Supplementary Information

The Effect of Comb Length on the *In vitro* and *In vivo* Properties of Self-Assembled Poly(Oligoethylene Glycol Methacrylate)-Based Block Copolymer Nanoparticles

Andrew Singh[1], Andrew Lofts[1], Ramya Krishnan[2], Matthew Campea[1], Lan Chen[2], Yonghong Wan[2] and Todd Hoare[1]*

[1]Department of Chemical Engineering, McMaster University, 1280 Main St. W., Hamilton, Ontario, Canada L8S 4L7

[2]Department of Pathology and Molecular Medicine, McMaster University, 1280 Main St. W., Hamilton, Ontario, Canada L8S 4L7

* To whom correspondence should be addressed: hoaretr@mcmaster.ca

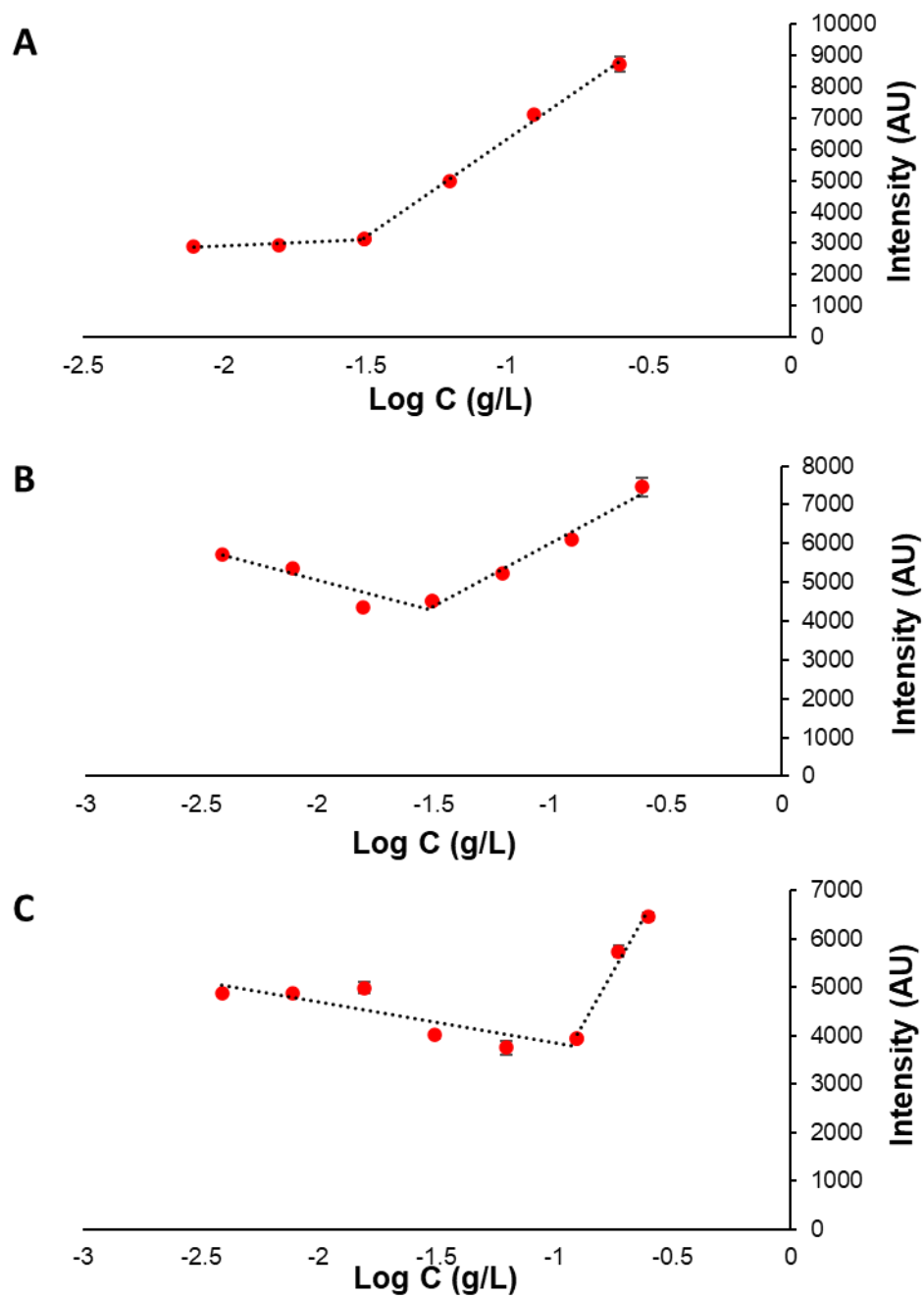| Polymer	CMC (mg/L)
P(L)LA$_{10K}$ -b-PEG$_{10K}$	22.0
P(L)LA$_{10K}$-b-POEGMA475$_{10K}$	21.8
P(L)LA$_{10K}$-b-POEGMA2000$_{10K}$	39.4

