Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and Micellization of Redox-Responsive Dynamic Covalent Multi-block Copolymers

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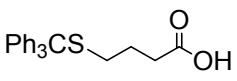
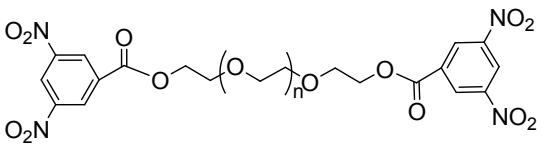
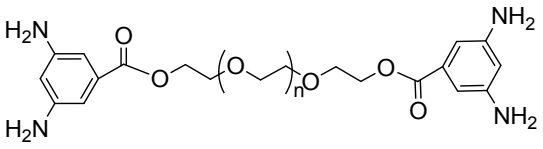
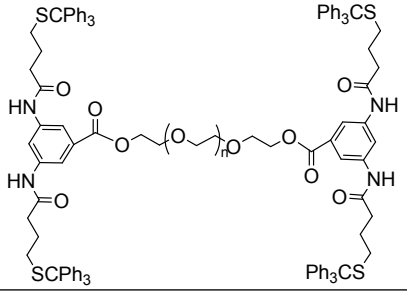
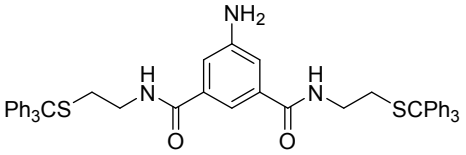
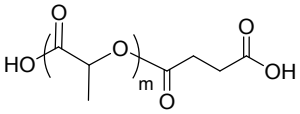
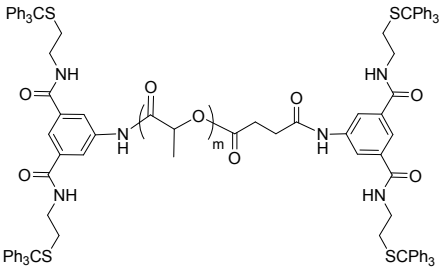
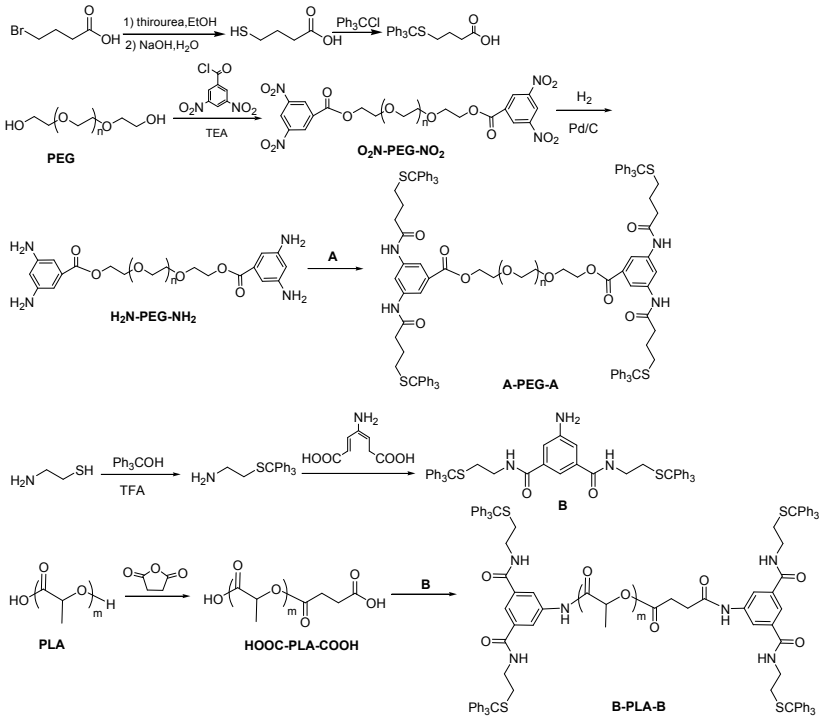
List of abbreviations

