{This document replaces the previous version which contained some errors in signal assignments in Fig. S1, S2, S3}

Supporting Information

Novel degradable amphiphilic 4-arm star PLA-*b*-POEOA and PLGA-*b*-POEOA block copolymers: synthesis, characterization and self-assembly

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Table S1. Architecture, composition and molecular weight parameters of the BCPs obtained by ICAR ATRP from polyester macroinitiators (prepared by ROP). Conditions: $[OEOA]_0/[polyester\text{-}Br]_0/[CuBr_2]_0/[Me_6TREN]_0/[V\text{-}50]_0$ = DP/1/0.16/0.32/1.2 (molar); $[OEOA]_0$ = 1 M; Solvent: DMF; T = 60 ^{0}C

Entry	Polymer	DP_{OEOA}	Time (h)	Conv. (%)	M_n^{NMR} x 10^{-3}	M_n^{SEC} x 10^{-3}	M_w/M_n
1	$(PLA_5\text{-}b\text{-}POEOA_{13})_4$	52	7.5	99	27.9	16.0	1.33
2	$(PLA_6\text{-}b\text{-}POEOA_{31})_4$	150[a]	24	84	65.1	22.6	1.62
3	$(PLGA_6\text{-}b\text{-}POEOA_{12})_4$ (PLGA 50:50)	48	24	99	26.2	14.9	1.41
4	$(PLGA_6\text{-}b\text{-}POEOA_{11})_4$ (PLGA 75:25)	50	4	91	26.1	18.8	1.31
5	$(PLGA_6\text{-}b\text{-}POEOA_{25})_4$ (PLGA 75:25)	150[a]	5	67	52.6	26.9	1.30
6	$(PLGA_7\text{-}b\text{-}POEOA_{32})_4$ (PLGA 50:50)	147[a]	5	87	65.7	33.4	1.20
7	Linear $PLA_{22}\text{-}b\text{-}POEOA_{50}$	51	24	99	27.9	17.3	1.34
8	Linear $PLGA_{27}\text{-}b\text{-}POEOA_{38}$ (PLGA 50:50)	52	6.5	74	22.2	13.7	1.32
9	Linear $PLGA_{23}\text{-}b\text{-}POEOA_{39}$ (PLGA 75:25)	51	6.5	77	22.3	11.0	1.31

[a] $[CuBr_2]_0/[Me_6TREN]_0$= 0.48/0.96 (molar)

