

Biodegradable multiblock polyurethane micelles with tunable reduction-sensitivity for on-demand intracellular drug delivery

Xueling He,^{‡^a} Mingming Ding,^{‡^b} Jiehua Li,^b Hong Tan,^{*^b} Qiang Fu^b and Liang Li^{*^a}

^a *Institute of Biomedical Engineering, West China School of Preclinical and Forensic Medicine, Sichuan University, Chengdu, 610041, China*

^b *College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China*

Supporting Information

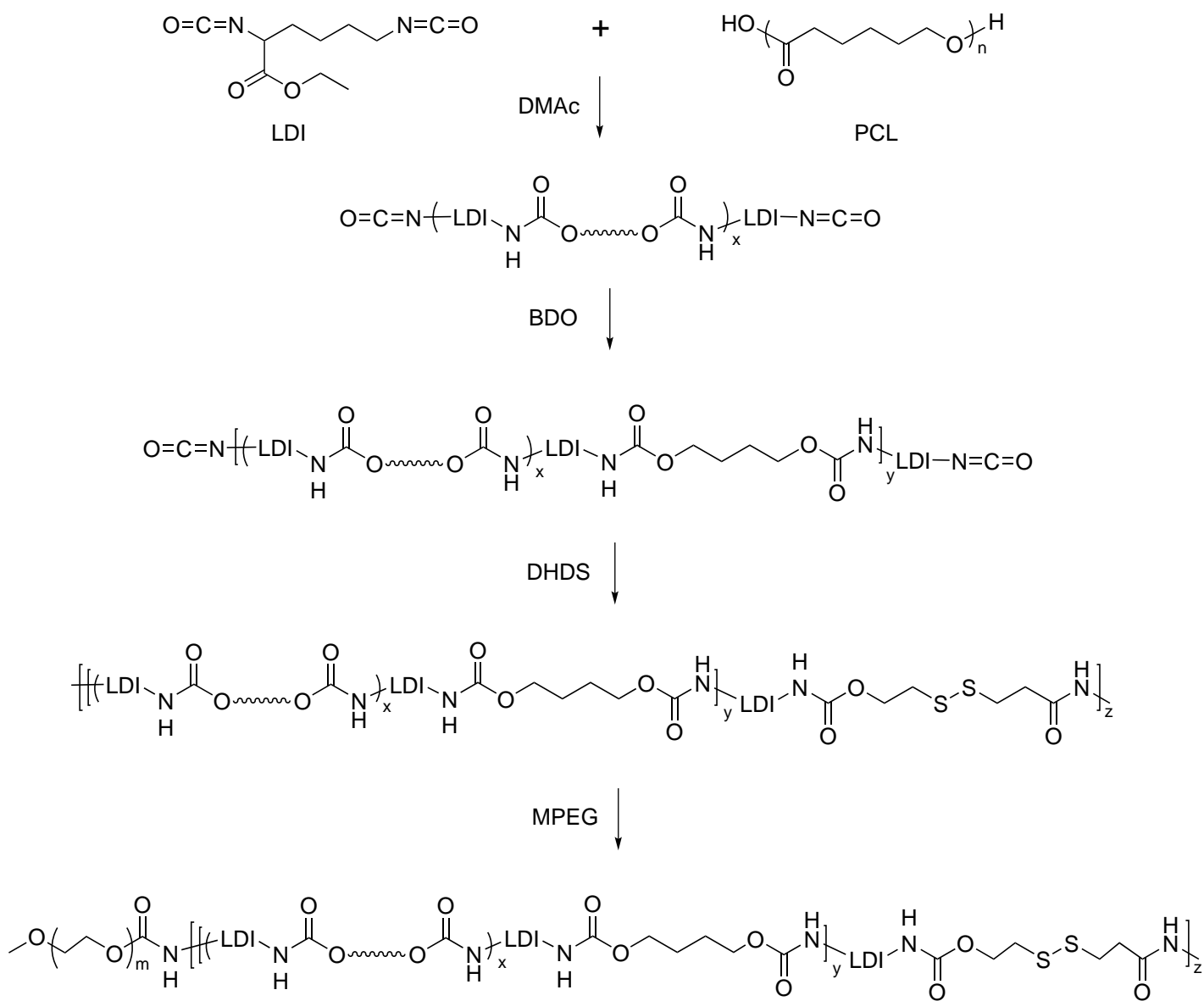


Fig. S1. Synthesis of reduction-sensitive biodegradable multiblock polyurethanes, $x, y, z, m = 1, 2,$

$3, \dots$, --- represents PCL segment.