Abbreviations		Full Name
Measures	NMR	Nuclear Magnetic Resonance
	GPC	Gel Permeation Chromatography
	DLS	Dynamic Light Scattering
	TLC	Thin-Layer Chromatography
	MTT	3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2-H-tetrazolium bromide
	CMC	Critical Micelle Concentration
	DLC	Drug Loading Content
	DLE	Drug Loading Efficiency
	PDI	Polydispersity Index
	MWCO	Molecular Weight Cut Off
Reagents	PEG	Polyethylene glycol
	PLA	Polylactic acid
	DOX	Doxorubicin
	GSH	Glutathione
	BSO	Buthionine Sulfoxide
	DMF	N,N-dimethylformamide
	DMSO	Dimethyl Sulfoxide
	DCM	Dichloromethane
	THF	Tetrahydrofuran
	HATU	2-(7-Aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
	NMM	N-methylmorpholine
	DMAP	4-dimethylamiopryidine
	DPH	1,6-diphenylhexa-1,3,5-triene
	TEA	Triethylamine
	PBS	Phosphate Buffered Saline
	DTT	DL-Dithiothreitol
	DMEM	Dulbecco's modified Eagle's medium
	FBS	Fetal Bovine Serum
Abbreviations		**Structures**
Intermediates	strand A	
	O_2N-PEG-NO_2	

	H_2N-PEG-NH_2	
	A-PEG-A	
	strand B	
	HOOC-PLA-COOH	
	B-PLA-B	



Scheme S1. Synthetic route of the end-modified polymer **A-PEG-A** and **B-PLA-B**