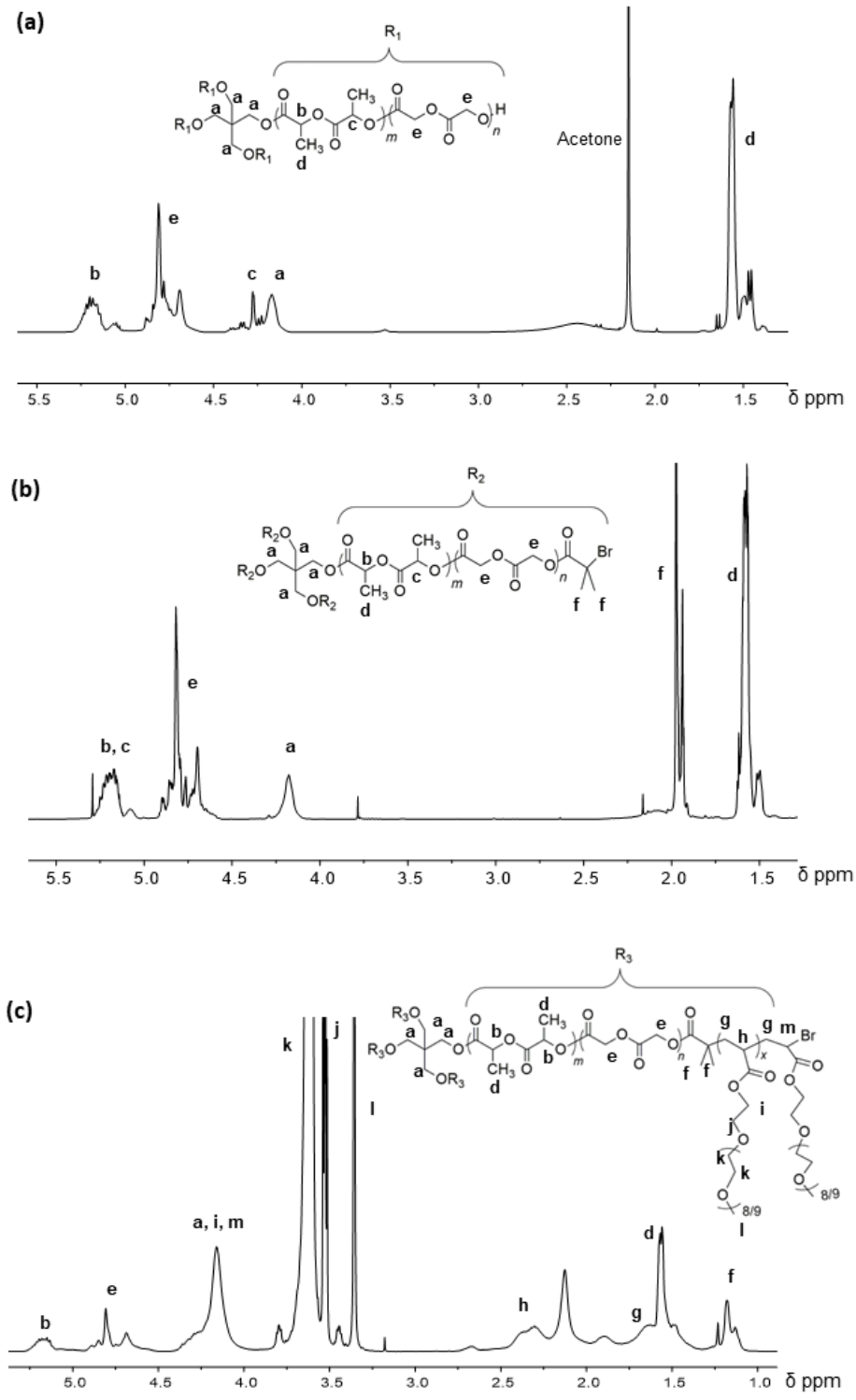

Figure S1. ^{1}H NMR spectra of 4-arm star PLGA-OH (a), 4-arm star PLGA-Br (b) and 4-arm star PLGA-*b*-POEOA (PLGA 50:50) BCP (c) in $CDCl_3$.

