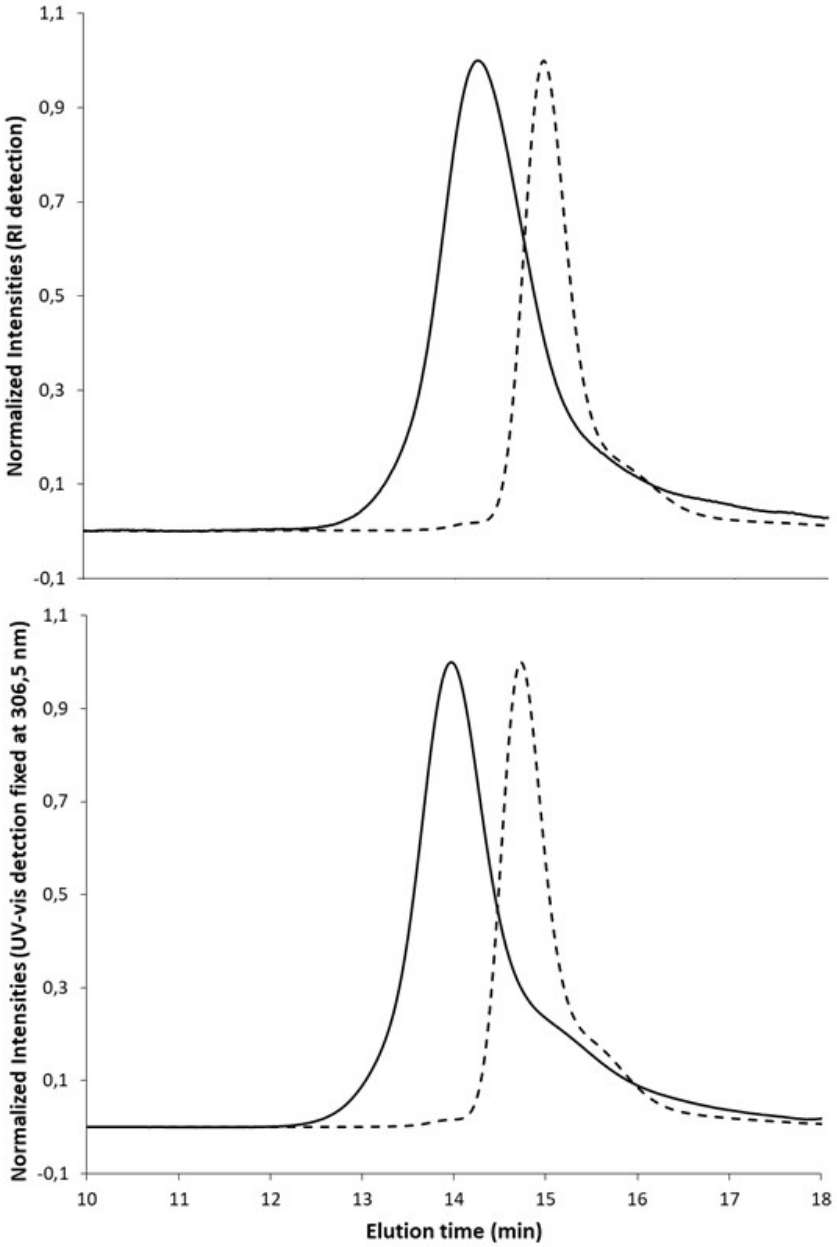

Figure S4. Overlaid SEC traces using RI detection (top) and UV-vis detection (fixed at 309 nm, bottom) of lPEG-CTA (dash line) and lPEG-*b*-P(DMAEA-*co*-*t*BocAEA) (solid line) synthesized by RAFT copolymerization of DMAEA and *t*BocAEA using lPEG-CTA and ACVA at 70 °C in 1,4-dioxane and DMF with $[DMAEA]_0/[tBocAEA]_0/[lPEG\text{-}CTA]_0/[ACVA]_0 = 50/50/1/0.2$.

