Supplementary Materials: Bactericidal Effect of Lauric Acid-Loaded PCL-PEG-PCL Nano-Sized Micelles on Skin Commensal *Propionibacterium acnes*

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1. Supplements of Triblock Copolymer: $^1$H NMR Spectra and DSC Thermograms
Figure S1. The $^1$H NMR spectra of triblock copolymers: (a) PC$_{20}$E$_{40}$C$_{20}$; (b) PC$_{50}$E$_{40}$C$_{50}$; (c) PC$_{100}$E$_{40}$C$_{100}$. 
Figure S2. DSC thermograms of triblock copolymers: (a) PC20E40C20; (b) PC50E40C50 and (c) PC100E40C100. The upper half of the thermogram represents the second cooling curve and the other displayed the second heating curve.

2. Preparation and Characterization of Diblock PEG-PCL Copolymer

In this section, mPEG-PCL diblock copolymers were synthesized by ring-opening polymerization reaction using Sn(Oct)₂ as a catalyst and mPEG (5000 Da) as an initiator. Theoretical molecular weights of PCL segment were designed to be 7500, 10000, 15000 Da corresponding to PC75, PC100 and PC150, respectively. The reaction was carried out at 130 °C for 5 h. Moreover, the ratios of hydrophilic segment: hydrophobic segment were 1:0.75, 1:1, 1:2, respectively. The physicochemical properties of copolymers were characterized by ¹H NMR, FTIR and DSC, respectively. Lastly, the
micelles were prepared and characterized by particle size analyzer. These results were used to compare to that of triblock copolymers PCL-PEG-PCL.

3. Characterization of mPEG-PCL Diblock Copolymers

3.1. Critical Micelle Concentration of the Micelles

Regarding to the pyrene 1:3 ratio method, CMCs of copolymer were determined based on the relationship of \( I_1/I_3 \) intensity ratio of pyrene included in micelles and concentrations. As shown in Figure S7, the CMC was determined at the center point of the sigmoid. It was found that the CMCs of PC75, PC100, PC150 (shown in Table S1) were 16.4 \( \times 10^{-3} \), 8.91 \( \times 10^{-3} \) and 4.47 \( \times 10^{-3} \) wt %, respectively. Apparently the CMCs reduced from 16.4 \( \times 10^{-3} \) to 4.47 \( \times 10^{-3} \) (wt %) when the molecular weight (chain length) of the hydrophobic PCL segment increased from 2500 Da to 10,000 Da. The values of polymeric micelles mainly depend on the hydrophobic segment of copolymers. The comparison of CMC of diblock and triblock copolymer is described in details in Section 3.2.1 of the main text.
3.2. \textit{\textsuperscript{1}H NMR and FT-IR Characterization of Molecular Structure of Diblock Copolymers}

mPEG-PCL diblock copolymers were synthesized using the ring-opening polymerization of ε-CL in the presence of mPEG. The hydroxyl end group initiated the ring opening of ε-CL. The Chemical structure of mPEG-PCL diblock copolymers was determined by \textit{\textsuperscript{1}H NMR in CDCl\textsubscript{3}. The presence of CH\textsubscript{2} group in PCL was observed around 1.3 ppm, 1.6 ppm, 2.3 ppm and 4 ppm as shown in Figure S4. The methoxy protons (OCH\textsubscript{3} group) of mPEG was observed at 3.4 ppm and the peak at 3.64 ppm was assigned as the methylene protons (CH\textsubscript{2} group) of mPEG. Table S1 summarized the characteristics of synthesized diblock copolymers.
Figure S4. The $^1$H-NMR spectra of diblock copolymers: PC$_{75}$ (a); PC$_{100}$ (b); PC$_{150}$ (c).

Functional groups of mPEG-PCL diblock copolymers were characterized by FT-IR spectrophotometer. As one can see in Figure S5, all spectra show typical peaks of C–H stretching in PCL segment at 2890.7–2946.7 cm$^{-1}$. In addition, typical peaks of C=O groups in PCL segment appeared at 1722.8–1731.7 cm$^{-1}$. Lastly, a specific peak at 1110.8–1180.2 cm$^{-1}$ indicated C–O–C stretching in PEG segment. Moreover, when increasing molecular weight of PCL segment in the diblock copolymer, the intensity of C=O of PCL became stronger.
Figure S5. FT-IR spectra of diblock copolymers: (a) PC75; (b) PC100 and (c) PC150.

Table S1. Molecular characteristics of the synthesized diblock copolymers.

| Copolymer | Feeding ratio of PEG/ɛ-CL | $M_w$ a (Da) | $M_n$ b (Da) | CMC (wt %) |
|-----------|---------------------------|-------------|-------------|------------|
| PC75      | 2                         | 7,500       | 6959        | $1.6 \times 10^{-3}$ |
| PC100     | 1                         | 10,000      | 9359        | $8.91 \times 10^{-3}$ |
| PC150     | 0.5                       | 15,000      | 14,139      | $4.47 \times 10^{-3}$ |

a: the theoretical molecular weight of copolymer. b: the molecular weight of copolymer determined by $^1$H NMR.

3.3. DSC Thermograms of Diblock Copolymers

As observed in Figure S6, the components of hydrophobic segment affected the melting point of copolymers. Particularly, the melting point decreased from 56.65 to 54.83 °C, when increasing molecular weight of PCL segment from 2500 to 10,000 Da.
Figure S6. DSC Thermograms of PC75 (a); PC100 (b) and PC150 (c) diblock copolymers; the upper half side of the diagram represents for the second cooling curve and the other displays the second heating curve.

3.4. Particle Size and Distribution of the Micelles
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Average diameter = 10.13 µm

(c) Micellar formations

(d) Micellar formations

PC75
PC100
PC150

PC75
PC100
PC150
Figure S7. The properties of the micelles: (a) the suspension solution of LA-loaded micelles; (b) the particle morphology of LA-loaded micelle (PC75LA) observed under the upright microscopy, the scale bar is 10 μm; (c) the particle size of blank micelle and (d) the particle size of LA-loaded micelle determined by DLS (PDI < 0.3). Please refer to the section 3.2.2 for the results and discussion for this figure.

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