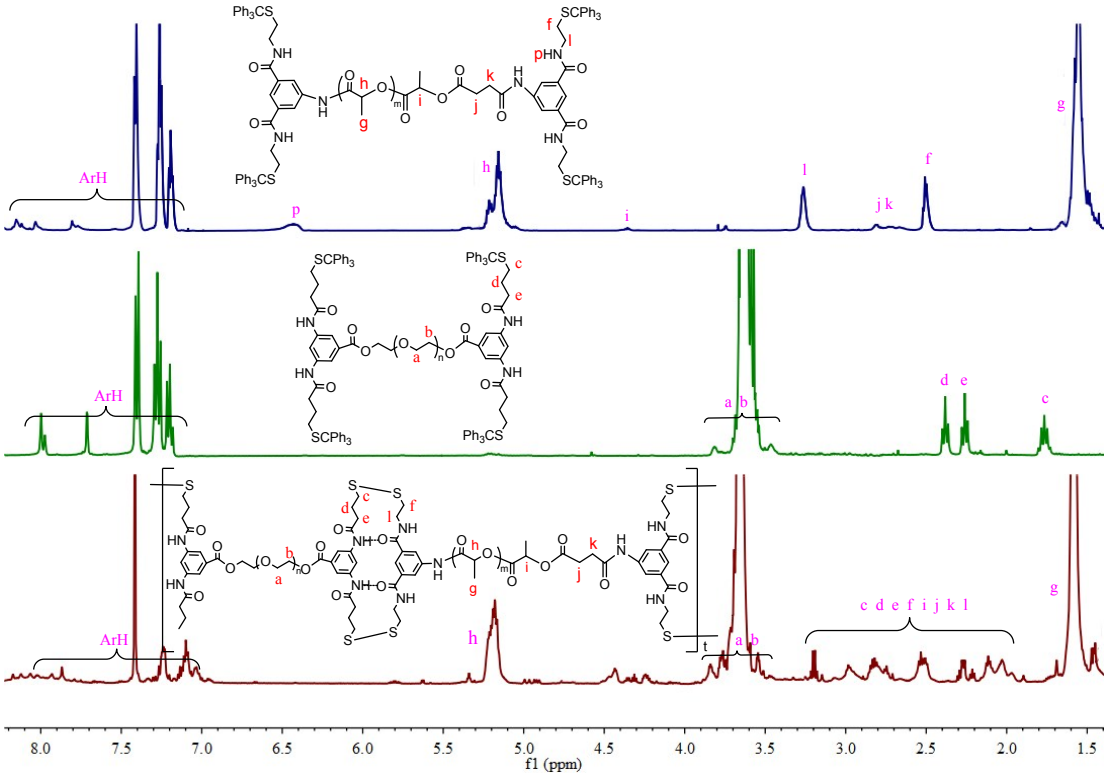


Figure S1. ^{1}H-NMR (400 MHz) spectra of B-PLA$_{3000}$-B, A-PEG$_{4000}$-A and [PLA$_{3000}$-PEG$_{4000}$]$_t$ in $CDCl_3$.

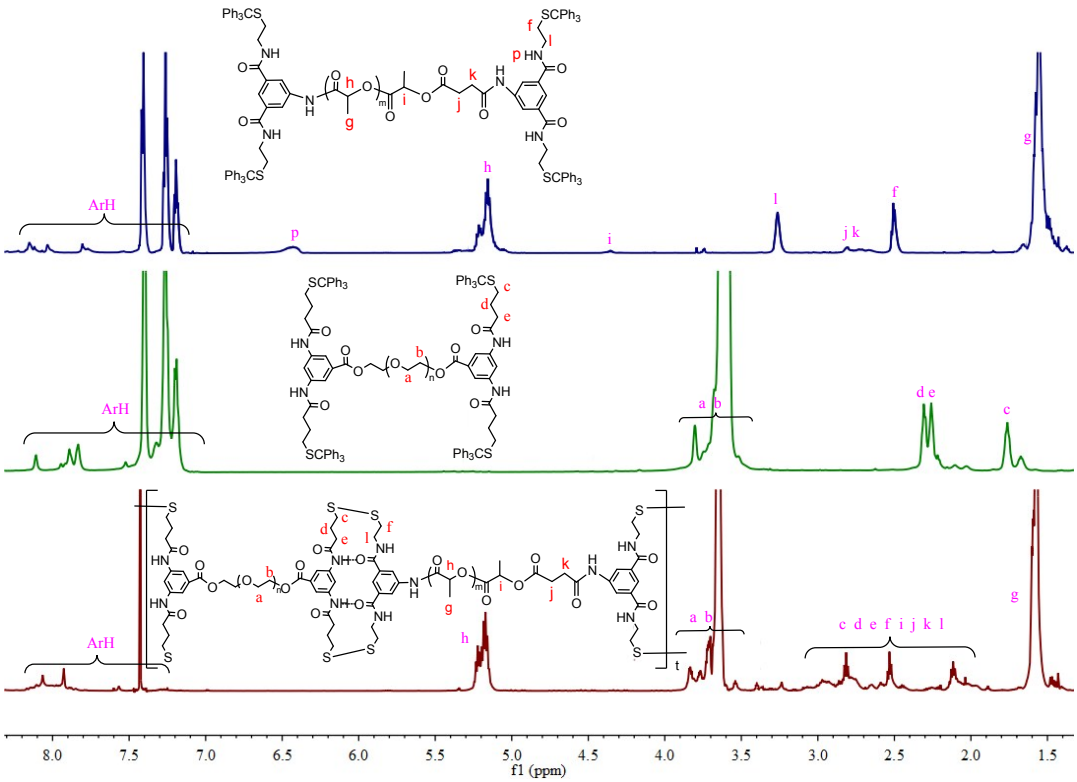


Figure S2. ^{1}H-NMR (400 MHz) spectra of B-PLA$_{3000}$-B, A-PEG$_{2000}$-A and [PLA$_{3000}$-PEG$_{2000}$]$_t$ in $CDCl_3$

