Supporting Information

Dual location disulfide degradable interlayer-crosslinked micelles with extended sheddable coronas exhibiting enhanced colloidal stability and rapid release

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Figure S1. First-order kinetic plot for ARGET ATRP of OEOMA initiated with PLA-ss-PHMssEt-Br macroinitiator in the presence of $CuBr_2$/TPMA complex in anisole at 40 °C. Conditions: $[OEOMA]_0/[$ PLA-ss-PHMssEt-Br$]_0/[CuBr_2]_0/[TPMA]_0/[Sn(Oct)_2]_0 = 100/1/0.05/0.15/0.4$; OEOMA/anisole = 0.16/1 wt/wt. The straight dotted lines are linear fits in (a) and the theoretically predicted molecular weight over conversion in (b).
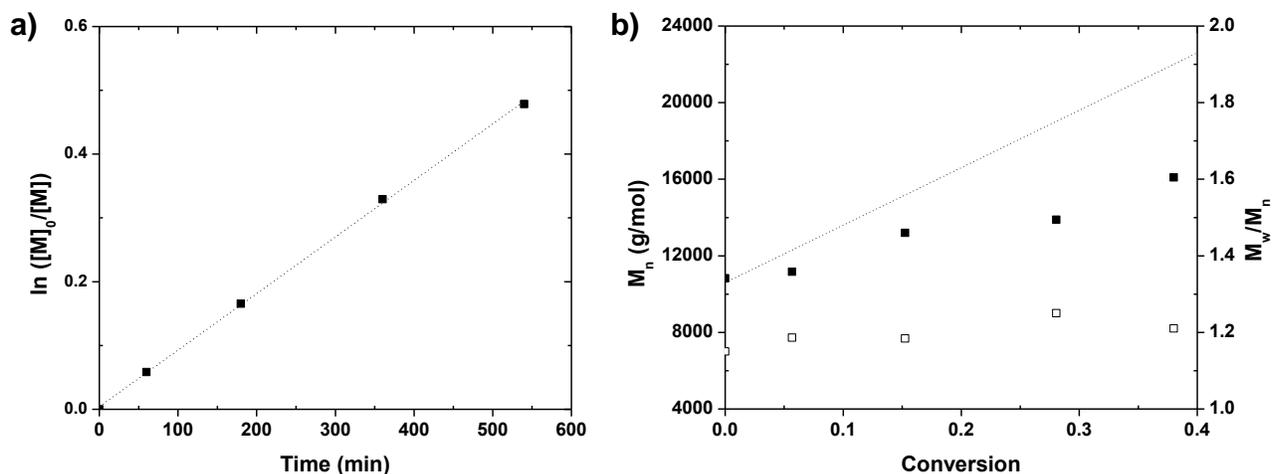
Synthesis of PHMssEt homopolymer using ARGET ATRP.
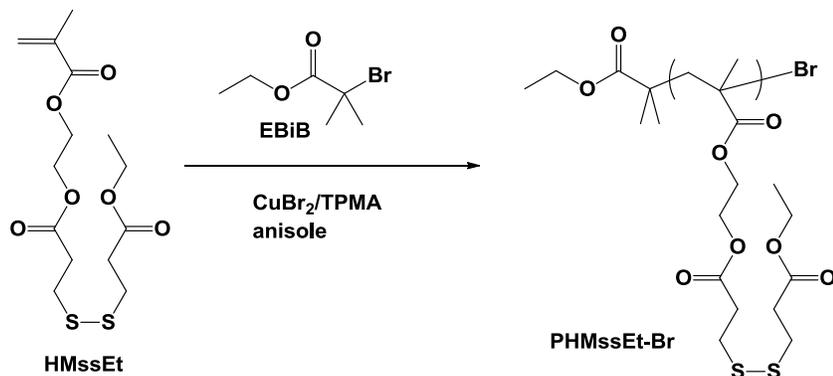
PHMssEt homopolymer was synthesized by ARGET ATRP of HMssEt in anisole at 40 °C mediated by a CuBr$_2$/TPMA complex. Ethyl 2-bromoisobutyrate (6.95 mg, 0.036 mmol), HMssEt (0.75 g, 2.14 mmol), TPMA (1.6 mg, 5.4 µmol), CuBr$_2$ (0.4 mg, 1.8 µmol), and anisole (3.5 g) were mixed in a 10 mL Schlenk flask. The mixture was deoxygenated by purging under nitrogen for 1 hr, and then placed in an oil bath at 40 °C. A pre-purged solution of Sn(Oct)$_2$ (5.8 mg, 14 µmol) dissolved in anisole (0.5 g) was injected into the Schlenk flask to initiate polymerization. Polymerization was stopped by cooling the reaction vessel and exposing the contents to air. The polymer solution was then diluted with acetone and passed through a column packed with alumina to remove any residual copper species. The purified solution was concentrated under rotary evaporation, and precipitated in cold hexane 3 times. The final polymer was dried under vacuum at room temperature for 18 hrs to yield PHMssEt homopolymer with M_n = 13 kg/mol and M_w/M_n = 1.21 as determined by GPC using DMF as eluent.