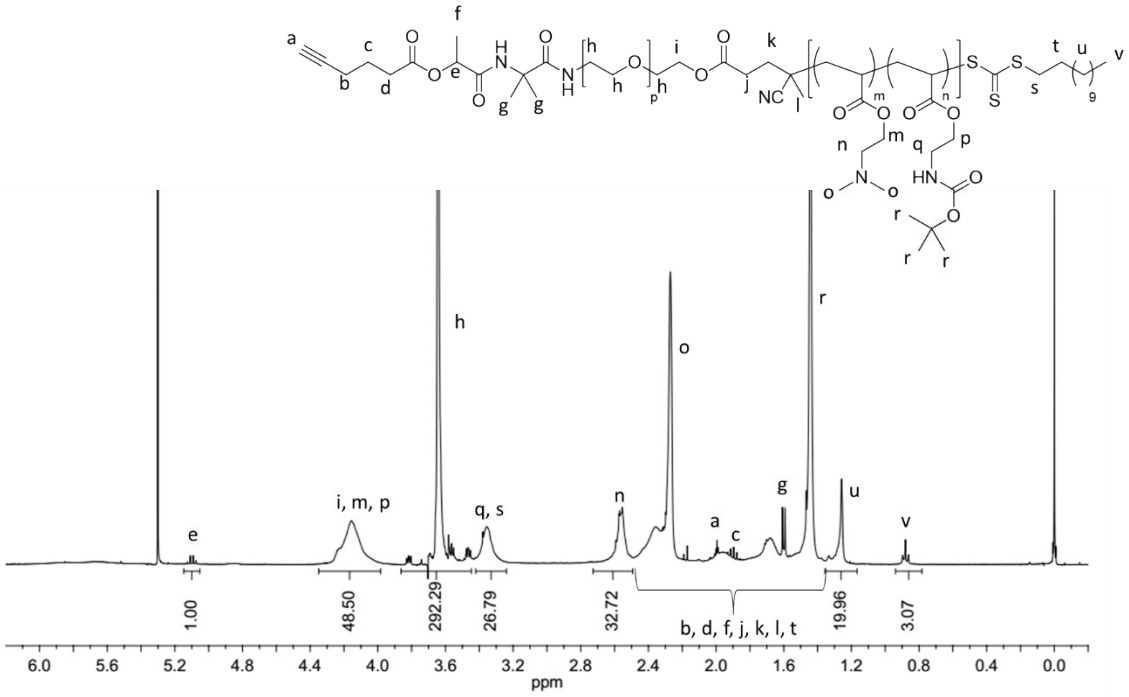

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified lPEG-*b*-P(DMAEA-*co*-*t*BocAEA) synthesized by RAFT copolymerization of DMAEA and *t*BocAEA using lPEG-CTA as the macromolecular chain transfer agent and ACVA as the initiator in 1,4-dioxane and DMF at 70 °C with $[DMAEA]_0/[tBocAEA]_0/[lPEG\text{-}CTA]_0/[ACVA]_0$ = 50/50/1/0.2. $DP_{n,PDMAEA}$ (= 11) and $DP_{n,tBocAEA}$ (= 12) were determined by comparing the integration area values of the signal of $CH_3CHC(=O)NH$ at 5.10 ppm, of the signal of $OCH_2CH_2NHC(=O)O$ and of $SCH_2(CH_2)_{10}CH_3$ at 3.35 ppm and of the signal of $CH_2CH_2OC(=O)$, of $OCH_2CH_2N(CH_3)_2$ and of OCH_2CH_2NH at 4.16 ppm.

