Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

SUPPLEMENTARY DATA

Size effects of self-assembled block copolymers spherical micelles and vesicle on cellular uptake in human colon carcinoma cells

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Table S1: Summary of results of the homopolymerization of POEGMEMA in toluene at 70˚C in the presence of CPADB RAFT at a ratio of 1:100.

Polymerization Time (h)	Conversion* (%)	M_n (Theo) g/mol	M_n (GPC) g/mol	PDI
1.5	13	4180	3580	1.20
2	20	6280	9600	1.23
5	42	12880	14200	1.19
8	57	17380	19500	1.12

* The monomer conversion was calculated from the ^{1}H NMR of the reaction mixture as seen in Figure S1. The theoretical molecular weight was calculated from linear relationship between molecular weight and conversion by Equation 2

$$M_n = ([M]_O/[RAFT]_O) * x * Mw_{monomer} + Mw_{RAFT} \quad \text{(Eq 2)}$$

where

$[M]_O$ = Monomer Concentration
[RAFT]o) = RAFT Agent Concentration
X = Monomer Conversion
$Mw_{monomer}$ = Molecular Weight of Monomer
Mw_{RAFT} = Molecular Weight of RAFT Agent

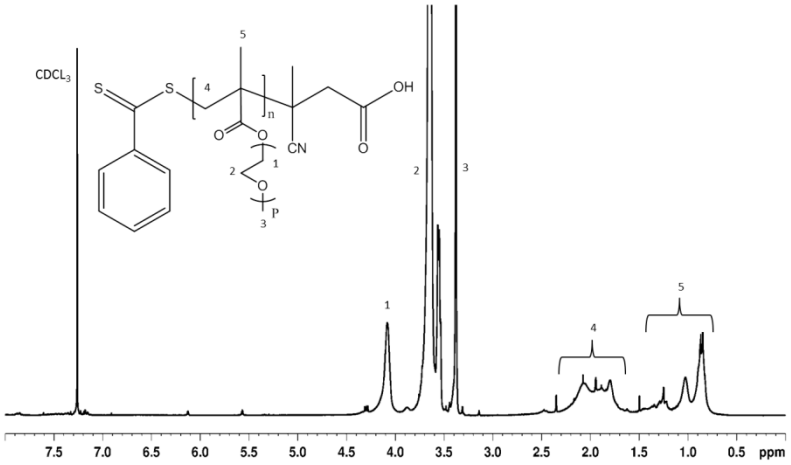


Figure S1: ^{1}H NMR spectroscopy of the "marcoRAFT" from the hydrophilic monomer POEGMEMA and RAFT agent CPADB.

