Supporting Information

Biodegradable pH-sensitive polyurethane micelles with different polyethylene glycol (PEG) location for anti-cancer drug carrier applications

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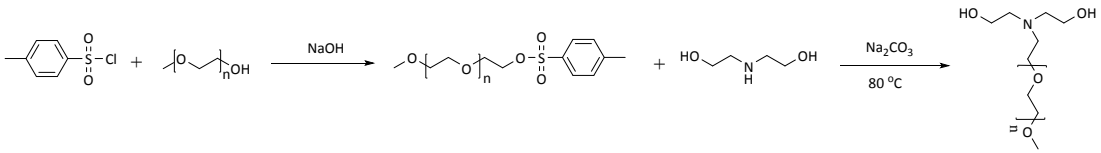
Synthesis

Scheme 1S



Preparation of $CH_3(OCH_2CH_2)_nOTs$.[1] A slurry of p-TsCl (3.813 g, 0.02mol), NaOH (1.6 g, 0.04mol) and MPEG (*M*n=1000, 1 g, 0.01 mol)was pestled in a mortar for 30 min. The mixture was poured into CH_2Cl_2 (400 mL) and the organic layer was washed with water (200 mL) and reduced to minimum volume by evaporation in vacuum. MPEG-OTs were thus prepared with at least 90% purity and were used as obtained in 92% yield.^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.75 (d, J = 8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 4.08 (t, J = 4 Hz, 2H), 3.54 (d, J = 4.4 Hz, 2H), 3.45 (m, 88H), 3.21 (s, 3H), 2.39 (s, 3H); MS (m/z): [186+44n+Na^+].

Preparation of PEGylated diethanolamine (MPEG-DEAM).[1] Diethanolamine (5.25 g, 0.05 mol) and Na_2CO_3 (2.9 g, 0.0275 mol) were placed in a three-necked, N_2-flushed flask. This mixture was held at 80 °C while the MPEG-OTs (2.32 g 0.002 mol) was added over 2 h. The reaction mixture was stirred vigorously (80 °C) for 20 h and cooled to room temperature, CH_2Cl_2 (100 mL) was added, and the salts were filtered and then washed with additional CH_2Cl_2 (150 mL). The CH_2Cl_2 was evaporated in vacuo. The crude MPEG-DEAM thus obtained and

was purified by Column chromatography (DCM /MeOH=20/1) to afford MPEG-DEAM as a white powder (1.31 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.8-3.5 (m, 93H), 3.01 (s, 2H), 2.96 (s, 4H); MS (m/z): [119+44n+H^+].

Supplemental Figures

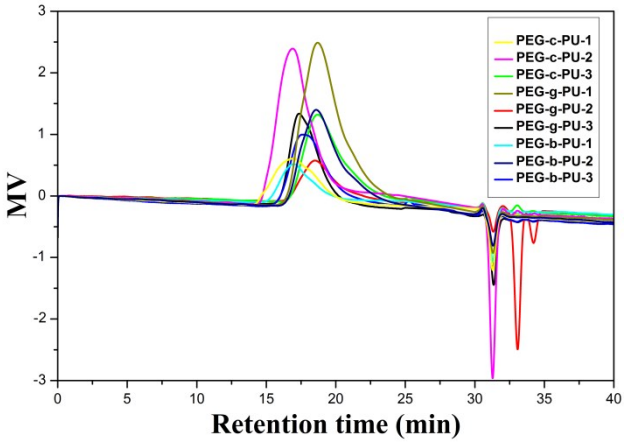


Fig. S1 GPC curves of purified PU

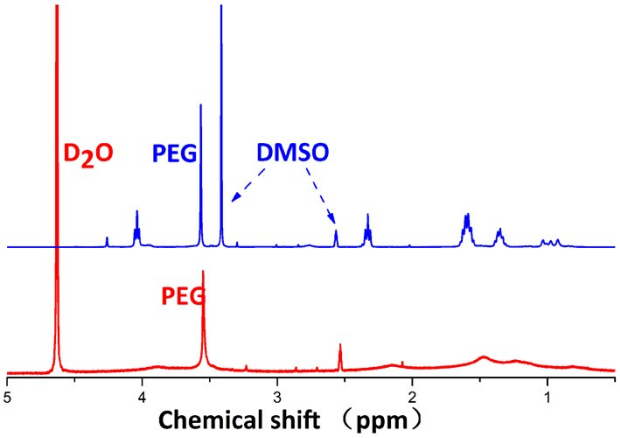


Fig. S2 ^{1}H NMR spectra of pH-sensitive polyurethane in DMSO-d_6 and its micelles in D_2O

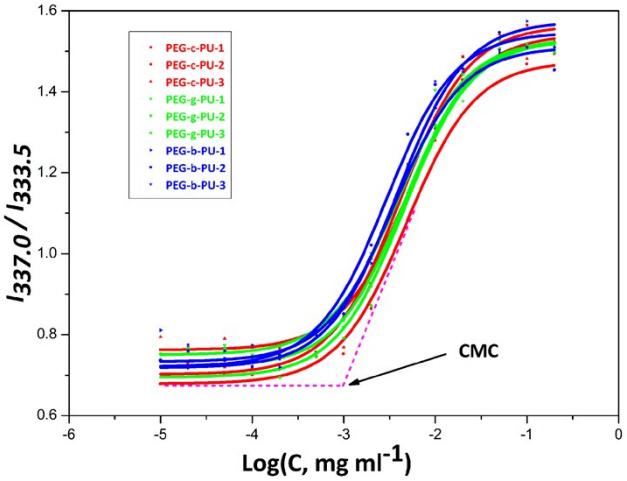


Fig. S3 $I_{337.0}/I_{333.5}$ ratios in the excitation spectra as a function of micellar concentrations (Log C), the CMCs are obtained from the intersection of the two tangent lines shown by the arrows.

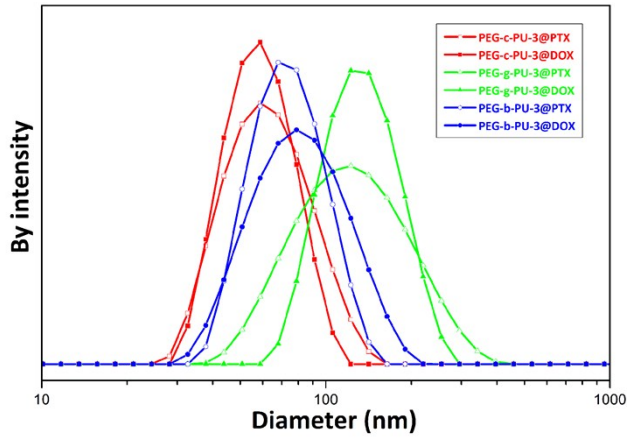


Fig. S4 Size distribution of pH-sensitive polyurethanes determined by DLS

1. R. A. Schultz, B. D. White, D. M. Dishong, K. A. Arnold and G. W. Gokel, *Journal of the American Chemical Society*, 1985, **107**, 6659-6668.