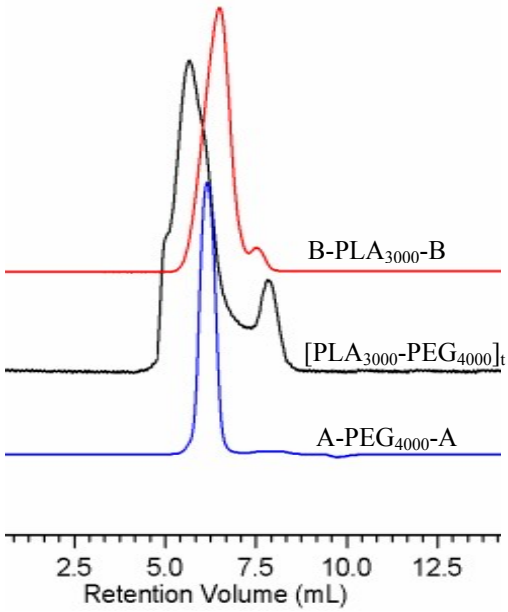


Figure S3. Gel permeation chromatography (GPC) traces of **B-PLA$_{3000}$-B**, **[PLA$_{3000}$-PEG$_{4000}$]$_t$** and **A-PEG$_{4000}$-A**

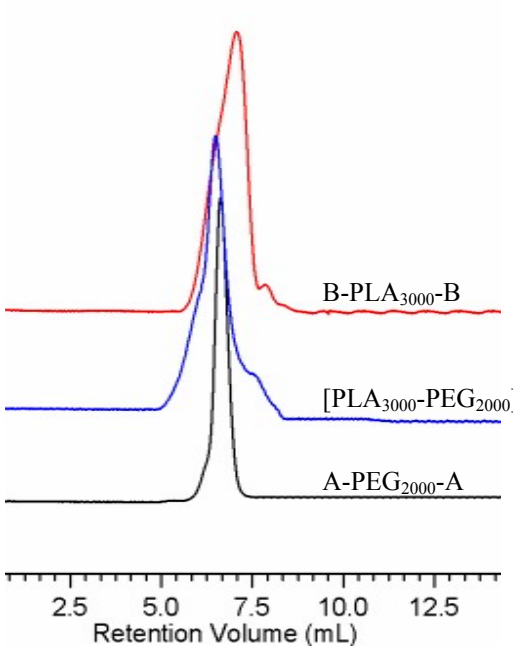


Figure S4. Gel permeation chromatography (GPC) traces of **B-PLA$_{3000}$-B**, **[PLA$_{3000}$-PEG$_{2000}$]$_t$** and **A-PEG$_{2000}$-A**

Table S1. The block numbers of multi-block copolymers

Copolymers	M_n	PDI	Num (avg. number of blocks)
[PLA$_{5000}$-PEG$_{4000}$]$_t$	18300	1.21	4.26
[PLA$_{3000}$-PEG$_{4000}$]$_t$	15600	1.19	4.59
[PLA$_{3000}$-PEG$_{2000}$]$_t$	9700	1.21	4.04
Estimated by GPC (THF, 1 mL/min) using polystyrene standards			

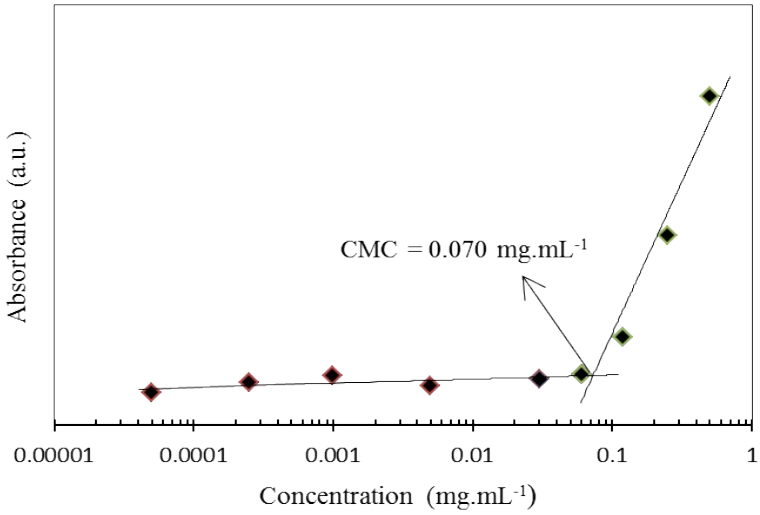


Figure S5. Relationship of the absorbance intensity of DPH as a function of the copolymer concentration of **[PLA$_{3000}$-PEG$_{4000}$]$_t$** in aqueous solution at room temperature