Figure S2. First-order kinetic plot for ARGET ATRP of HMssEt initiated with ethyl α-bromoisobutyrate (EBiB) in the presence of $CuBr_2$/TPMA complex in anisole at 40 °C. Conditions: $[HMssEt]_0/[EBiB]_0/[CuBr_2]_0/[TPMA]_0/[Sn(Oct)_2]_0 = 100/1/0.05/0.15/0.4$; HMssEt/anisole = 0.16/1 wt/wt. The straight dotted lines are linear fits in (a) and the theoretically predicted molecular weight over conversion in (b).
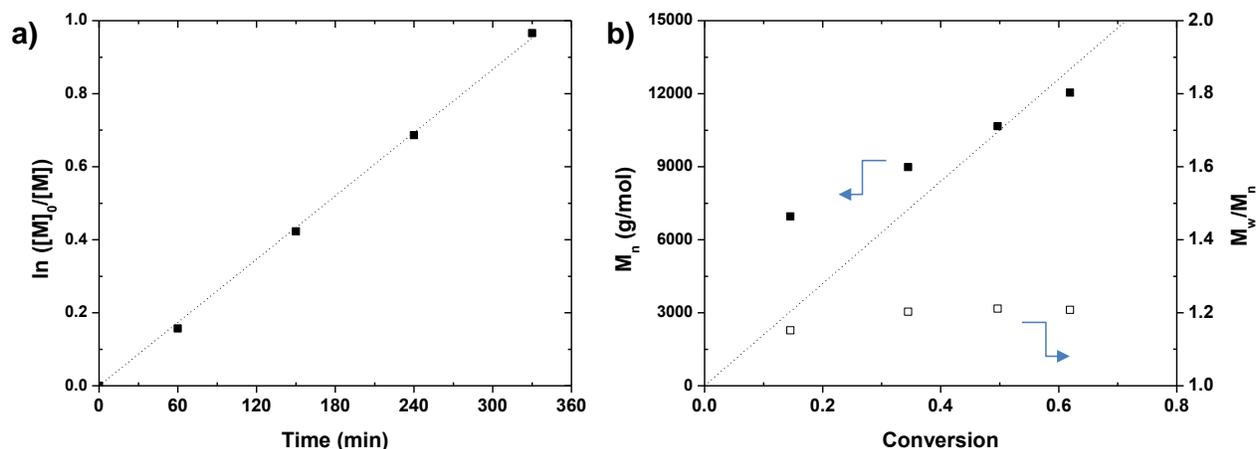
Figure S3 Peak analysis by deconvolution method for GPC trace of degraded products of PssDL in the presence of excess DTT in DMF.

Peak Analysis

Data Set:[Book4]Sheet1!B   Date:28/03/2013

BaseLine:0.

Chi^2=2.56359E-004   Adj. R-Square=9.99275E-001   # of Data Points=498.

SS=1.25360E-001   Degree of Freedom=489.

Fitting Results

Peak #	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	0.49261	0.39331	1.17874	4.00423	49.43812
2	Gaussian	0.48856	0.31231	1.46965	4.33634	49.03164
3	Gaussian	0.01525	0.06245	0.22938	4.5114	1.53024

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Figure S4. DLS diagram of NR-loaded micelles at 2.2 mg/mL in aqueous solution.

