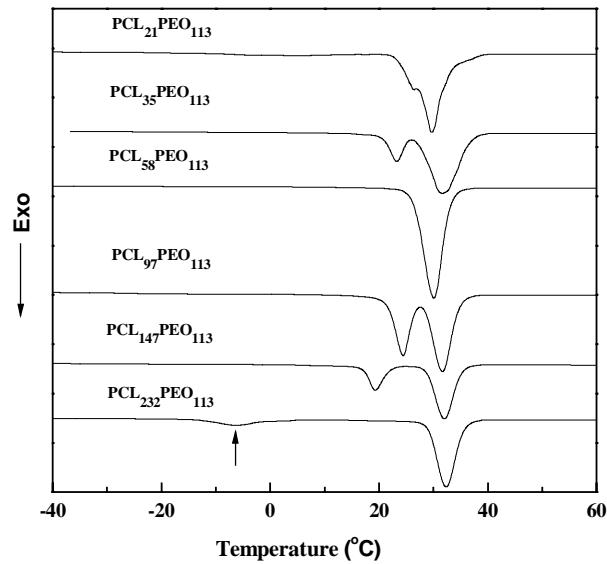
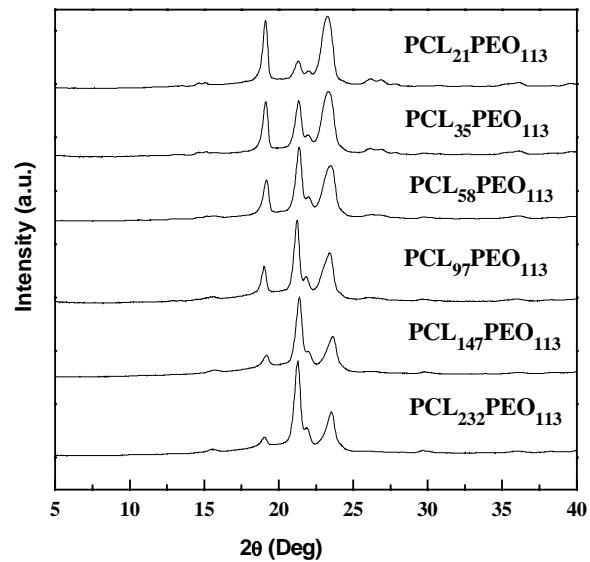


The supporting material includes the DSC non-crystallization curves and WAXD patterns of PCL<sub>n</sub>PEO<sub>113</sub> in the bulk and electron diffraction pattern of PCL<sub>40</sub>PEO<sub>44</sub> micelles. The DSC non-crystallization curves and WAXD patterns of PCL<sub>n</sub>PEO<sub>44</sub> in the bulk can be found in ref.[46] (Du, Z. X.; Xu, J. T.; Yang, Y.; Fan, Z. Q. *J Appl Polym Sci* **2007**, *105*, 771.). The DSC curves of WAXD patterns of PCL<sub>n</sub>PEO<sub>44</sub> and PCL<sub>n</sub>PEO<sub>113</sub> in the bulk show that both PCL and PEG blocks are crystallizable.