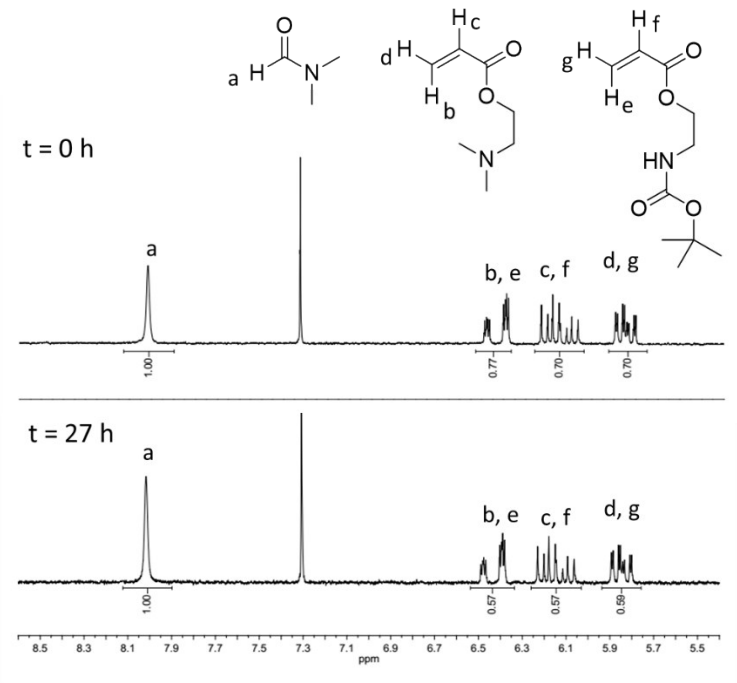

Figure S6. Overlaid ^{1}H NMR spectra (400 MHz, $CDCl_3$) between 5.4 and 8.6 ppm of the crude mixture of RAFT polymerization of DMAEA and *t*BocAEA using bPEG-CTA as the macromolecular chain transfer agent and ACVA as the initiator in 1,4-dioxane and DMF at 70 °C using $[DMAEA]_0/[tBocAEA]_0/[bPEG\text{-}CTA]_0/[ACVA]_0$ = 50/50/1/0.2. Total conversion of DMAEA and *t*BocAEA were determined to be 20% by comparing the integration areas of vinylic proton of DMAEA and *t*BocAEA at 5.79-6.52 ppm and with the integral area value of the CH of DMF at 8.02 ppm.

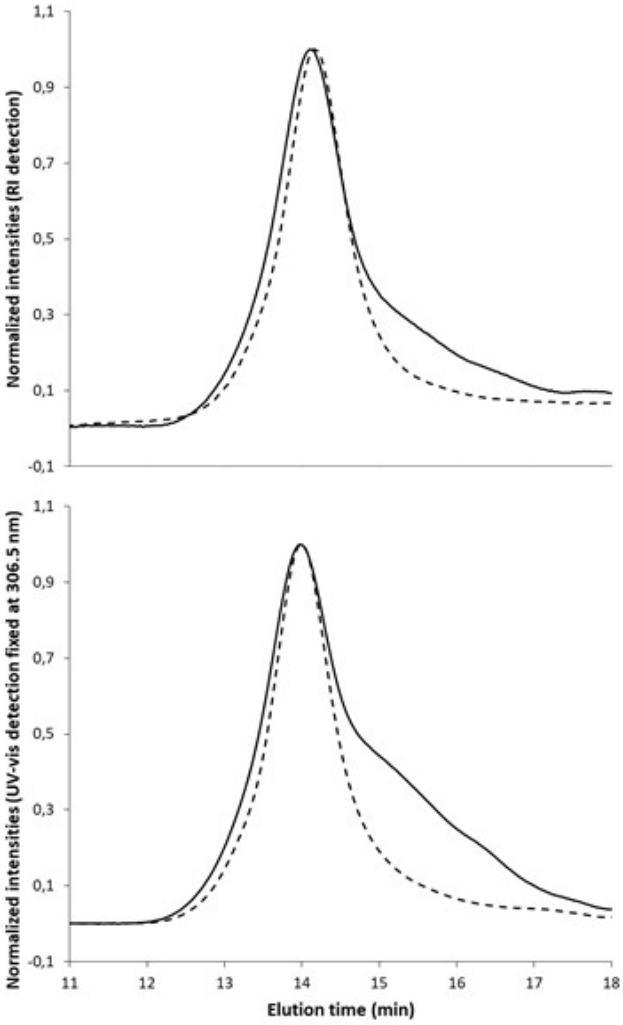

Figure S7. Overlaid of SEC traces using RI detection (top) and UV-vis detection (fixed at 309 nm, bottom) of bPEG-CTA (dash line) and bPEG-*b*-P(DMAEA-*co*-*t*BocAEA) (solid line) synthesized by RAFT copolymerization of DMAEA and *t*BocAEA using bPEG-CTA and ACVA in 1,4-dioxane and DMF at 70 °C with $[DMAEA]_0/[tBocAEA]_0/[bPEG\text{-}CTA\text{-}CTA]_0/[ACVA]_0 = 50/5/1/0.2$.