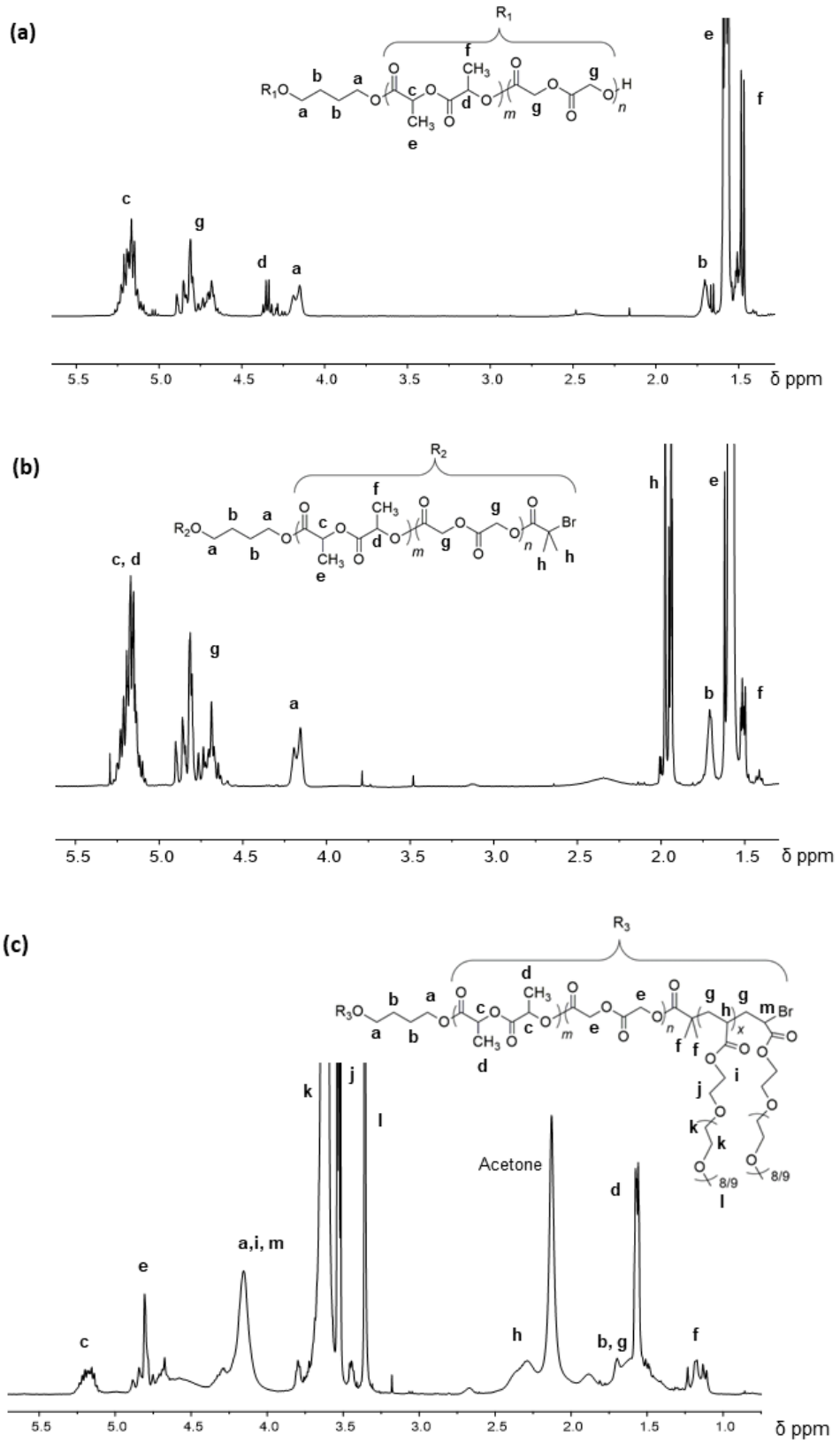

Figure S2. ^{1}H NMR spectra of linear PLGA-OH (a), linear PLGA-Br (b) and linear PLGA-*b*-POEOA (PLGA 50:50) BCP (c) in $CDCl_3$.