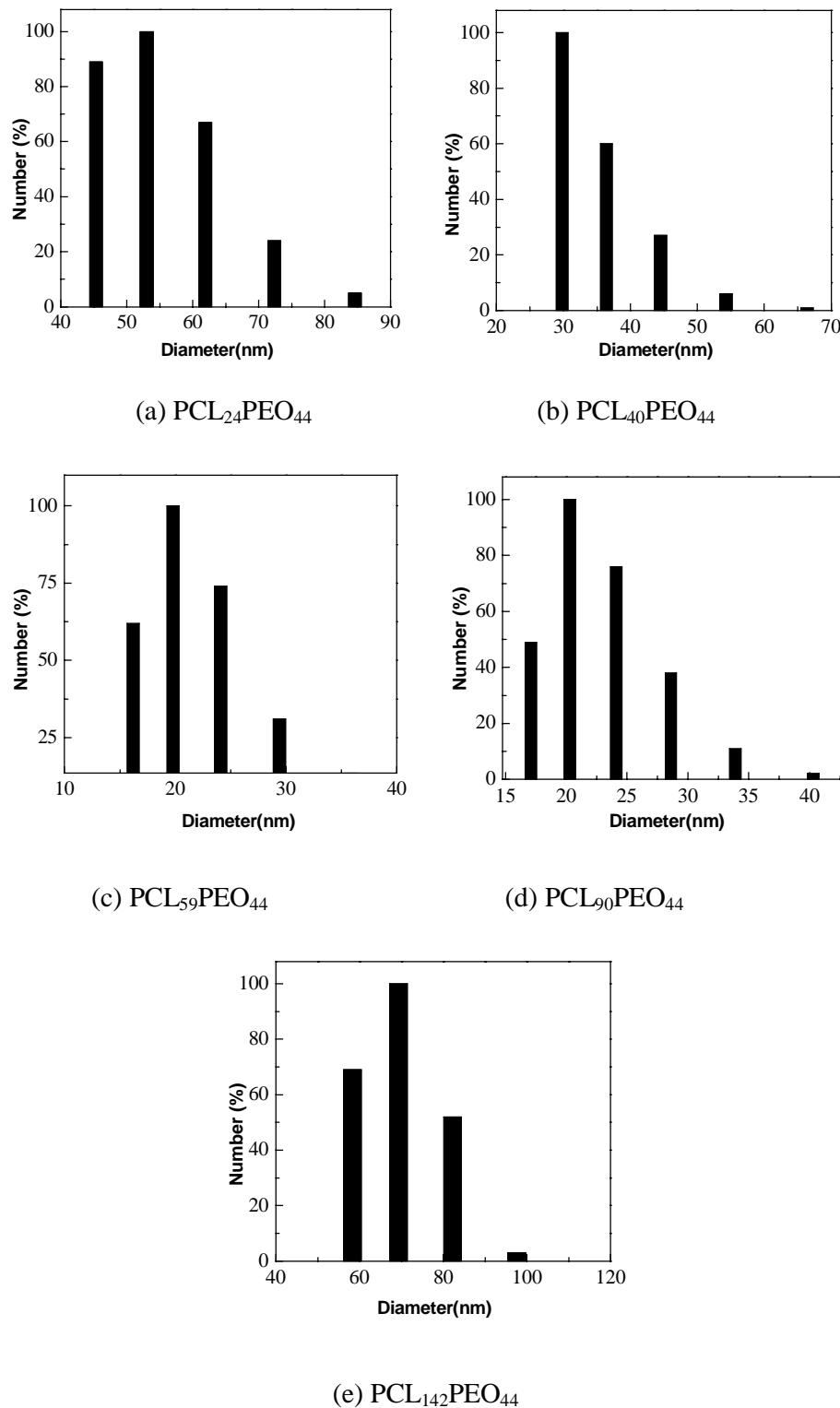
The hydrodynamic diameter and size distribution of the micelles were determined by dynamic light scattering (DLS) using a Brookhaven 90 Plus particle size analyzer. Each analysis lasted for 3 min and was performed at 25 °C with a detection angle of 90°. All micelle solutions had a final polymer concentration of about 0.1 mg/mL. Prior to the light scattering measurements, the solutions were filtered through 0.45 μm filters firstly. The size of micelles is calculated from DLS data according to ref.42.



**Figure S1.** Non-isothermal crystallization DSC traces of PCL<sub>n</sub>PEO<sub>113</sub> diblock copolymers in the bulk. The cooling rate is 10 °C/min.