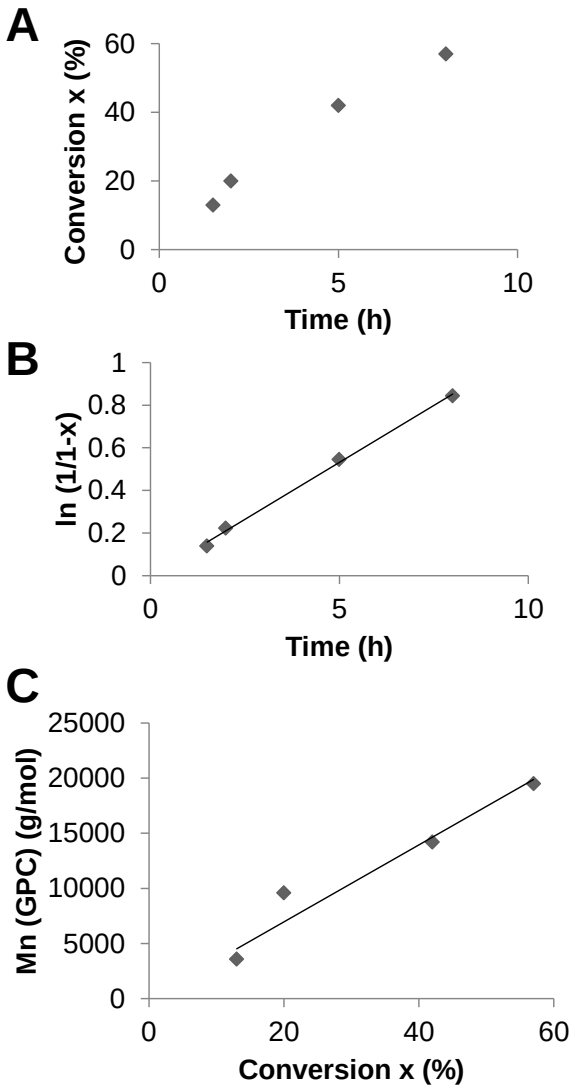


Figure S2: RAFT polymerization of POEGMEMA using CPADB RAFT in toluene at 70˚C ([M] : [RAFT] : [AIBN] = 100 : 1 : 0.2). (A) Monomer conversion at different time intervals (B)A pseudo-first-order kinetic plot for the homopolymerization (C) Molecular Weight M_n as obtained by DMAc GPC.

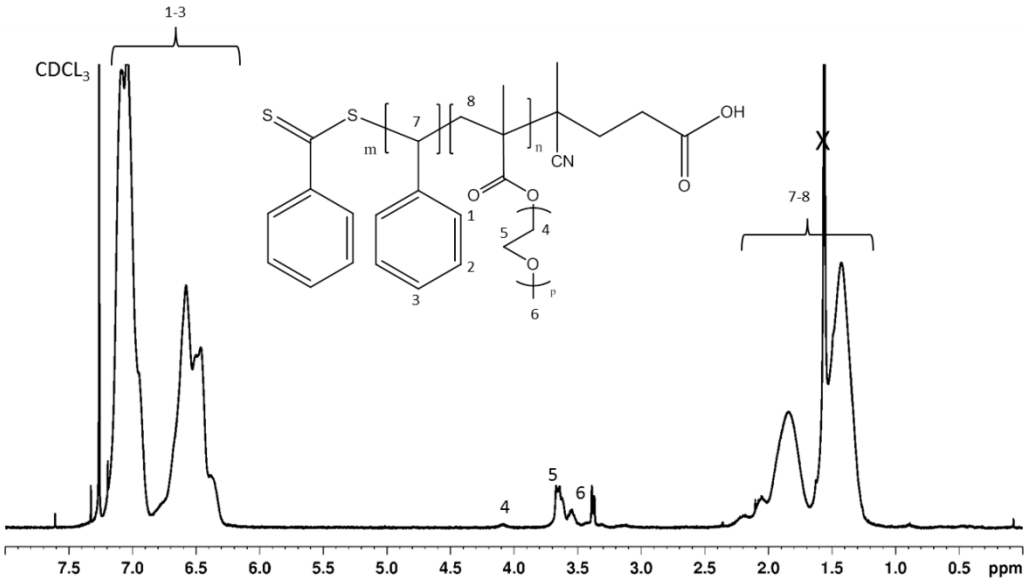


Figure S3: ^{1}H NMR spectroscopy of the block copolymer from the hydrophobic monomer styrene and the marcoRAFT.