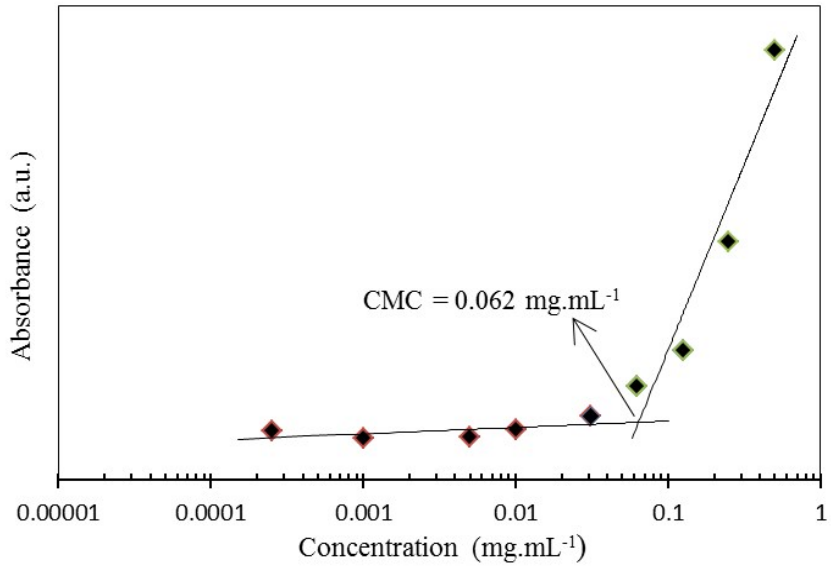


Figure S6. Relationship of the absorbance intensity of DPH as a function of the copolymer concentration of **[PLA$_{3000}$-PEG$_{2000}$]$_t$** in aqueous solution at room temperature

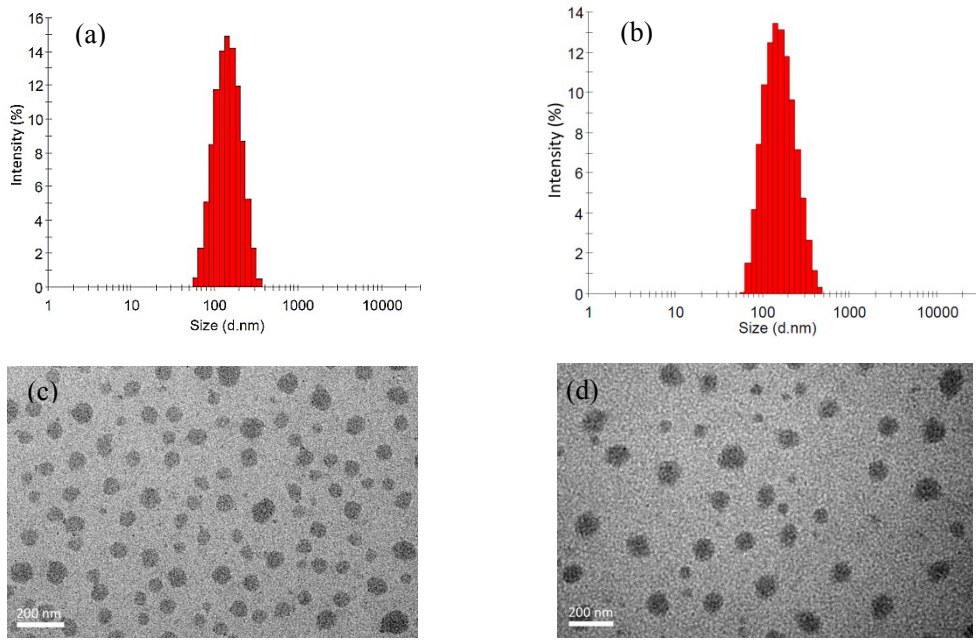


Figure S7. DLS plots and TEM images of of blank (a), (c) and DOX-loaded (b), (d) **[PLA$_{3000}$-PEG$_{4000}$]$_t$** micelle