$D_n = 26 \pm 0.8$ nm
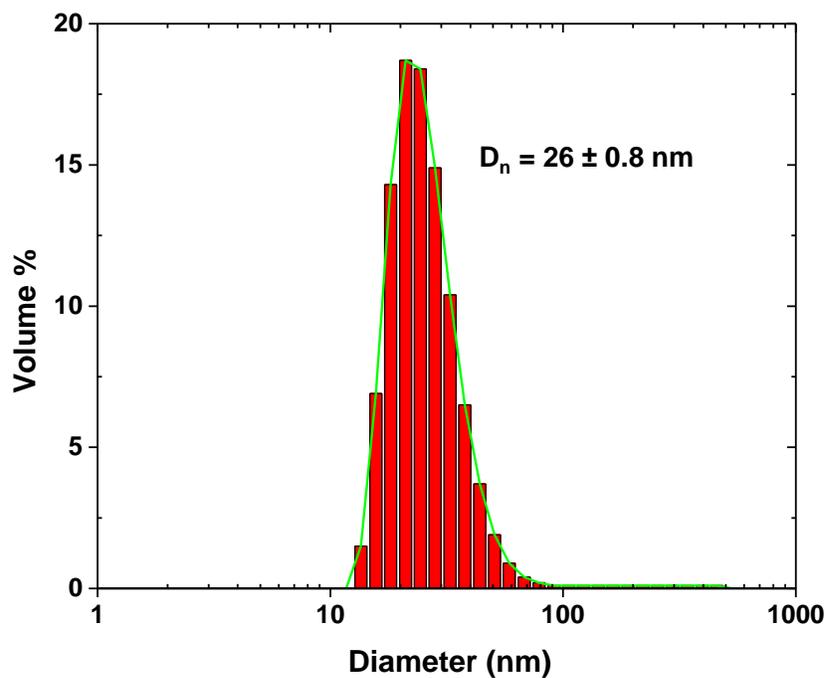
Figure S5. Overlaid fluorescence spectra of NR in mixtures of PssDL-based micelles without (a) and with (b) excess DTT in water.
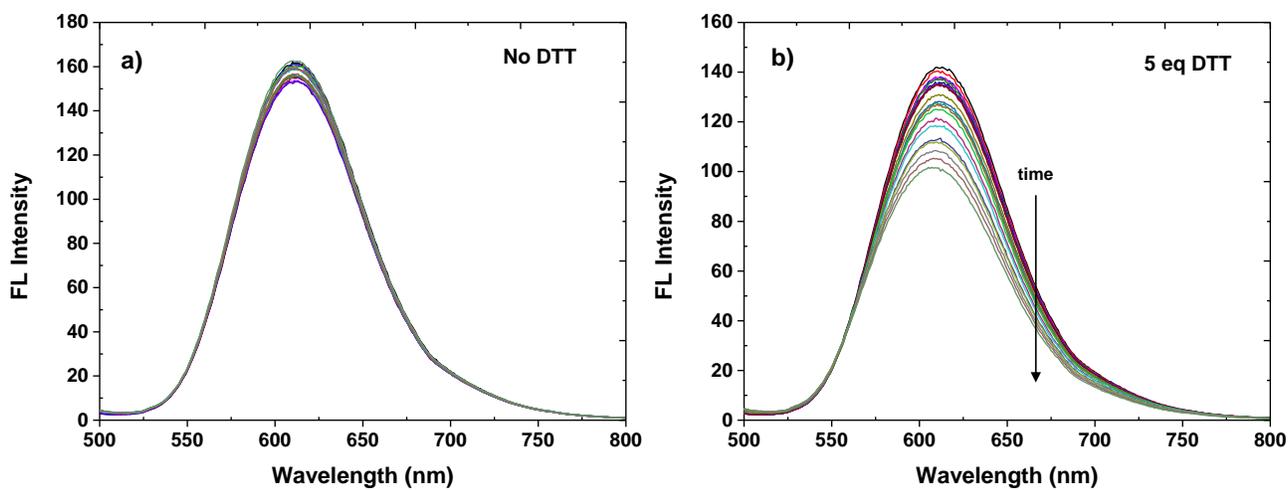
Figure S6. Overlaid UV spectra (a) and absorbance at λ_{max} = 497 nm (b) of DOX at various concentrations (µmol/L) in a mixture of DMF/water (5/1 v/v) to construct a calibration curve.
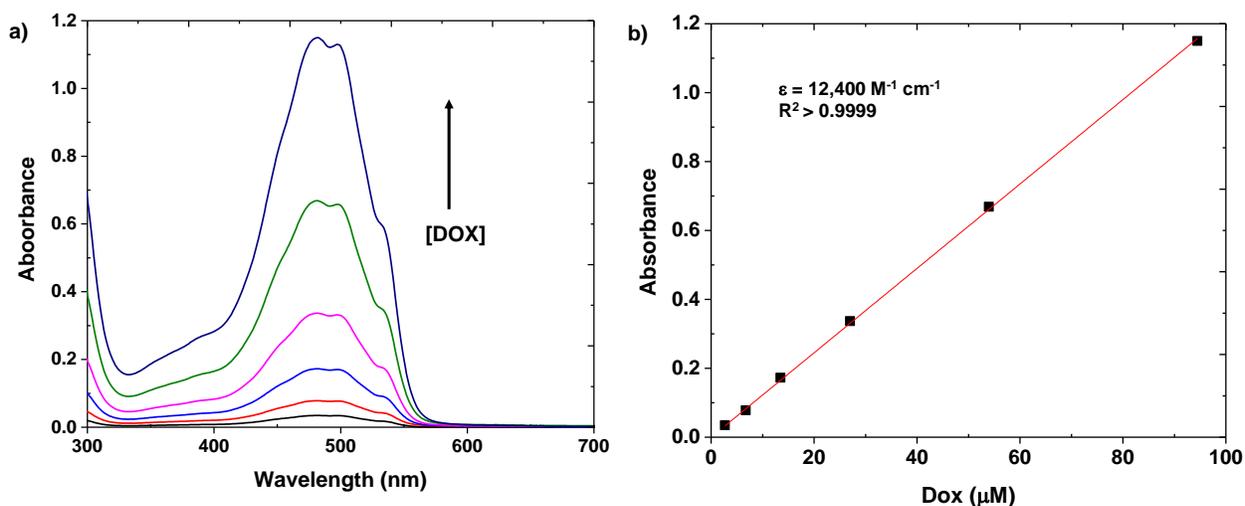
Figure S7. A typical UV/Vis spectrum of DOX-loaded PssDL-micelles in a mixture of DMF/water (5/1 v/v).