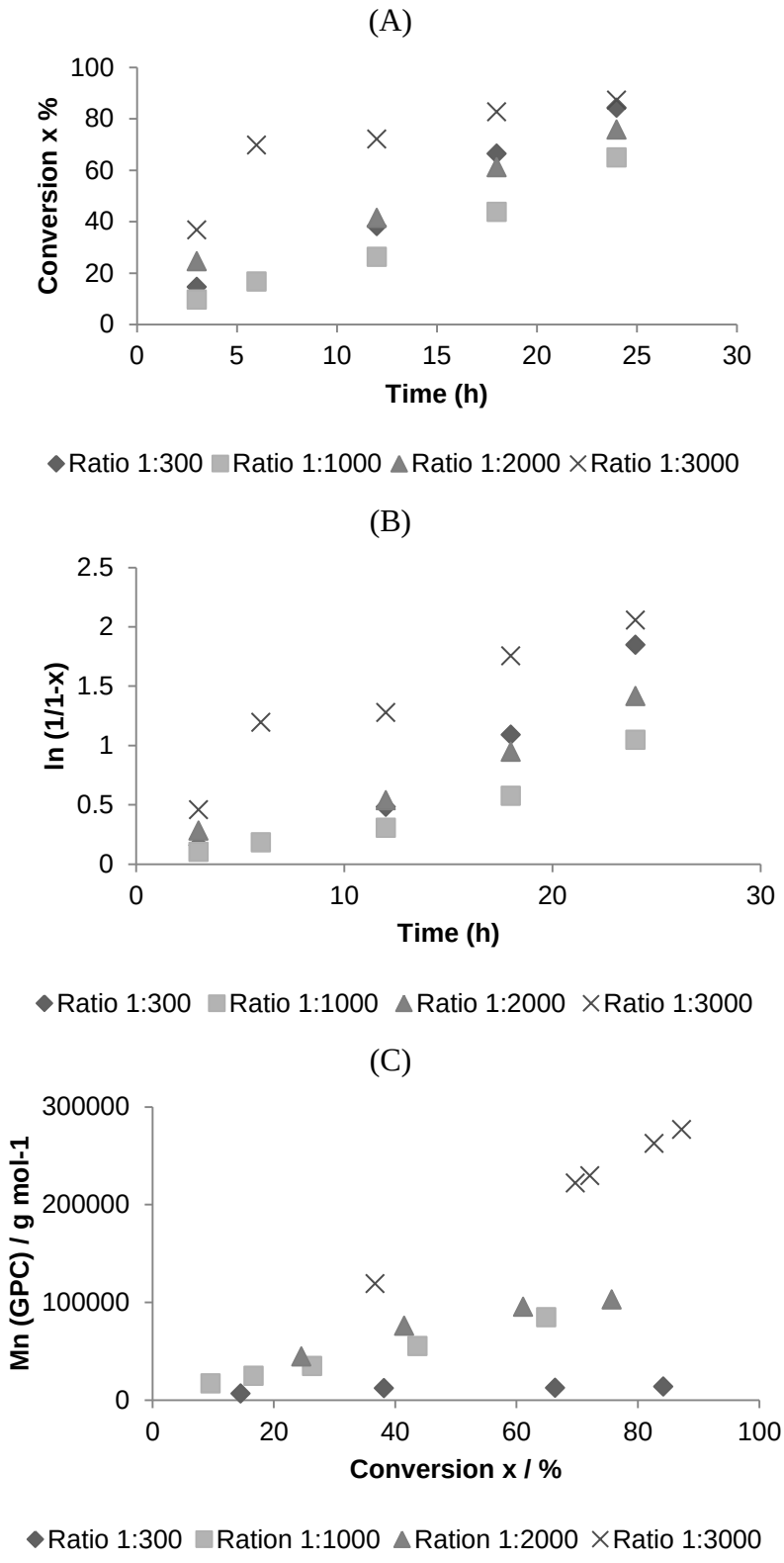


Figure S4: (A) Time vs. monomer conversion, (B) pseudo-first order kinetic plot, (C) and Mn vs. monomer conversion of the polymerization of styrene in the presence of POEGMEMA macroRAFT agent (Mn(theo)=3879.38 g mol^{-1}) in toluene at 70˚C ([POEGMEMA macroRAFT] : [Styrene] : [AIBN] =1 : 300-3000 : 0.1).