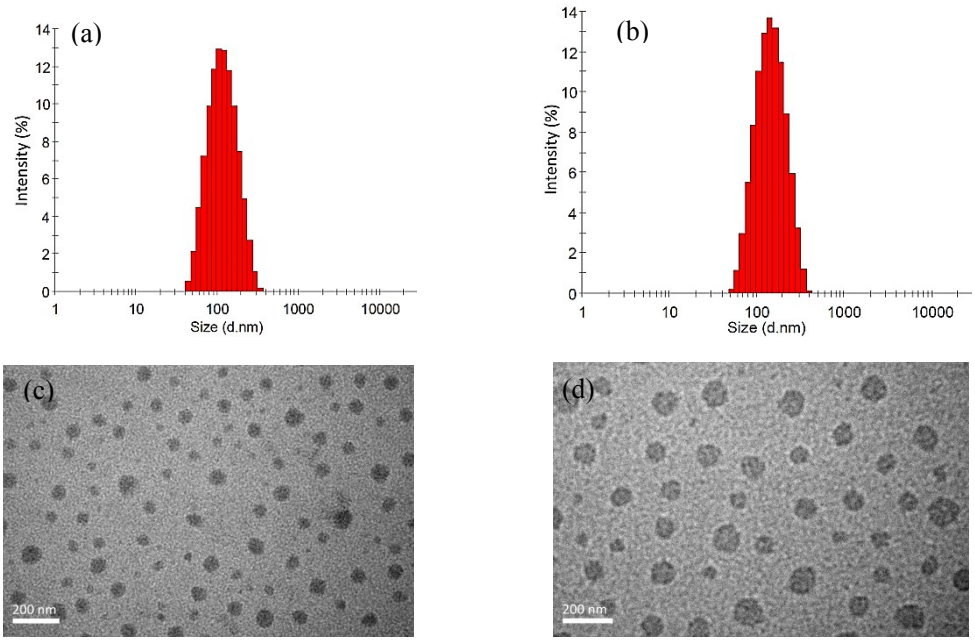
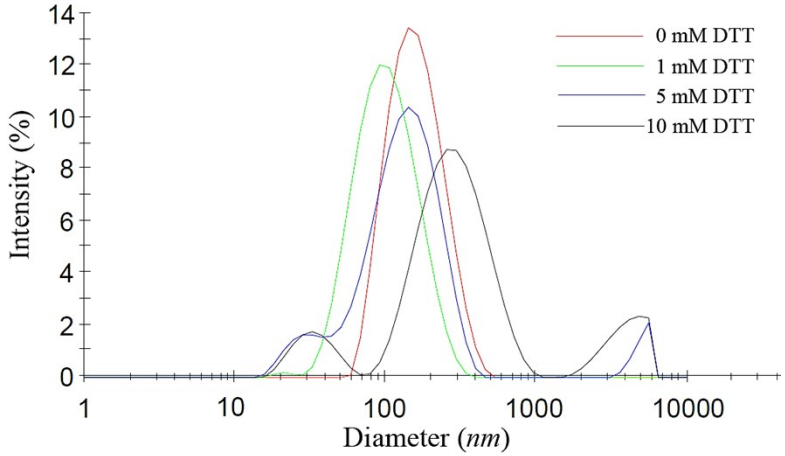
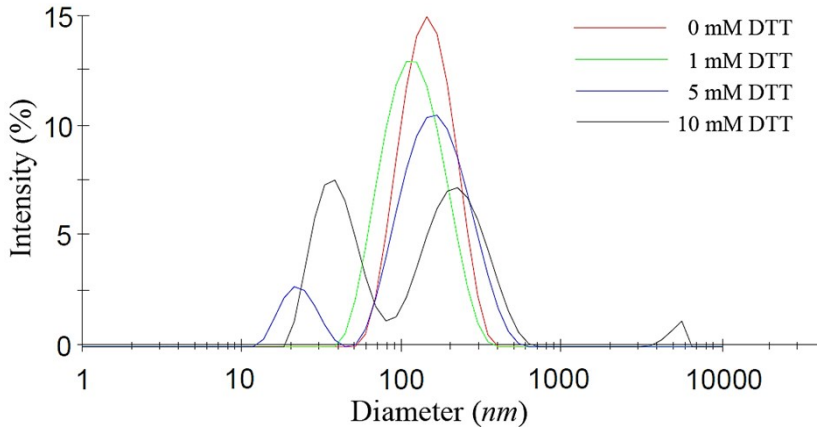