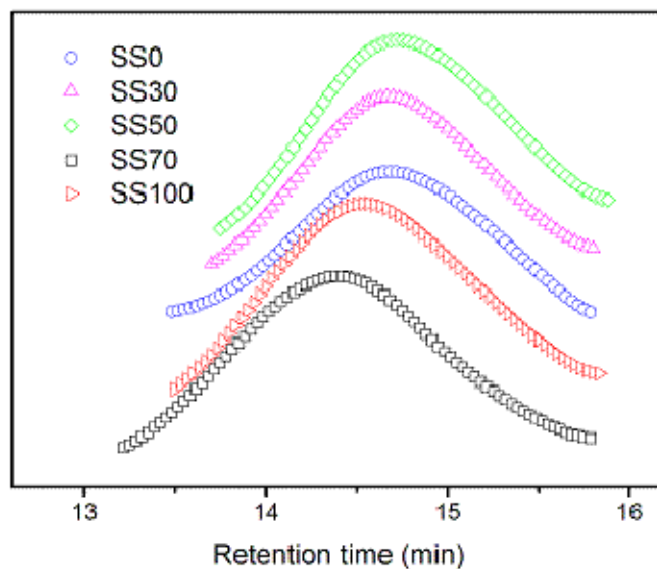


Fig. S2. GPC diagrams of reduction-sensitive biodegradable multiblock polyurethanes.

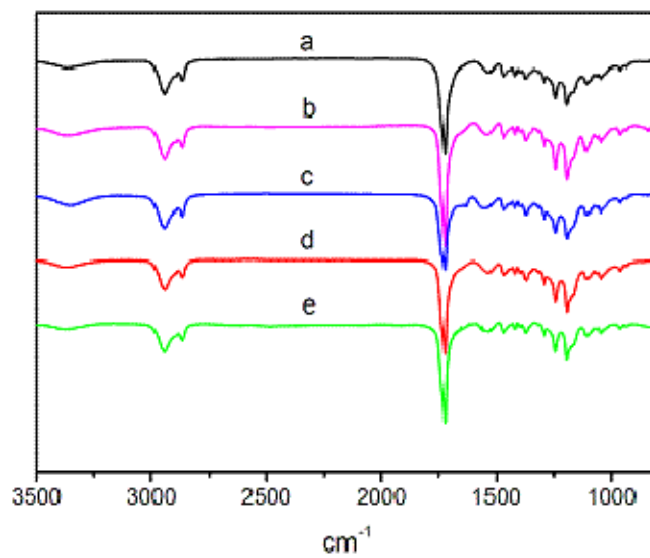


Fig. S3. FTIR spectra of reduction-sensitive biodegradable multiblock polyurethanes: (a) SS0, (b) SS30, (c) SS50, (d) SS70 and (e) SS100.