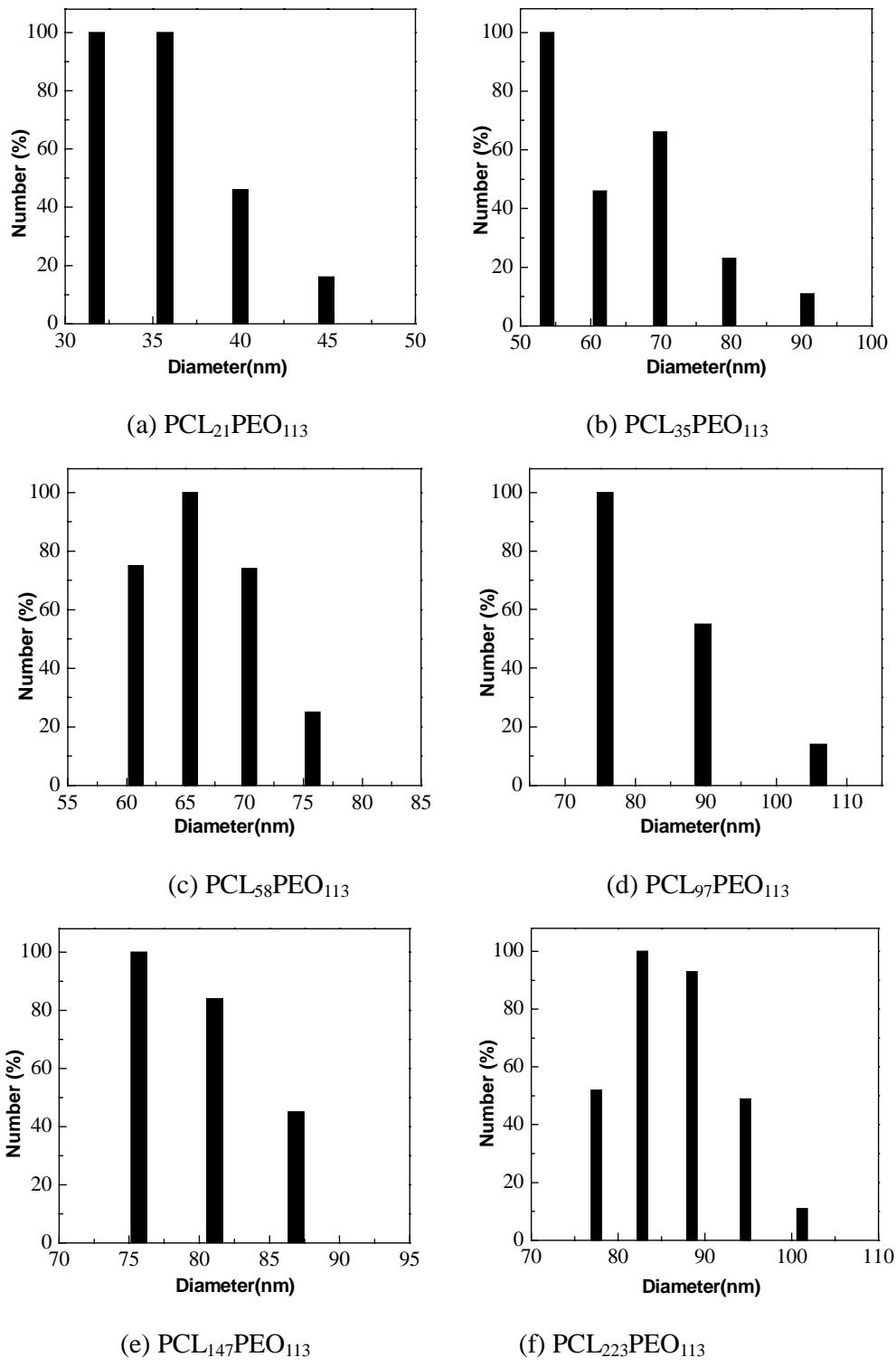


**Figure S2.** WAXD patterns of PCL<sub>n</sub>PEO<sub>113</sub> diblock copolymers in the bulk.



**Figure S3.** Particle size distributions of  $\text{PCL}_n\text{PEO}_{44}$  micelles. (a)  $\text{PCL}_{24}\text{PEO}_{44}$ , (b)

$\text{PCL}_{40}\text{PEO}_{44}$ , (c)  $\text{PCL}_{59}\text{PEO}_{44}$ , (d)  $\text{PCL}_{90}\text{PEO}_{44}$ , (e)  $\text{PCL}_{142}\text{PEO}_{44}$ .



**Figure S4.** Particle size distributions of PCL<sub>n</sub>PEO<sub>113</sub> micelles. (a) PCL<sub>21</sub>PEO<sub>113</sub>, (b) PCL<sub>35</sub>PEO<sub>113</sub>, (c) PCL<sub>58</sub>PEO<sub>113</sub>, (d) PCL<sub>97</sub>PEO<sub>113</sub>, (e) PCL<sub>147</sub>PEO<sub>113</sub> (f) PCL<sub>232</sub>PEO<sub>113</sub>.