Figure S1. CMC based on plots of the fluorescence intensity of pyrene at 336 nm vs. log C in (A) P(L)LA$_{10K}$ -b-PEG$_{10K}$; (B) P(L)LA$_{10K}$-b-POEGMA475$_{10K}$; (C) P(L)LA$_{10K}$-b-POEGMA2000$_{10K}$
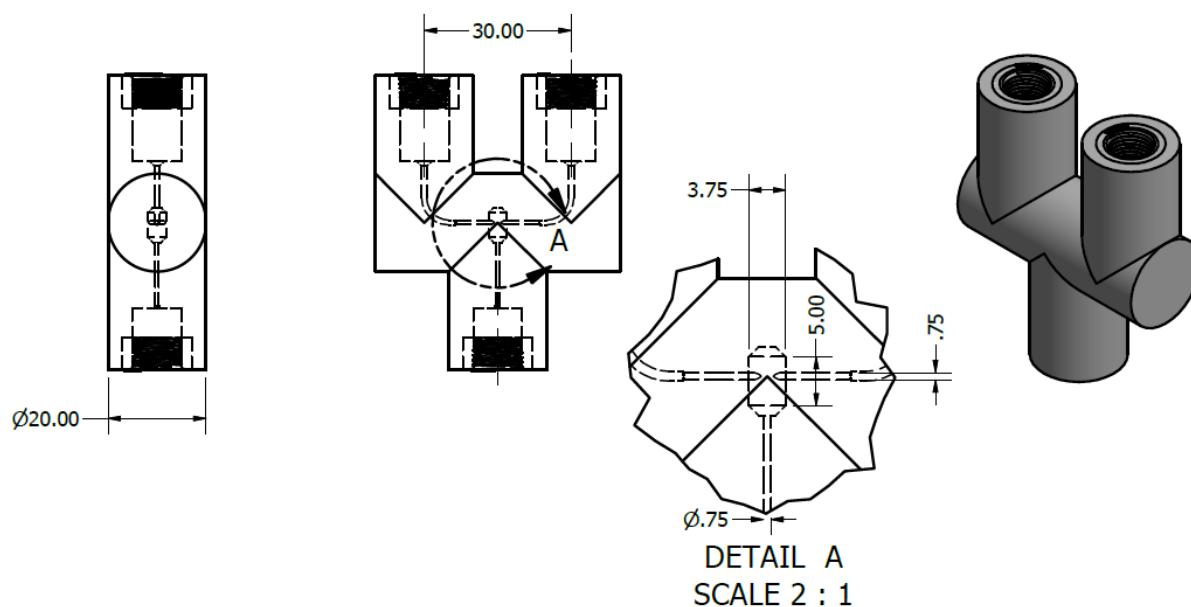
Figure S2. Schematic and picture of the CIJ-M device used to assemble the P(L)LA-b-POEGMA copolymers into nanoparticles. Solvent and aqueous solutions flow through the two inlets, the flow of which is impinged at the center of the device to trigger flash nanoprecipitation and induce the self-assembly of block copolymers into nanoparticles
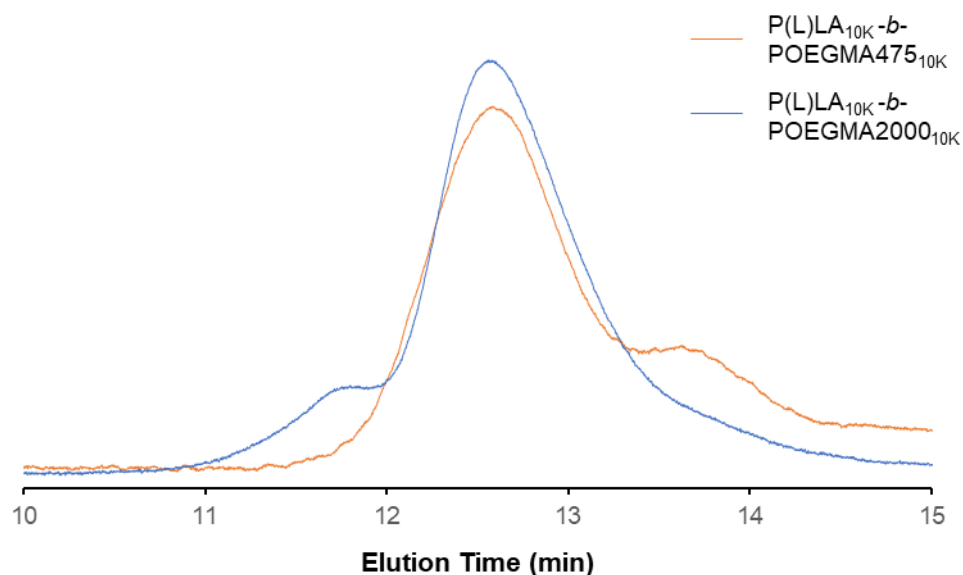