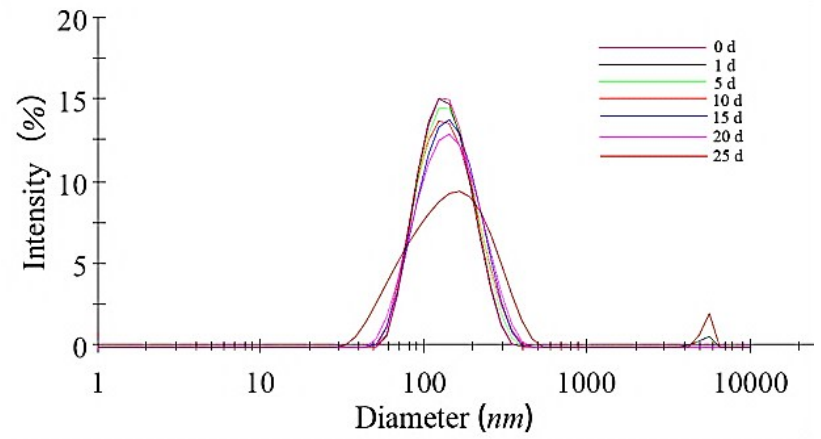
Figure S8. DLS plots and TEM images of of blank (a), (c) and DOX-loaded (b), (d) **[PLA$_{3000}$-PEG$_{2000}$]$_t$** micelle



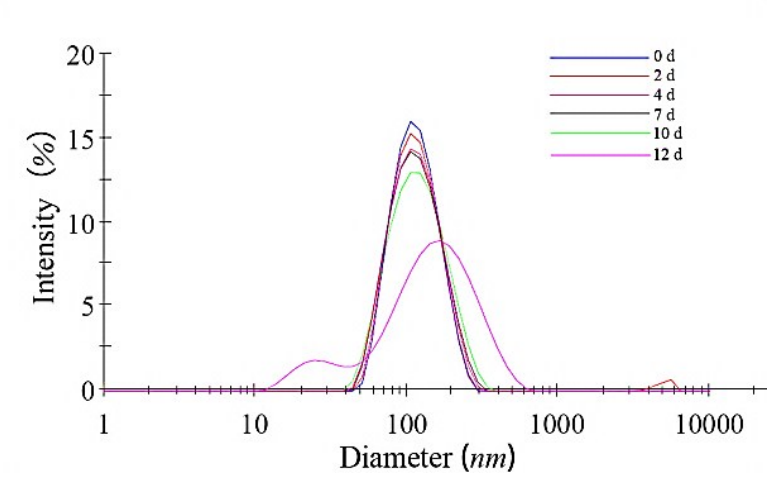
Figuer S9. DLS plot of **[PLA$_{3000}$-PEG$_{4000}$]$_t$** micelles after being incubated with 1.0 mM, 5.0 mM and 10 mM DTT for 2 h



Figuer S10. DLS plot of **[PLA$_{3000}$-PEG$_{2000}$]$_t$** micelles after being incubated with 1.0 mM, 5.0 mM and 10 mM DTT for 2 h