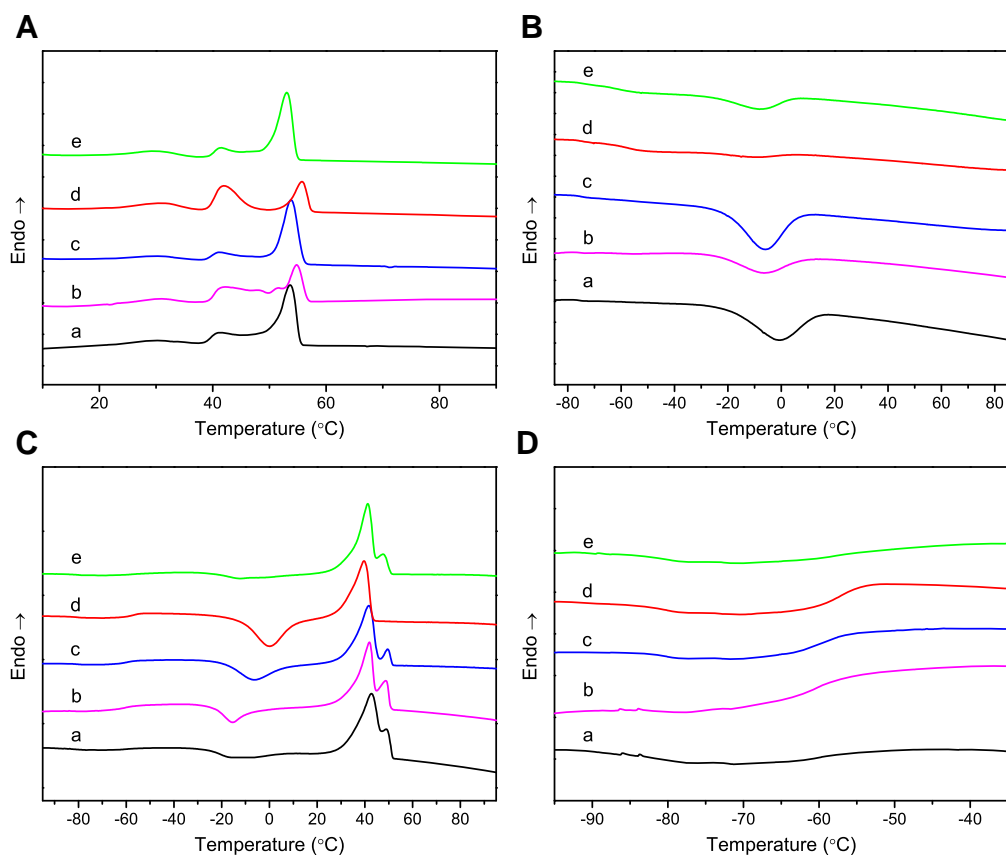


Fig. S4. DSC thermograms of reduction-sensitive biodegradable multiblock polyurethanes: (a) SS0, (b) SS30, (c) SS50, (d) SS70 and (e) SS100. A, B, C and D represent curves for first heating, first cooling, second heating procedures and glass transition regions in the second heating curves, respectively.

Table S1. Thermal properties of reduction-sensitive biodegradable multiblock polyurethanes.^a

Samples ^b	T_g ^c (°C)	T_{cc} ^d (°C) [ΔH_c (J g ⁻¹)]	T_{m1} ^e (°C) [ΔH_m (J g ⁻¹)]	T_{c2} ^f (°C) [ΔH_c (J g ⁻¹)]	T_{m2} ^e (°C) [ΔH_m (J g ⁻¹)]
SS0	-58.73	—	53.6 [58.4]	-1.1 [26.1]	42.8 [55.6]
SS30	-60.36	-15.5 [13.4]	54.8 [49.5]	-6.8 [15.1]	42.0 [53.4]
SS50	-60.25	-6.7 [19.4]	53.9 [45.0]	-8.3 [9.5]	41.6 [38.3]
SS70	-58.17	-0.1 [30.8]	55.8 [51.0]	—	40.0 [35.7]
SS100	-54.83	—	53.1 [51.0]	-6.3 [30.2]	41.1 [52.6]

^a Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris Diamond DSC (Perkin-Elmer Instruments, USA) at a heating/cooling rate of 10 °C min⁻¹ in the range of -100 to 100 °C under a steady flow of nitrogen. ^b Reduction cleavable polyurethanes are denoted as SSX, where SS is for DHDS, X is the molar content of DHDS in chain extender. ^c T_g is defined as the midpoint of the glass transition. ^d Cold crystallization temperature. ^e T_{m1} and T_{m2} represent the melting temperatures on the first heating and second heating curves, respectively. ^f The crystallization temperature on the first cooling curve.