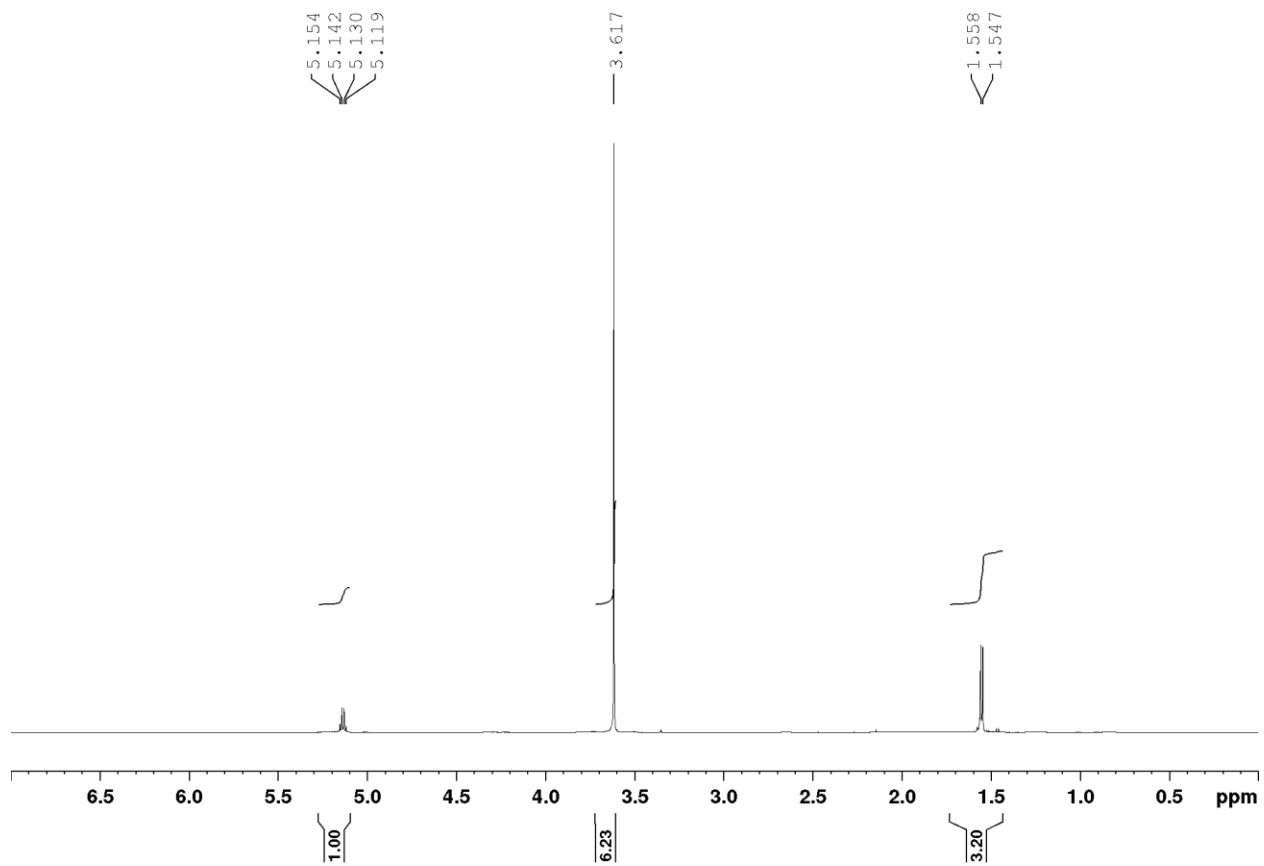*Figure S3. GPC traces of the P(L)LA-b-POEGMA linear-comb block copolymers synthesized*

