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Electronic Supplementary Information for:

Star-shaped amphiphilic block copolymer with dual responses:

synthesis, crystallization, self-assembly, redox and LCST-UCST

thermoresponsive transition

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Synthesis of Linear PCL

CL (5.136 g, 45 mmol), benzyl alcohol (0.108 g, 1 mmol), and a catalytic amount of $Sn(Oct)_2$ (45 µmol) were added to a fire-dried polymerization tube quickly. The tube was then connected to a Schlenk line, where exhausting-refilling processes were repeated for three times. The tube was put into an oil bath at 115 $^{\circ}$ C under argon atmosphere with stirring and cooled to room temperature after polymerization for 24 h. The resulting product was dissolved in chloroform and precipitated two times in methanol. The purified polymer was dried in vacuum at room temperature.

 $M_{\rm n}$ =4960 g/mol, $M_{\rm w}/M_{\rm n}$ =1.32