Figuer S11. DLS plot of size change of **[PLA$_{3000}$-PEG$_{4000}$]$_t$** micelle over time at physiological temperature 37 ^{o}C



Figuer S12. DLS plot of size change of **[PLA$_{3000}$-PEG$_{2000}$]$_t$** micelles over time at physiological temperature 37 ^{o}C

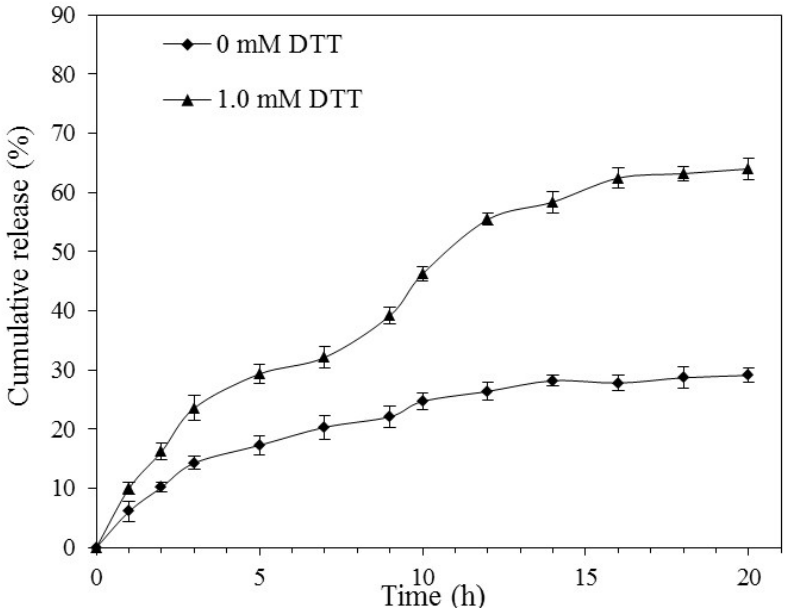


Figure S13. DOX released from DOX loaded **$[PLA_{3000}\text{-}PEG_{4000}]_t$** micelle against 1.0 mM DTT as monitored with the fluorescence intensity of DOX (EX: 485nm, EM: 590 nm)

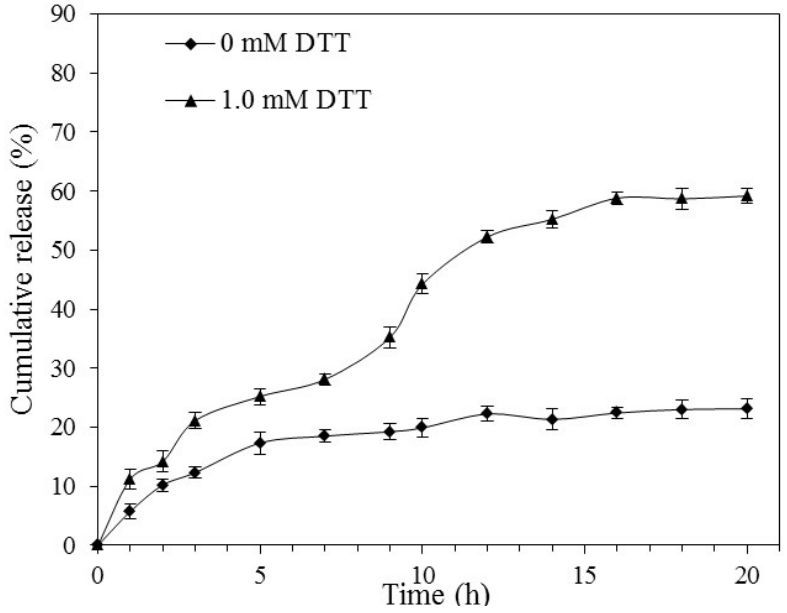


Figure S14. DOX released from DOX loaded **$[PLA_{3000}\text{-}PEG_{2000}]_t$** micelle against 1.0 mM DTT as monitored with the fluorescence intensity of DOX (EX: 485nm, EM: 590 nm)