5.154
5.142
5.130
5.119

3.617

1.558
1.547

6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5   ppm

1.00

6.23

3.20

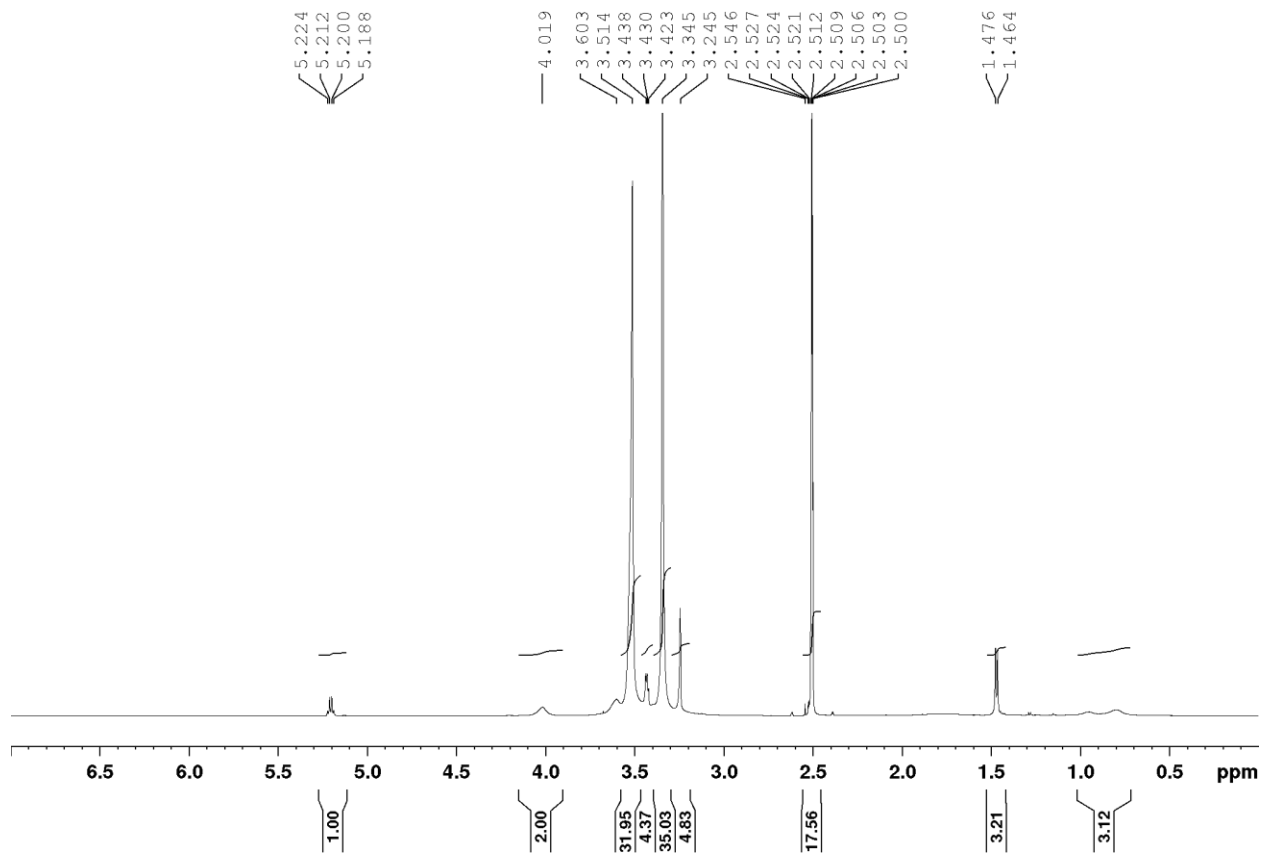*Figure S4. ^1H NMR spectrum of P(L)LA$_{10K}$ -b-PEG$_{10K}$ in CDCl$_3$*