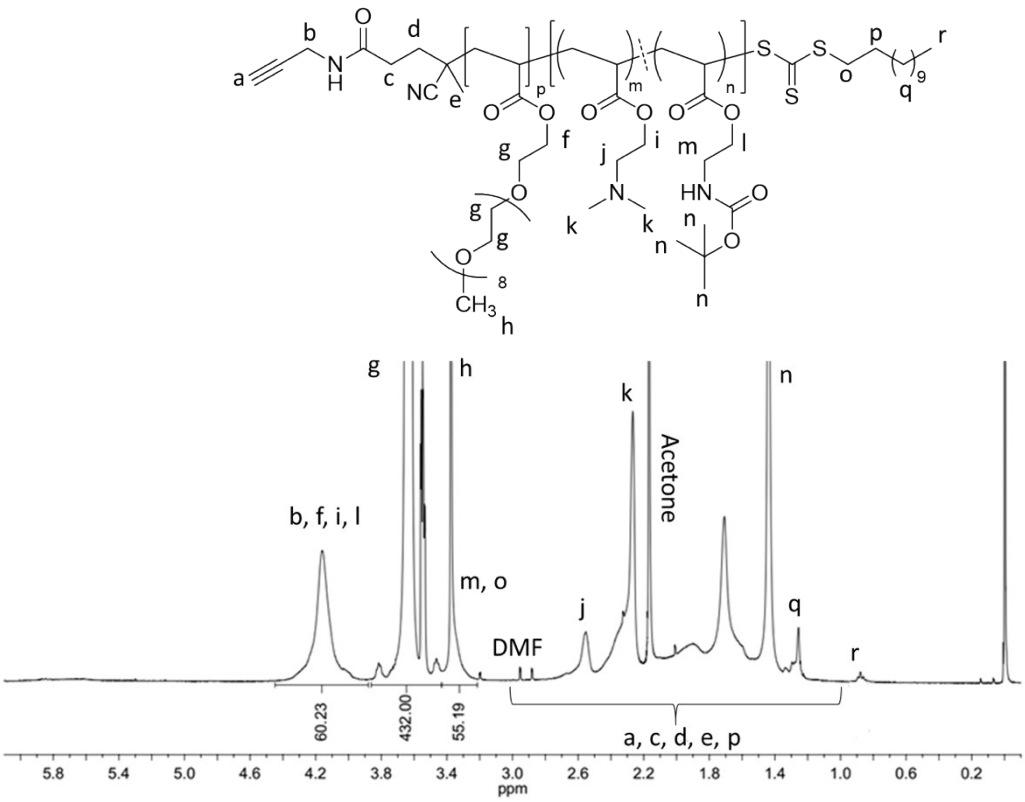

Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of bPEG-*b*-P(DMAEA-*co*-*t*BocAEA) synthesized by RAFT copolymerization of DMAEA and *t*BocAEA using bPEG-CTA as the macromolecular chain transfer agent and ACVA as the initiator in 1,4-dioxane and DMF at 70°C with $[DMAEA]_0/[tBocAEA]_0/[bPEG\text{-}CTA]_0/[ACVA]_0 = 50/50/1/0.2$. $DP_{n,PDMAEA}$ (= 10) and $DP_{n,tBocAEA}$ (= 10) were determined by comparing the integration area values of the signal of CH_2CH_2O units at 3.64 ppm, of the signal of $(CH_2CH_2O)_9CH_3$, of OCH_2CH_2NH, of $SCH_2(CH_2)_{10}CH_3$ at 3.38 ppm, and of the signal of $HC{\equiv}CCH_2NH$, of $OCH_2CH_2O(CH_2CH_2O)_8$ of $OCH_2CH_2N(CH_3)_2$, of OCH_2CH_2NH at 4.16 ppm.

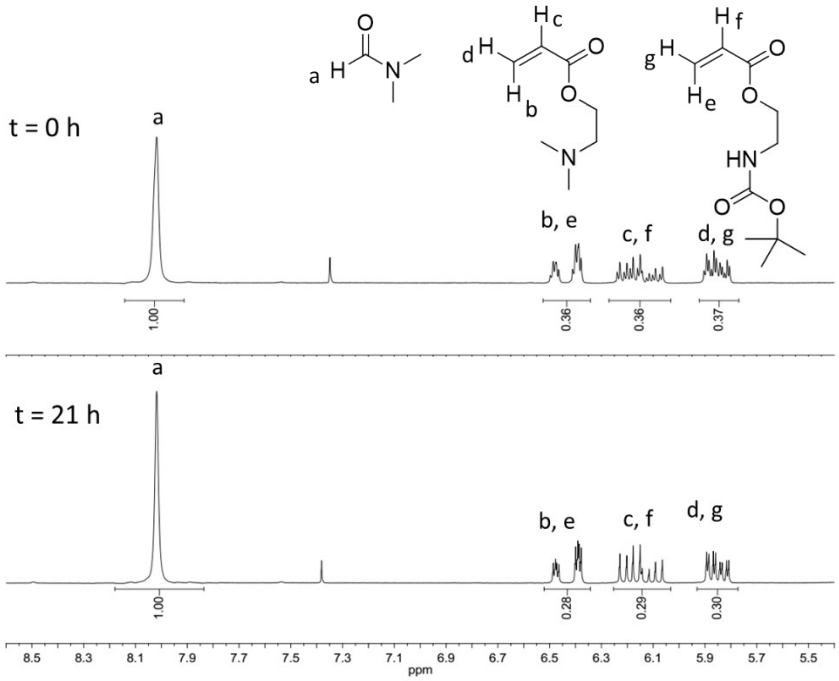

Figure S9. Overlaid of ^{1}H NMR spectra (400 MHz, $CDCl_3$) between 5.4 and 8.6 ppm of the crude mixture of RAFT copolymerization of DMAEA and *t*BocAEA using COPYDC as the chain transfer agent and ACVA as the initiator in 1,4-dioxane and DMF at 70 °C using $[DMAEA]_0/[tBocAEA]_0/[COPYDC]_0/[ACVA]_0$ = 50/50/1/0.2. Total conversion of DMAEA and *t*BocAEA were determined to be 19% by comparing the integration areas of vinylic proton of DMAEA and *t*BocAEA at 5.79-6.52 ppm and with the integral area value of the CH of DMF at 8.02 ppm.