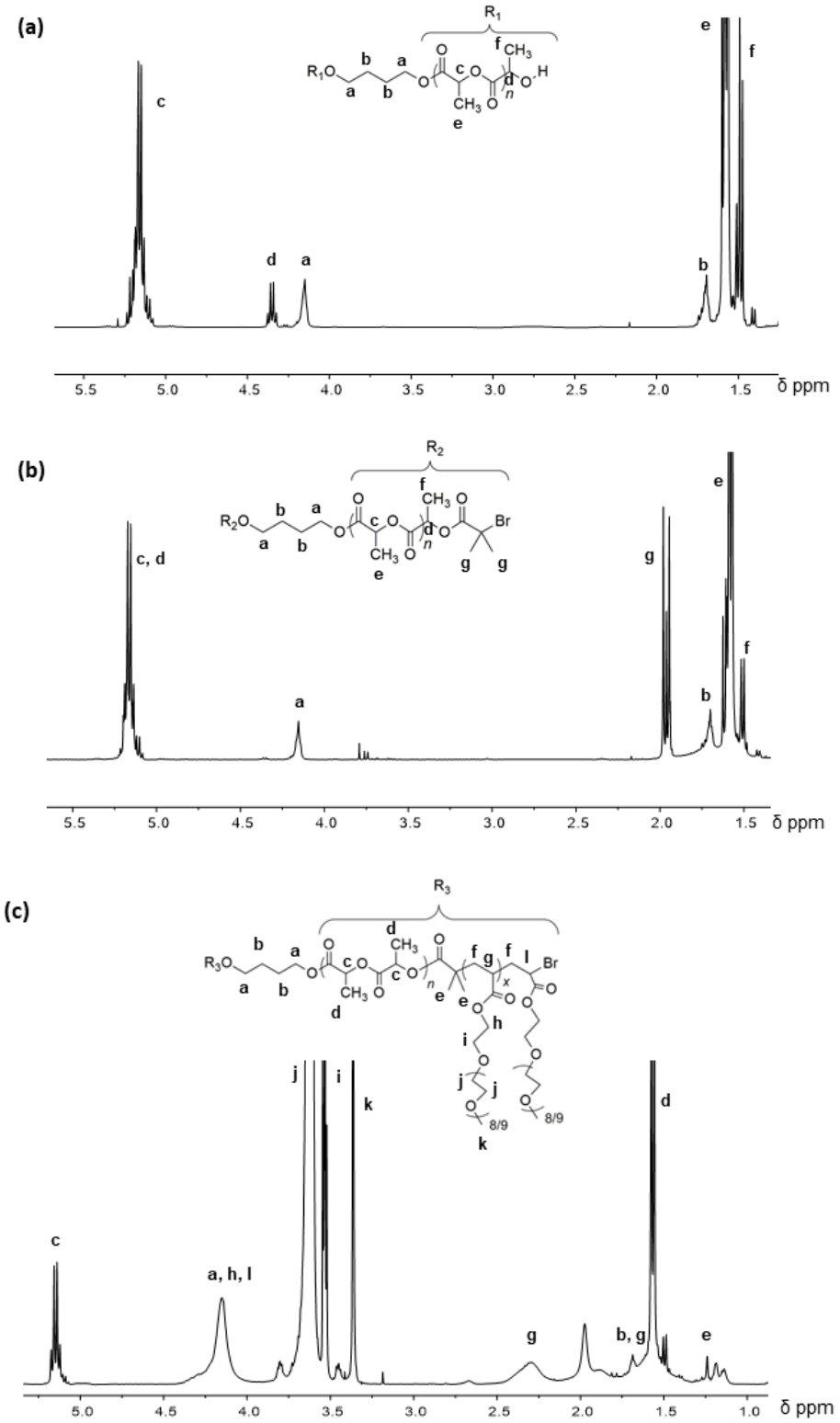

Figure S3. ^{1}H NMR spectra of linear PLA-OH (a), linear PLA-Br (b) and linear PLA-*b*-POEOA BCP (c) in $CDCl_3$.

The ATR-FTIR spectra in Figures S4, S5, S6 and S7 show the characteristic PLA and PLGA stretching vibration of the ester carbonyl at 1746 cm^{-1}, the OH stretching at 3516 $cm^{-1}$and the C-O-C stretching at 1084 cm^{-1}.[1] The peak at 1453 cm^{-1} corresponds to the vibration of methyl and the aliphatic C–H stretching is observed at 2873 cm^{-1}, which is attributed to the C–H bending vibrations.[1]

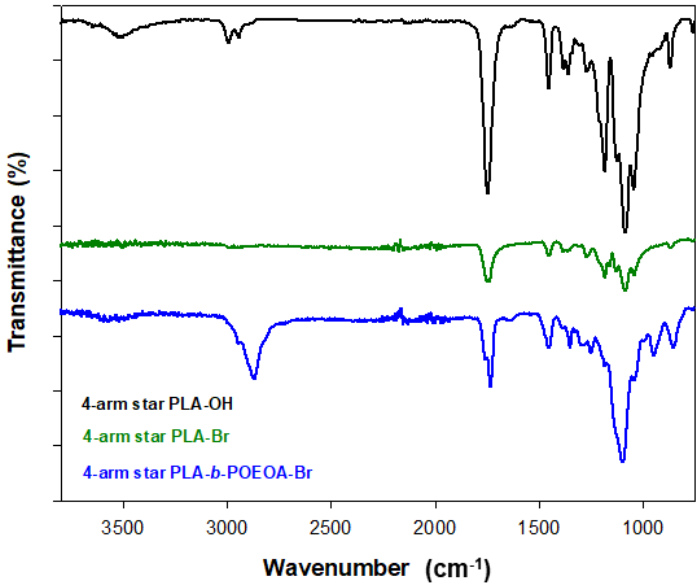

Figure S4. ATR-FTIR spectra of 4-arm star PLA-OH, 4-arm star PLA-Br and 4-arm star PLA-*b*-POEOA BCP.