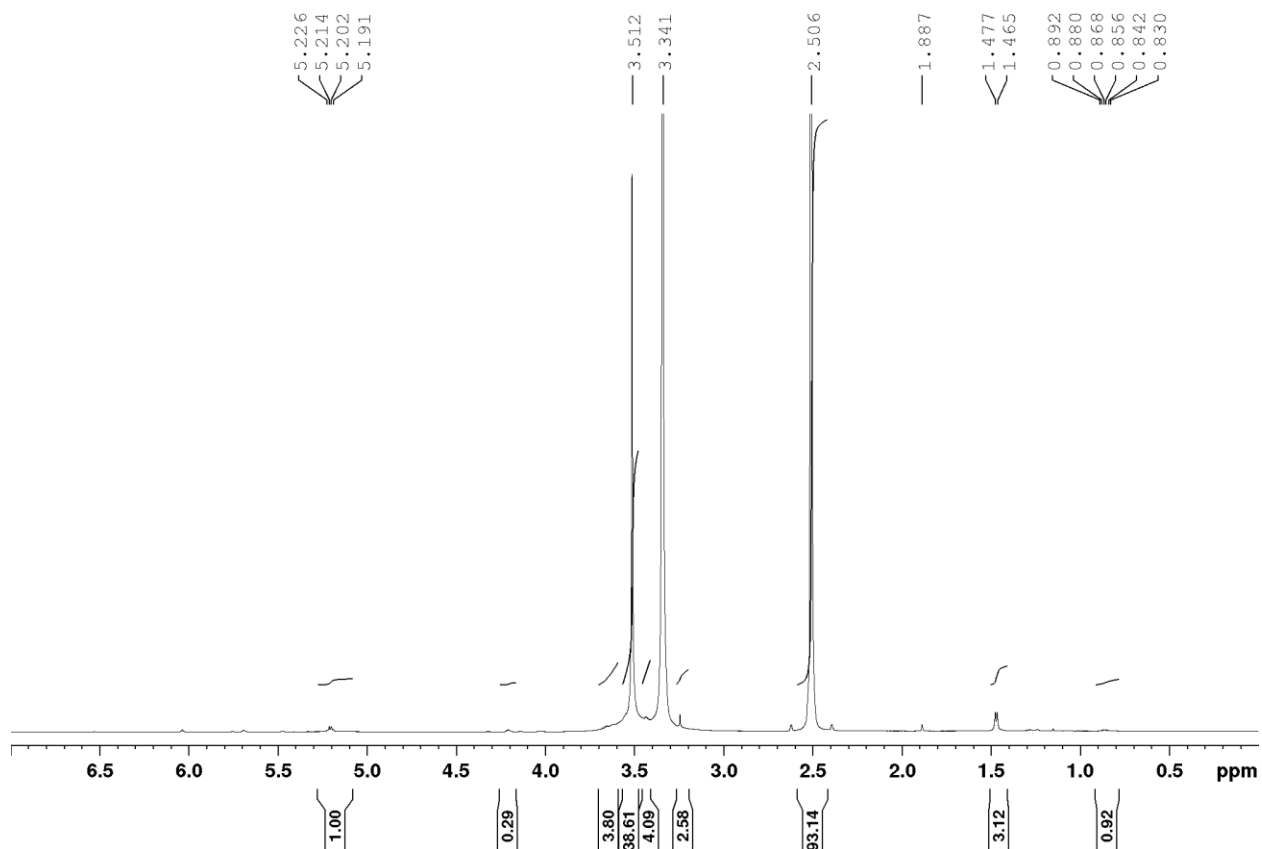*Figure S5. ^1H NMR spectrum of $P(L)LA_{10K}$ -b-$POEGMA475_{10K}$ in deuterated DMSO*