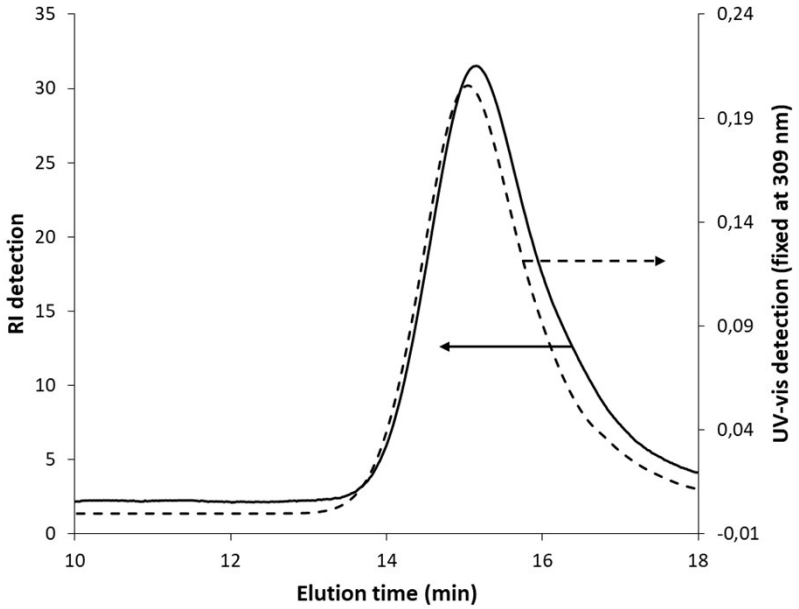

Figure S10. Overlaid SEC traces of purified P(DMAEA-*co*-*t*BocAEA) (solid line: RI response, dash line: UV-vis response at 309 nm) obtained by RAFT copolymerization of DMAEA and *t*BocAEA using COPYDC as RAFT agent, ACVA as the initiator in DMF at 70 °C. ($[DMAEA]_0/[tBocAEA]_0/[COPYDC]_0/[ACVA]_0 = 50/50/1/0.2$).