Table S3: Molecular weight and conversion of the copolymerization of styrene in the presence of POEGMEMA macroRAFT (Mn(theo) = 3879.38 g mol^{-1}, PDI = 1.20) at 100°C in bulk where RU=repeating units. (A) [styrene] = 7.67 mol L^{-1}, [POEGMEMA macroRAFT] = 2.54×10^{-2} mol L^{-1}, (B) [styrene] = 8.73 mol L^{-1}, [POEGMEMA macroRAFT] = 8.73×10^{-3} mol L^{-1} , (C) [styrene] = 8.74 mol L^{-1}, [POEGMEMA macroRAFT] = 4.37×10^{-3} mol L^{-1} , (D) [styrene] = 8.72 mol L^{-1}, [POEGMEMA macroRAFT] = 2.91×10^{-3} mol L^{-1}

(A)

Polymerization Time (h)	Conversion (%)	Styrene RU	M_n (Theo)	M_n (GPC)	PDI
6	14.56	44	8400	6500	1.18
12	38.17	115	16000	12000	1.29
18	66.36	199	24600	22300	1.29
24	84.21	253	30200	26700	1.29

(B)

Polymerization Time (h)	Conversion (%)	Styrene RU	M_n (Theo)	M_n (GPC)	PDI
3	9.6	96	14200	17000	1.31
6	16.7	167	21600	24800	1.32
12	26.3	263	31600	34800	1.31
18	43.7	437	49700	55000	1.38
24	64.9	649	71800	84500	1.41

(C)

Polymerization Time (h)	Conversion (%)	Styrene RU	M_n (Theo)	M_n (GPC)	PDI
6	24.53	490	51000	44300	1.27
12	41.47	829	86200	75800	1.40
18	61.12	1222	127000	95500	1.57
24	75.72	1514	157000	102800	1.65

(D)

Polymerization Time (h)	Conversion (%)	Styrene RU	M_n (Theo)	M_n (GPC)	PDI
3	36.7	1101	166000	183000	1.44
6	69.7	2091	222000	219000	1.77
12	72.1	2163	229000	193000	1.65
18	82.7	2481	263000	232000	1.54
24	87.2	2616	277000	245000	1.52

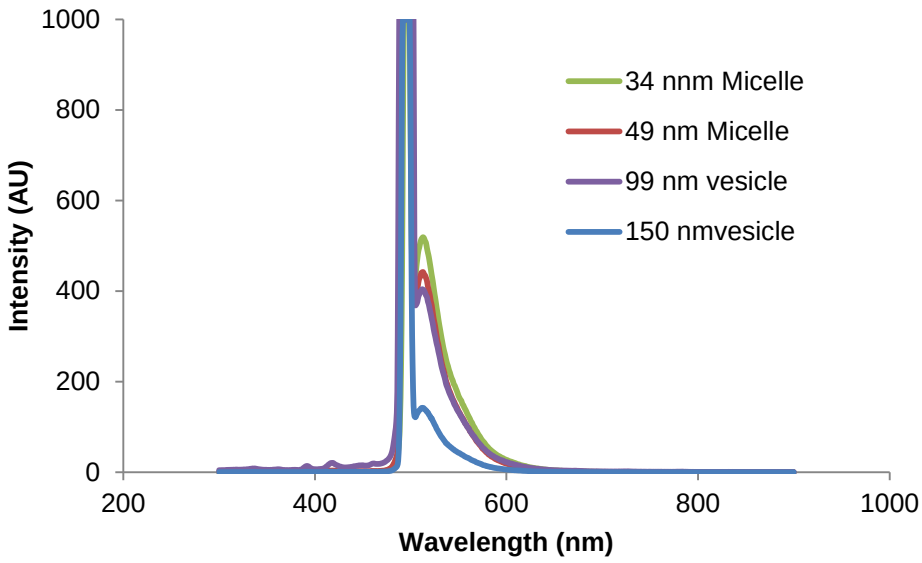
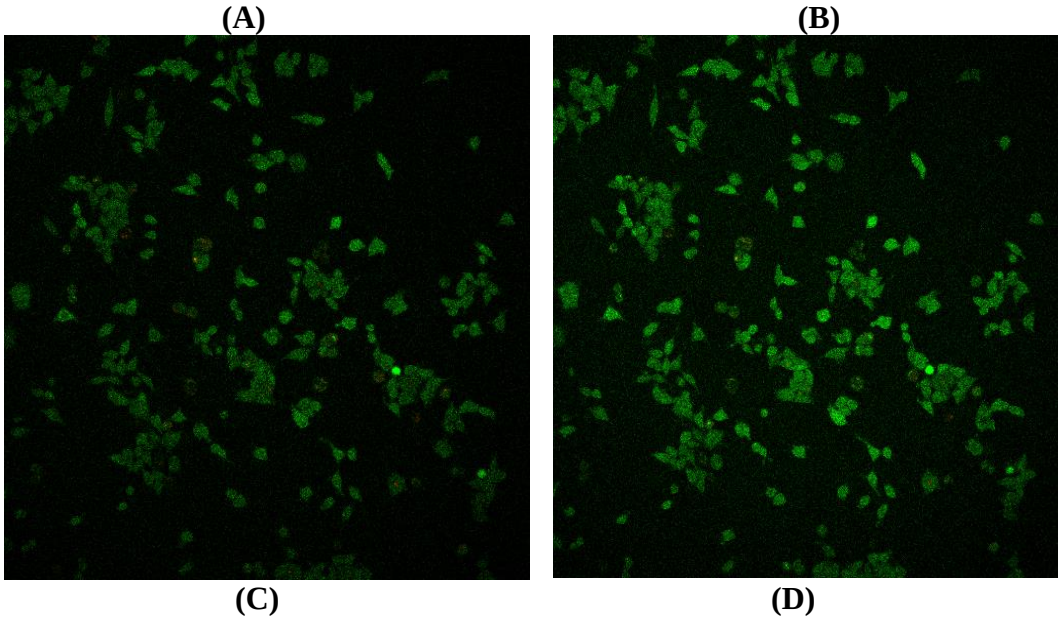


