



## Synthesis and self-assembly of poly(*N*-vinylcaprolactam)-*b*-poly(ε-caprolactone) block copolymers via the combination of RAFT/MADIX and ring-opening polymerizations

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## SUPPLEMENTARY MATERIALS



Figure S1. <sup>1</sup>H NMR spectrum of O-ethyl S-4-(hydroxymethyl)benzyl carbonodithioate.



**Figure S2. (a)** Plot of monomer conversion *vs* reaction time and **(b)** plots of the number average molar mass ( $M_n$ , filled symbol) and dispersity ( $\tilde{D}$ , empty symbol) *vs* monomer conversion for the polymerization of NVCL in 1.4-dioxane using [NVCL]:[CTA]:[AIBN] = 150:1:0.1 feed molar ratio at 70 °C. The solid line is the fit line for  $M_n$  determined by HPLC.



**Figure S3**. <sup>1</sup>H NMR spectra of PNVCL homopolymer before (X-PNVCL-OH, **a**) and after (PNVCL-OH, **b**) reaction with AIBN.



Figure S4. <sup>1</sup>H NMR spectra of (a) PNVCL-OH and (b) PNVCL-*b*-PCL (1).



**Figure S5.** Size distribution of the PNVCL-*b*-PCL micelles determined by DLS: (**a**) PNVCL-*b*-PCL (1) and (**b**) PNVCL-*b*-PCL (2) micelles.



**Figure S6**. Temperature dependence of the size and optical transmittance of the PCL-*b*-PVCL (1) micelles (2 mg mL<sup>-1</sup>).



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