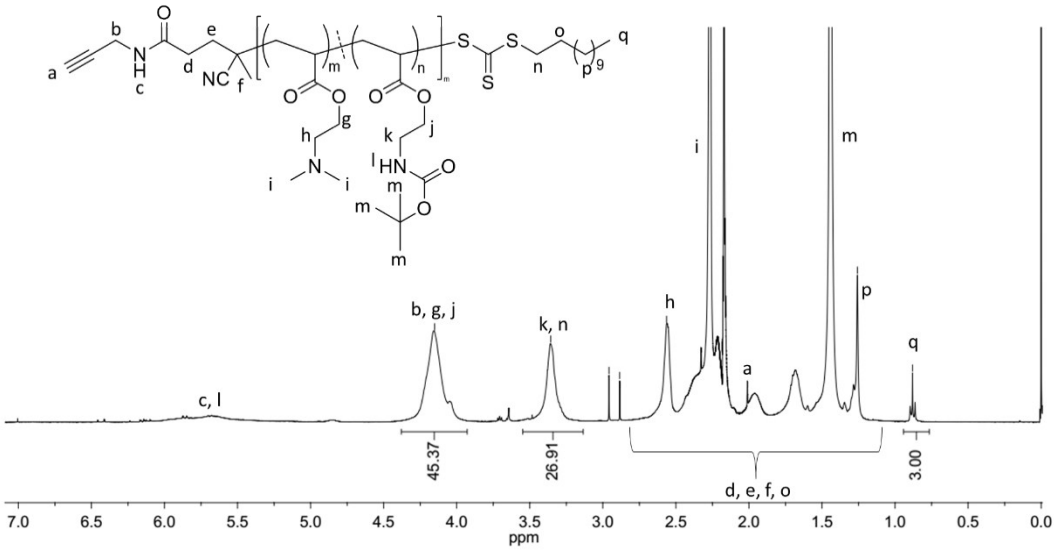

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of purified P(DMAEA-*co*-*t*BocAEA) synthesized by RAFT copolymerization of DMAEA and *t*BocAEA mediated through COPYDC as the chain transfer agent and ACVA as the initiator in DMF at 70 °C using $[DMAEA]_0/[tBocAEA]_0/[COPYDC]_0/[ACVA]_0$ = 50/50/1/0.2. $DP_{n,PDMAEA}$ = 10) and $DP_{n,tBocAEA}$ (= 12) were determined by comparing the integration area values of the signal of $SCH_2(CH_2)_{10}CH_3$ at 0.88 ppm, of the signal of OCH_2CH_2NH, of $SCH_2(CH_2)_{10}CH_3$ at 3.36 ppm and of the signal of $HC{\equiv}CCH_2NH$, of $OCH_2CH_2N(CH_3)_2$, of CH_2CH_2NH at 4.16 ppm.

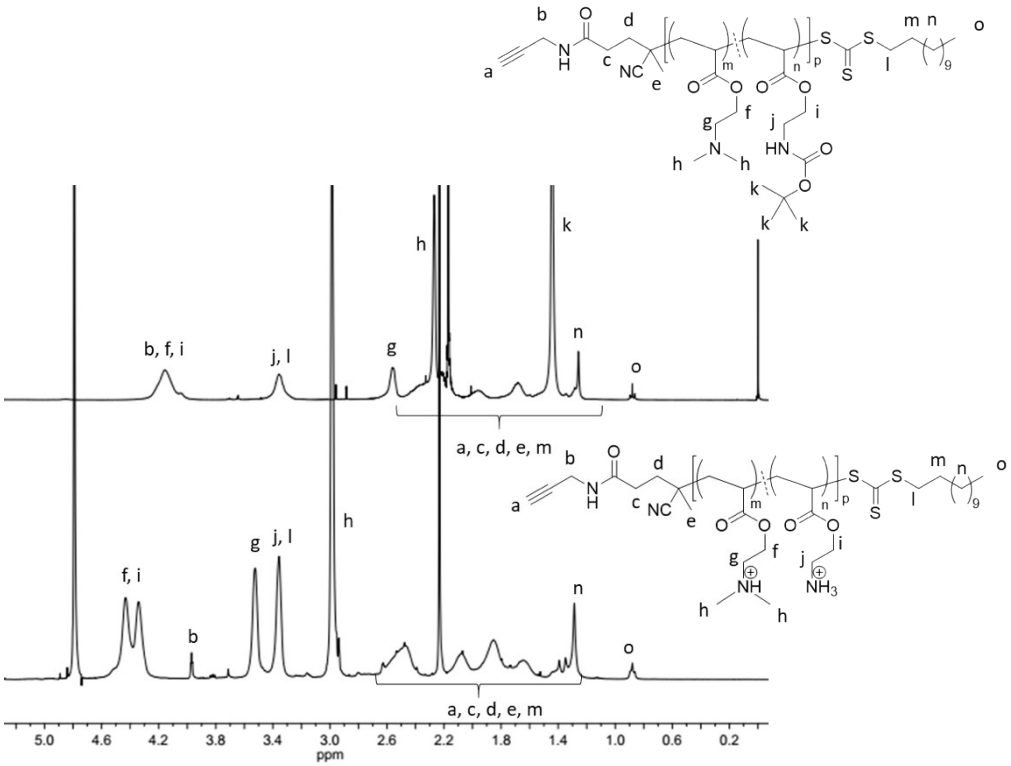

Figure S12. Overlaid ^{1}H NMR spectra (400 MHz) of P(DMAEA-*co*-*t*BocAEA) (top, $CDCl_3$) and P(DMAEA-*co*-AEA) (bottom, D_2O).