Figure S5: Fluorescence intensities of 150nm vesicles of polymers.



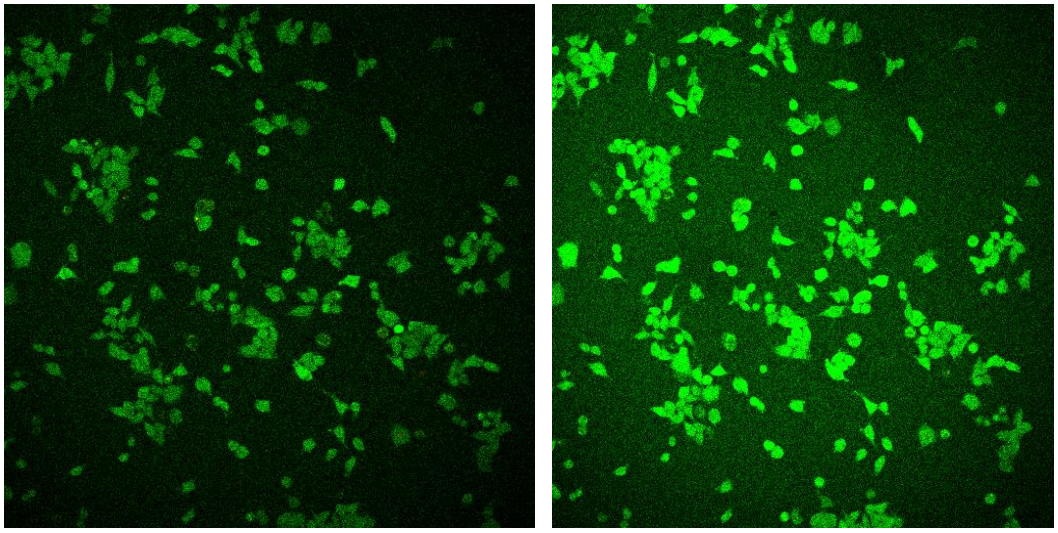


Figure S6: The green emissions within the cells are a result of the polymer uptake. The yellow is the overlap of the green aggregates and the red lysosomes. The polymers are internalized immediately and continue to enter the cell over time. A) 2 minutes, B) 10 minutes, C) 30 minutes, D) 120 minutes