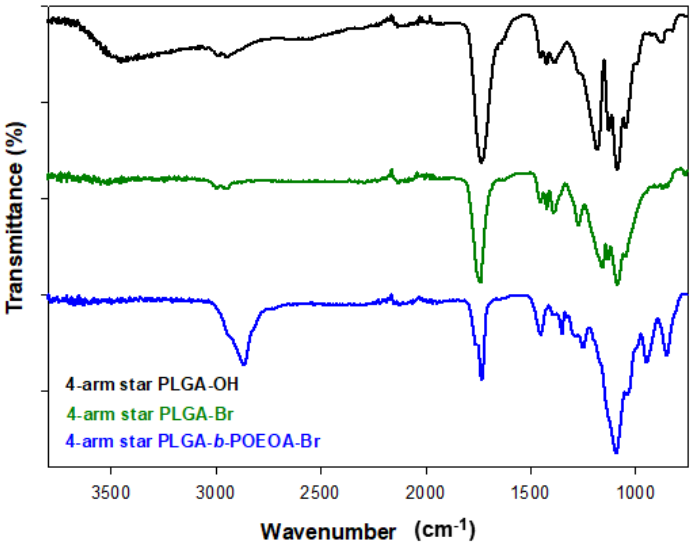

Figure S5. ATR-FTIR spectra of 4-arm star PLGA-OH, 4-arm star PLGA-Br and 4-arm star PLGA-*b*-POEOA BCP.

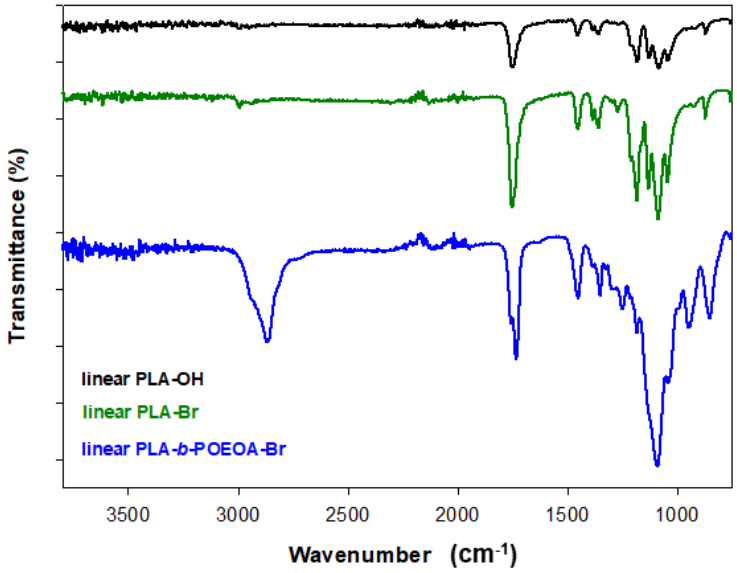

Figure S6. ATR-FTIR spectra of linear PLA-OH, linear PLA-Br and linear PLA-*b*-POEOA BCP.