Figure S6. ^1H NMR spectrum of P(L)LA$_{10K}$-b-POEGMA2000$_{10K}$ in deuterated DMSO

Table S1. Ratio of ethylene oxide (EO) repeat units:lactic acid (LA) repeat units from ^1H NMR analysis and corresponding estimate of molecular weight of the POEGMA block (PLA block = 10 kDa as per macroinitiator manufacturer specifications)

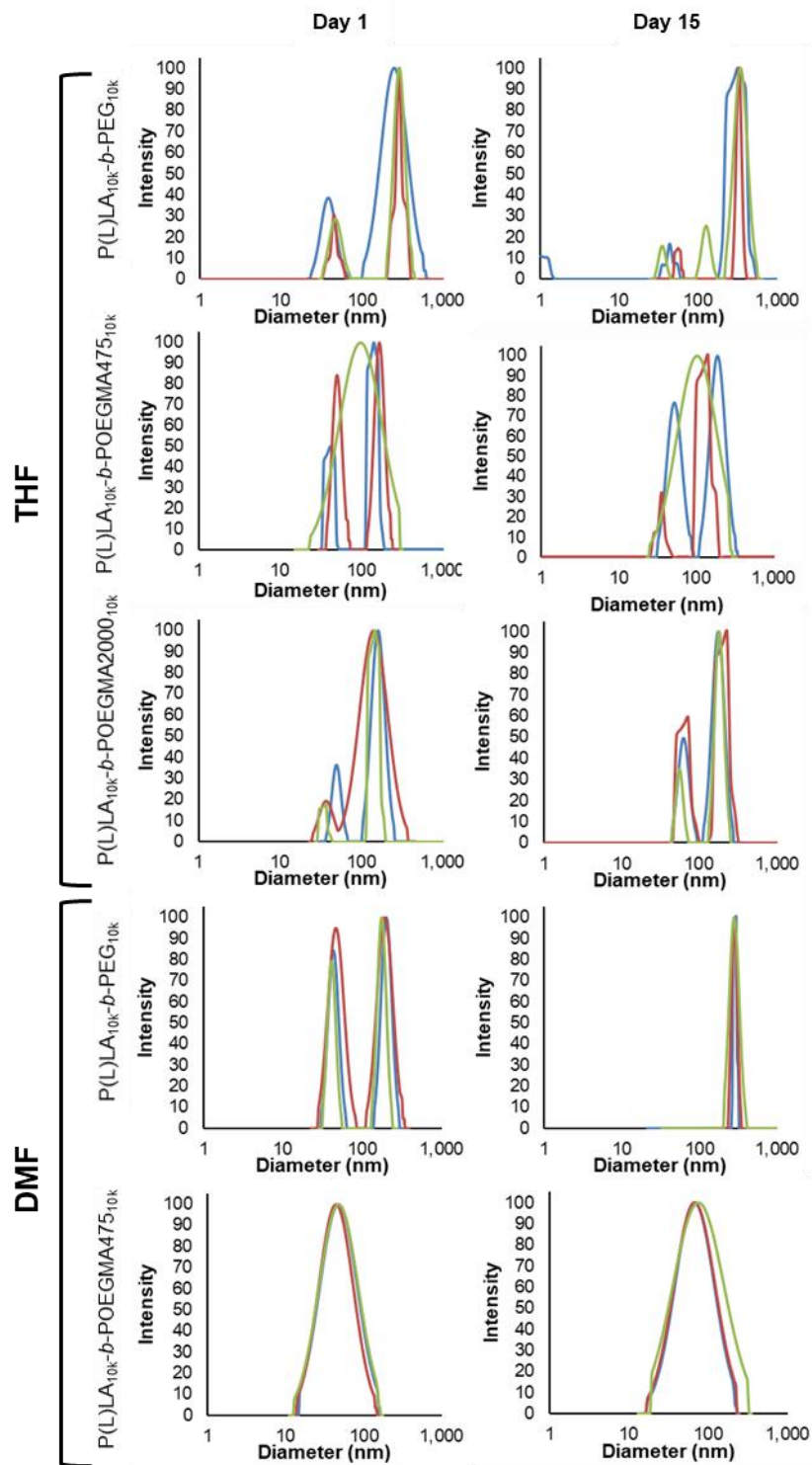| Polymer	LA:EO signal intensity	M$_n$ of PEG/POEGMA block
P(L)LA$_{10K}$-b-PEG$_{10K}$	1:6.2	9300
P(L)LA$_{10K}$-b-POEGMA475$_{10K}$	1:32	45700
P(L)LA$_{10K}$-b-POEGMA2000$_{10K}$	1:39	45900

