Effects of the oppositely charged moieties on the self-assembly and biophysicochemical properties of polyurethane micelles

Zhicheng Pan^a, Guangxuan Yang^a, Jian Liu^a, Jinfeng Yuan^a, Mingwang Pan^a, Jiehua Li^{*b} and Hong Tan^{*b}

- a Hebei Key Laboratory of Functional Polymers, Department of Polymer Materials and Engineering, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China
- b College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

*Corresponding author. Fax: +86-28-85405402; Tel: +86-28-85460961 E-mail: hongtan@scu.edu.cn, jiehua_li@scu.edu.cn

samples	molar ratio						molecular weights ^a		
	LDI	PCL	mPEG	Chain Extender			Ma	M	N
				EG8	TPT	CYSD	- IVIn	MW	WW/WIN
G0T50mE1900	4	1.6	0.8	0	1	1	49054	67321	1.37
G10T40mE1900	4	1.6	0.8	0.2	0.8	1	34632	49426	1.43
G25T25mE1900	4	1.6	0.8	0.5	0.5	1	48626	85308	1.75
G40T10mE1900	4	1.6	0.8	0.8	0.2	1	30477	40560	1.33
G50T0mE1900	4	1.6	0.8	1	0	1	16570	28415	1.71
G25T25mE0	4	2	0	0.5	0.5	1	20467	33051	1.61
G25T25mE500	4	1.6	0.8	0.5	0.5	1	33347	57928	1.74
G25T25mE5000	4	1.6	0.8	0.5	0.5	1	57157	73410	1.28

Table S1. Theoretical composition and molecular weights of polyurethanes



Figure S1. a) ¹H NMR spectra with full scale and b) GPC curves for all G*x*T*y*mE*z* polyurethanes.



Figure S2. FTIR spectrum of polyurethanes with oppositely charged moieties and different chain lengths of mPEG. The absorption band 3391 cm⁻¹ is assigned to the N-H stretching vibration in the urethane structure. The absorption band from 2800~3000 belongs to the saturated carbon C-H stretching vibration. The peak of 2890 and 1110 cm⁻¹ representing the C-H and C–O–C groups, which are corresponding to the mPEG segments, are obviously stronger with the mPEG chain length increased. There is no peak around 2200 cm⁻¹ which is assigned to the N=C=O stretching vibration in LDI, indicating that LDI is completely reacted. The absorption band 1650~1750 cm⁻¹ is assigned to the carbonyl region, in which 1726 and 1650 cm⁻¹ are contributed to the carbonyl of urethane and carbonyl in urea groups, respectively.



Figure S3. Change of size distribution of G25T25mE5000 for 1 h and 24 h in PBS buffer solution with 10 mM GSH.



Figure S4. A) Drug loading content (%) and encapsulation efficiency (%) of PTX in G25T25mE5000 micelles. B) Release profile of PTX from G25T25mE5000 micelles in the presence or absence of 10 mM GSH in PBS solution.



Figure S5. Cell viability of L929 mouse fibroblasts and HeLa cells after incubation with drug free G25T25mE5000 micelles for 24 h and 72 h.



Figure S6. Cytotoxicity of G25T25mE5000 micelles against HeLa cells after 24 h and 72 h of incubation. Insets show the IC_{50} values toward HeLa cells for 72 h of incubation, the unit of IC_{50} is µg/mL.



Figure S7. CLSM images of (A) Hela cells and RAW264.7 (B) incubated with polyurethane micelles containing various oppositely charged moieties for 1 h of incubation. All the images were tested under the same conditions.



Figure S8. CLSM images of Hela and RAW 264.7 cells incubated with G25T25mE5000 for 1 h and 3 h of incubation.