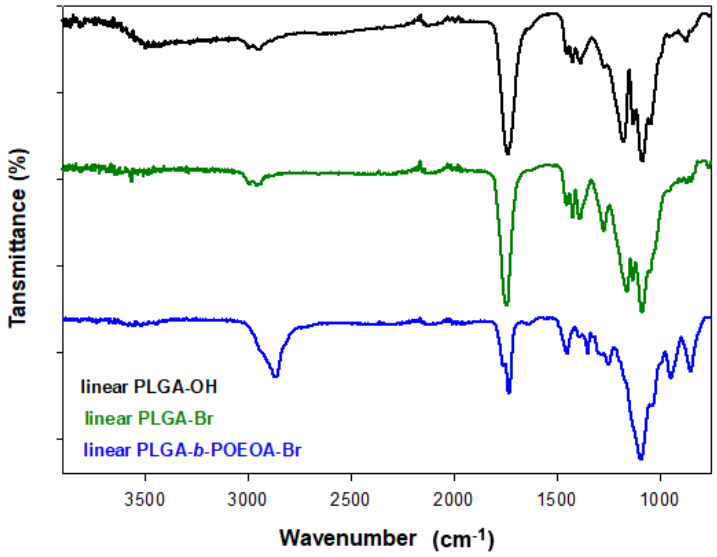

Figure S7. ATR-FTIR spectra of linear PLGA-OH, linear PLGA-Br and linear PLGA-*b*-POEOA BCP.

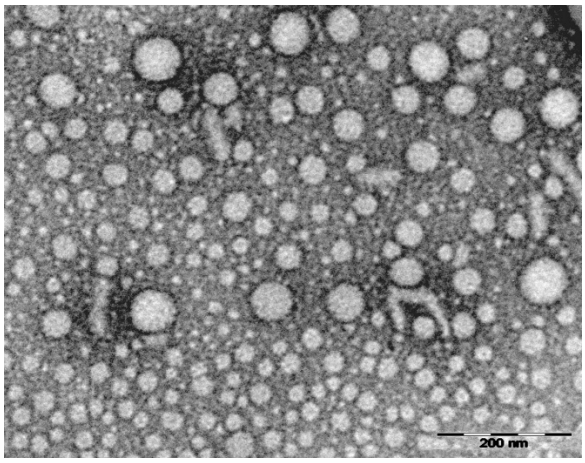

Figure S8. TEM image of micelles formed by $(PLA_5\text{-}b\text{-}POEOA_{13})_4$ BCP.

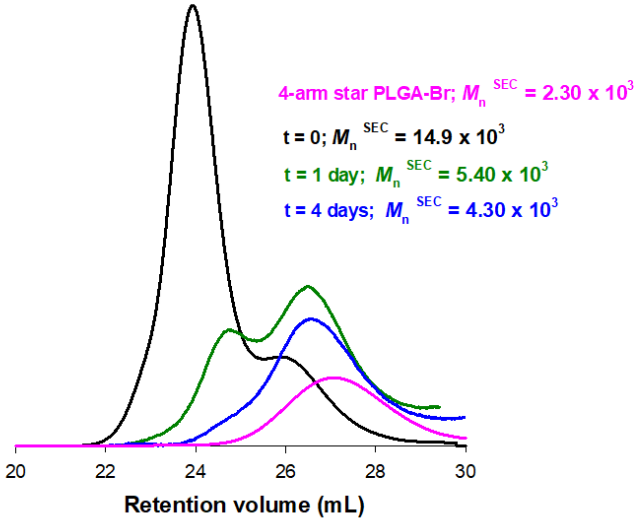

Figure S9. SEC traces (RI signal) of $(PLGA_6\text{-}b\text{-}POEOA_{12})_4$ (PLGA 50:50) BCP at different degradation times.

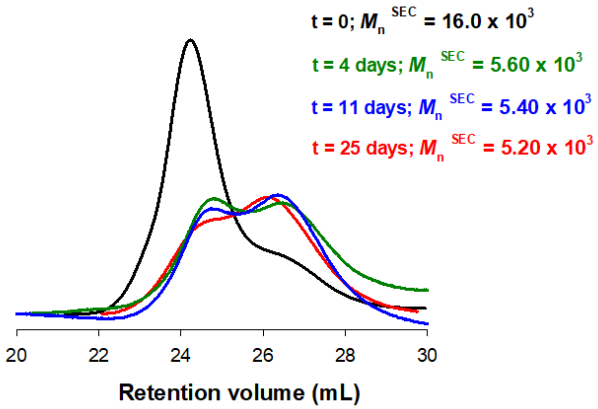

Figure S10. SEC traces (RI signal) of $(PLA_5\text{-}b\text{-}POEOA_{13})_4$ BCP at different degradation times.

References

1. Eldessouki, M., Buschle-DIller, G., Gowayed, Y. *Des. Monomers Polym.*, 2016, **19**, 180–192.