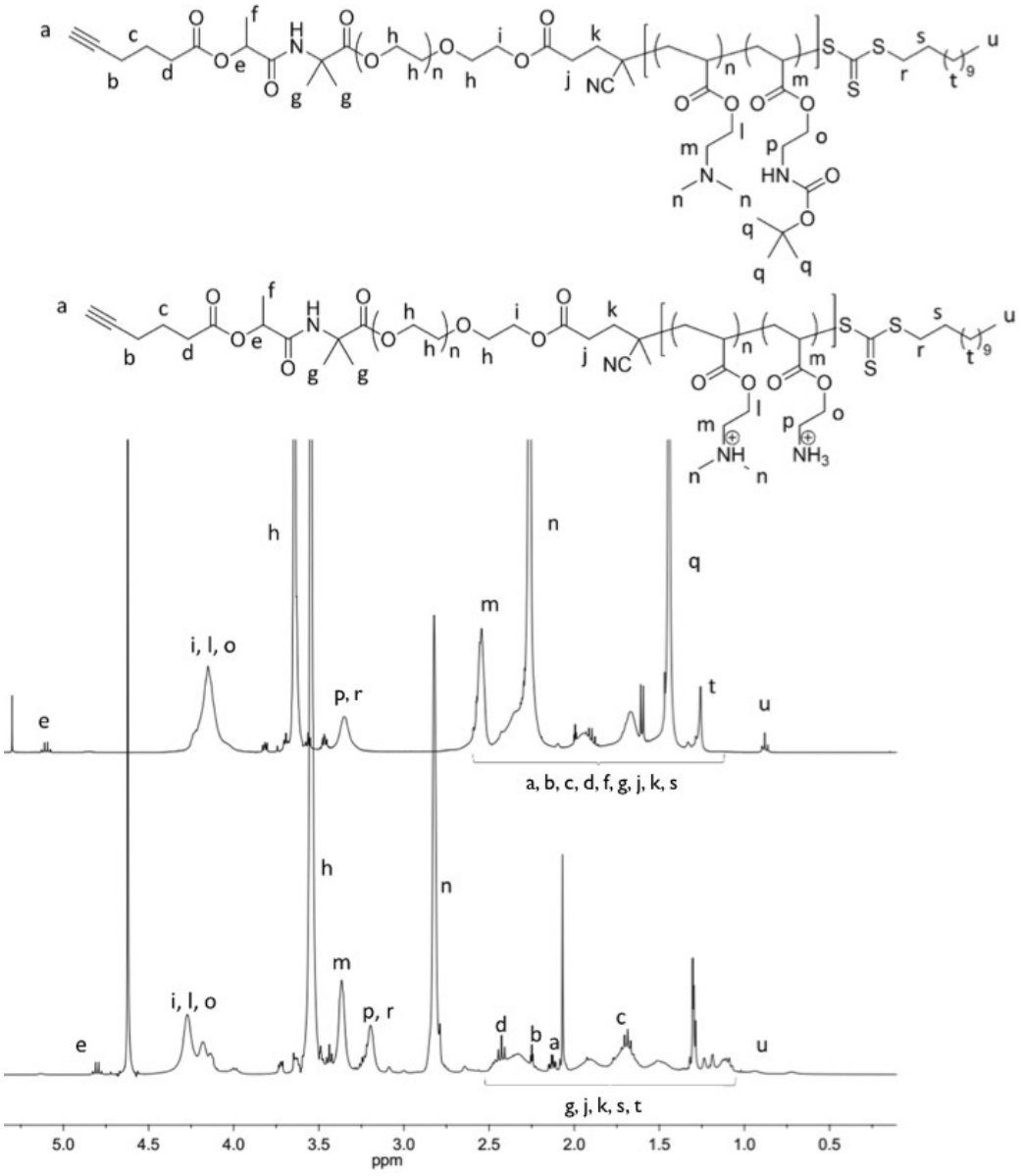

Figure S13. Overlaid of ^{1}H NMR spectra (400 MHz) of lPEG-*b*-P(DMAEA-*co*-*t*BocAEA) in $CDCl_3$ (top) and lPEG-*b*-P(DMAEA-*co*-AEA) in D_2O (bottom).