Figure S7. Raw intensity DLS traces of linear and comb block copolymer-based nanoparticles fabricated using THF or DMF
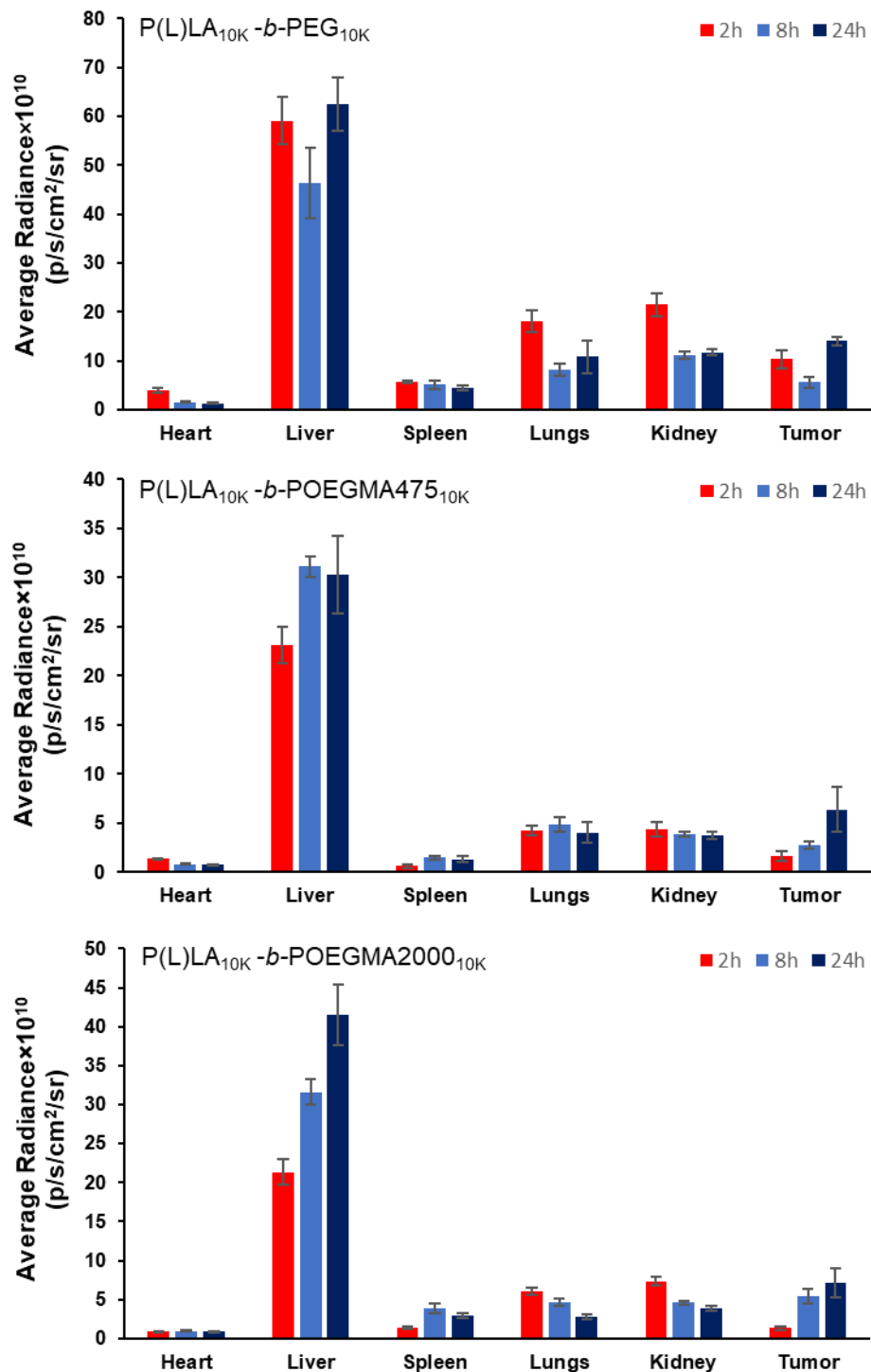
Figure S8. Radiance measurements from IVIS ex vivo organ imaging reflecting the biodistribution of polymer nanoparticles in whole organs of BALB/c mice implanted with CT26 tumors (n = 5 animals per group, data points represent the mean values, error bars represent the standard deviation)