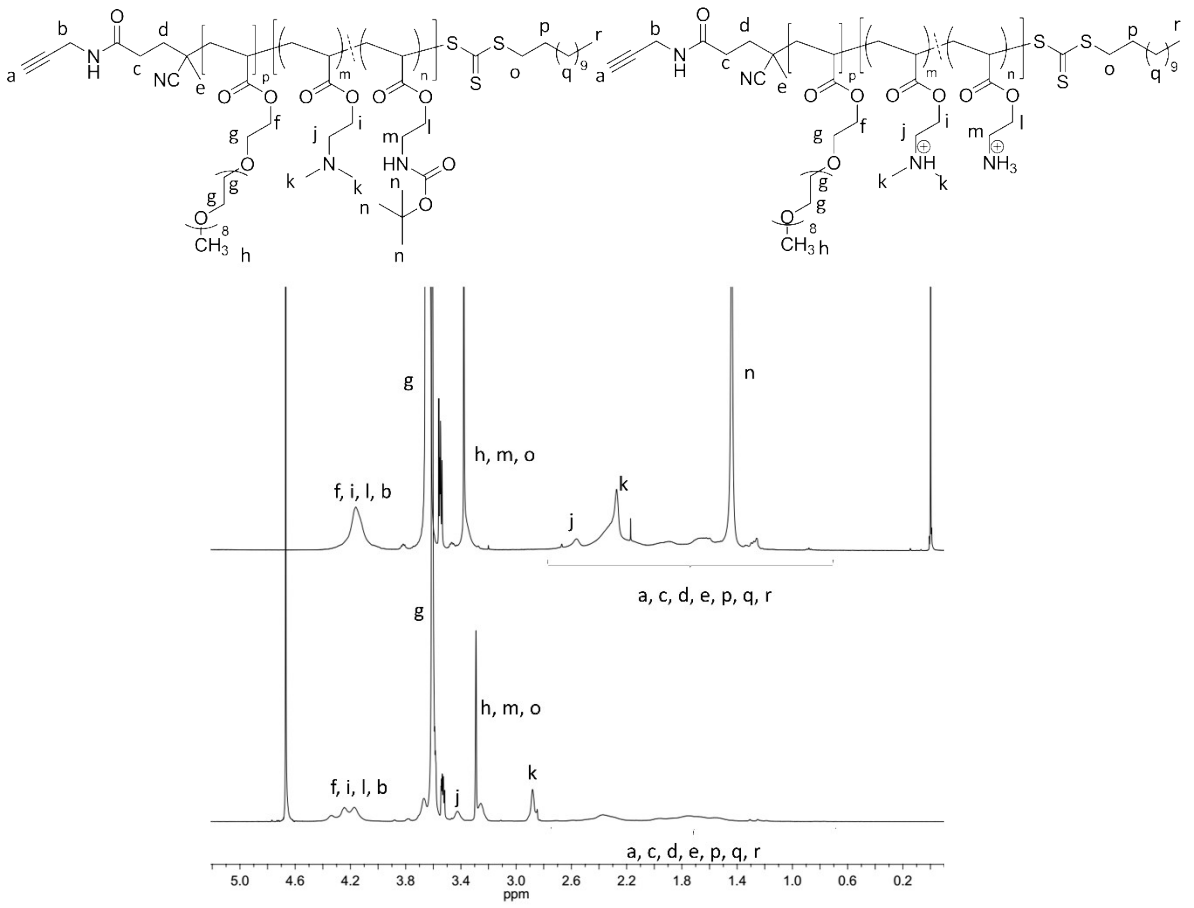

Figure S14. Overlaid ^{1}H NMR spectra (400 MHz) of bPEG-*b*-P(DMAEA-*co*-*t*BocAEA) ($CDCl_3$, top) and bPEG-*b*-P(DMAEA-*co*-AEA) (D_2O, bottom).

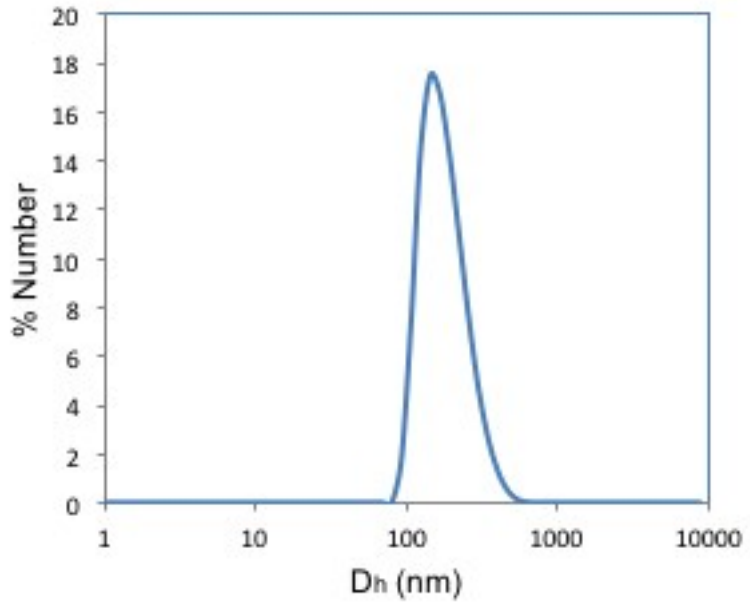

Figure S15. DLS number-average diameter distribution of the pDNA/lPEG-*b*-P(DMAEA-*co*-AEA) polyplex (N/P = 3)

Table S1. Preparation of pDNA/polymer polyplexes at different N/P ratios.

N/P	V_{pDNA} (μL)	$V_{DNA\ loading}$ (μL)	$V_{pH\ buffering}$ (μL)	$V_{copolymer\ solution}$ (μL)
0	2	2	7	0
1	2	2	5	2
2	2	2	3	4
3	2	2	1	6
4	2	2	0	8
5	2	2	0	10
6	2	2	0	12
7	2	2	0	14
8	2	2	0	16