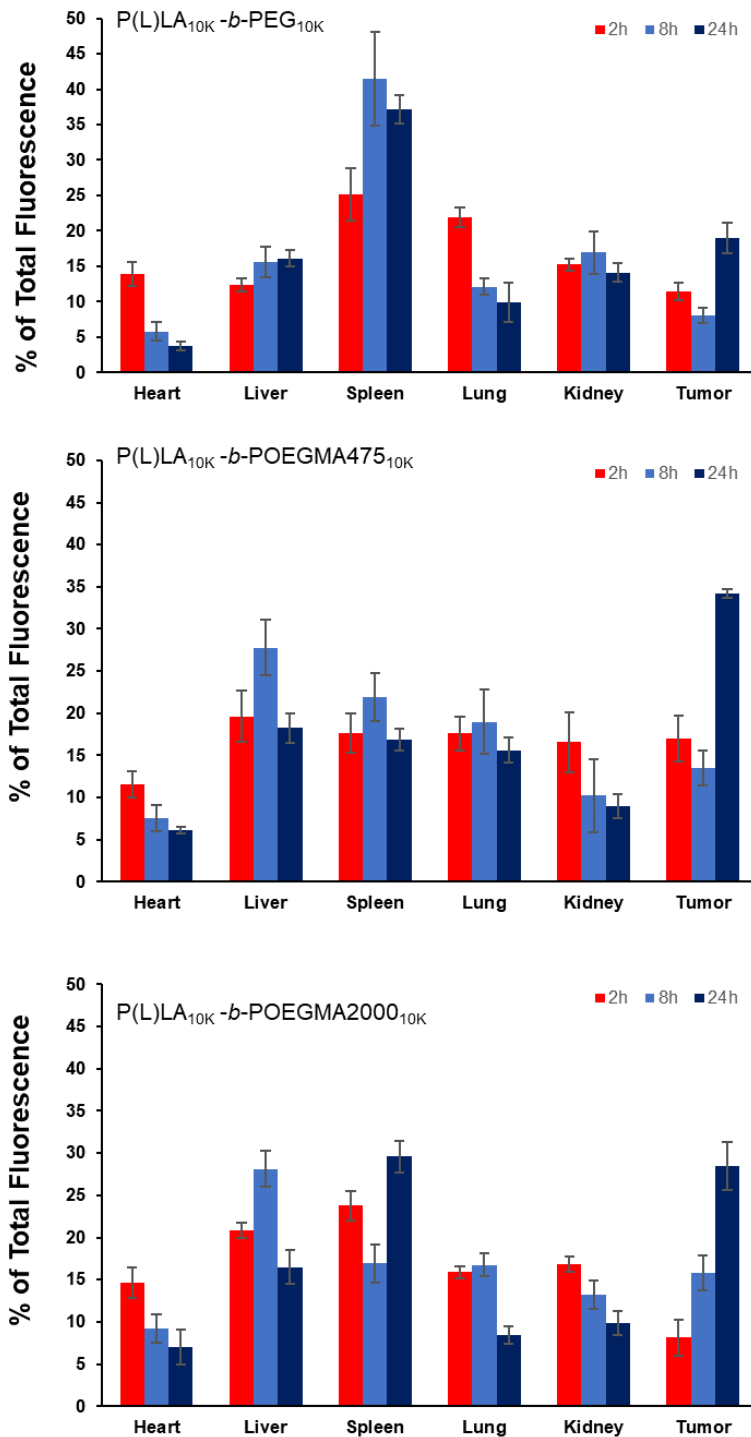
Figure S9. Biodistribution of Cy5-labeled polymer nanoparticles in ground organs of BALB/c mice implanted with CT26 tumors as a function of time post-injection measured as a percentage of total fluorescence (n = 5 animals per group, data points represent the mean values, error bars represent the standard deviation)