

Supporting Information

Self-Assemblies of Novel Lipid-Mimicking Brush Polymers in Nanoscale Thin Films

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Synthesis of PECH-PC_m polymers

All materials were purchased from Aldrich and used as received unless otherwise noted. The brush polymers with various numbers of bristle ends incorporating PC moieties were synthesized in four steps (Scheme S1).

In the first step, poly(epichlorohydrin) (PECH (**1**)) was synthesized by carrying out the cationic ring-opening polymerization of epichlorohydrin with triphenylcarbenium hexafluorophosphate (TCHP) as an initiator, as previously reported.^{1,2} Epichlorohydrin (40 mL, 512 mmol) was cooled to -5 °C under nitrogen. Triphenylcarbenium hexafluorophosphate (TCHP, 0.1 g, 0.256 mmol) was dissolved in dichloromethane and slowly added into the epichlorohydrin at -5 °C with stirring. Then, the reaction mixture was stirred at room temperature for 2 days. The reaction solution was poured into methanol, precipitating crude polymer product. The obtained crude polymer product was dissolved in dichloromethane and again precipitated into methanol. By repeating this dissolution and precipitation several times, the purified polymer product was obtained and finally

dried in vacuum at 40 °C for 12 h, then characterized by using a Bruker spectrometer (model AM300, Rheinstetten, BW, Germany) with ^1H and ^{13}C probes and an ATI Mattson FTIR spectrometer (model Research Series 2, Lakewood, NJ, USA). Yield: 65%. ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 3.89–3.49 (br, 3H, OCH, OCH₂, CH₂Cl); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 79.70, 70.32, 44.31; FTIR (in film): ν (cm^{-1}) = 2960, 2915, 2873, 1427, 1348, 1299, 1263, 1132, 750, 707.

For the obtained PECH polymer (**1**), molecular weights were determined using a gel permeation chromatography (model PL-GPC 210, Polymer labs, Amherst, MA, USA) equipped with two PL Gel Mixed-C columns (300 × 7.5 mm), which was calibrated with polystyrene standards ($\overline{M}_w = 690\text{--}1800$ kDa). $\overline{M}_w = 38500$ Da and \overline{M}_n (number-average molecular weight) = 22700 Da.

In the second step, poly(oxy(11-hydroxyundecylthiomethyl)ethylene-*ran*-oxy(*n*-dodecylthiomethyl)ethylene)s (PECH-OH m (**2a-2f**)) were prepared from the reaction of the above obtained PECH polymer (**1**) with sodium 11-hydroxyundecylthiolate and sodium *n*-dodecylthiolate in various mole fractions. For a typical synthetic example, the preparation of PECH-OH100 polymer (**2f**) is described as follows. A mixture of the obtained polymer **1** (3.38g, 36.5mmol) and sodium 11-hydroxyundecylthiolate (9.074g, 39.70mmol) in 40 mL of dimethylacetamide (DMAc) was stirred at room temperature. After 24 h the reaction solution was poured into 100 mL chloroform and then the used DMAc solvent was eliminated by washing with water several times. The solution was dried over anhydrous magnesium sulfate and filtered off. The filtrate was concentrated under reduced pressure. The obtained polymer product was poured into cold *n*-hexane and then the polymer product in white powder was filtered, followed by drying in vacuum. For the polymer product, the incorporation of 11-hydroxyundecyl groups was confirmed to be 100% by NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 3.70–3.59 (br, 3H, OCH, OCH₂), 2.75–2.52 (m, 4H, CH₂SCH₂), 1.57–1.13 (m, 18H, CH₂); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) =

79.36–78.72, 63.07, 39.23, 33.26, 32.82, 29.75–28.53, 25.76; IR (in film): ν (cm⁻¹) = 3590–3100, 2960, 2854, 1460, 1110, 732.

In similar manner, the other PECH-OH m polymers were synthesized: PECH-OH0 (**2a**: **4a**), PECH-OH20 (**2b**), PECH-OH40 (**2c**), PECH-OH60 (**2d**), and PECH-OH80 (**2e**) (Scheme S1). The obtained polymers were characterized by ¹H and ¹³C NMR spectroscopy. In particular, ¹H NMR spectroscopy analysis confirmed that these bristles were incorporated with 100% yield into the PECH polymers. In this analysis, there were used the proton peaks at 2.75–2.52 ppm (–CH₂SCH₂– unit in the bristle) and 3.70–3.59 ppm (–OCH– and –OCH₂– units in the backbone). For each brush polymer, the proportions of the two different incorporated bristles were determined from the proton peaks around 0.90 ppm (–CH₃ end group in the *n*-dodecylthiomethyl bristle) and at 2.75–2.52 ppm (–CH₂SCH₂– unit in the bristles). This analysis found that the proportion of 11-hydroxyundecylthiomethyl bristle is 0 mole % for PECH-OH0, 16 mole % for PECH-OH20, 38 mole % for PECH-OH40, 57 mole % for PECH-OH60, 78 mole % for PECH-OH80, and 100 mole % for PECH-OH100 (Scheme S1).

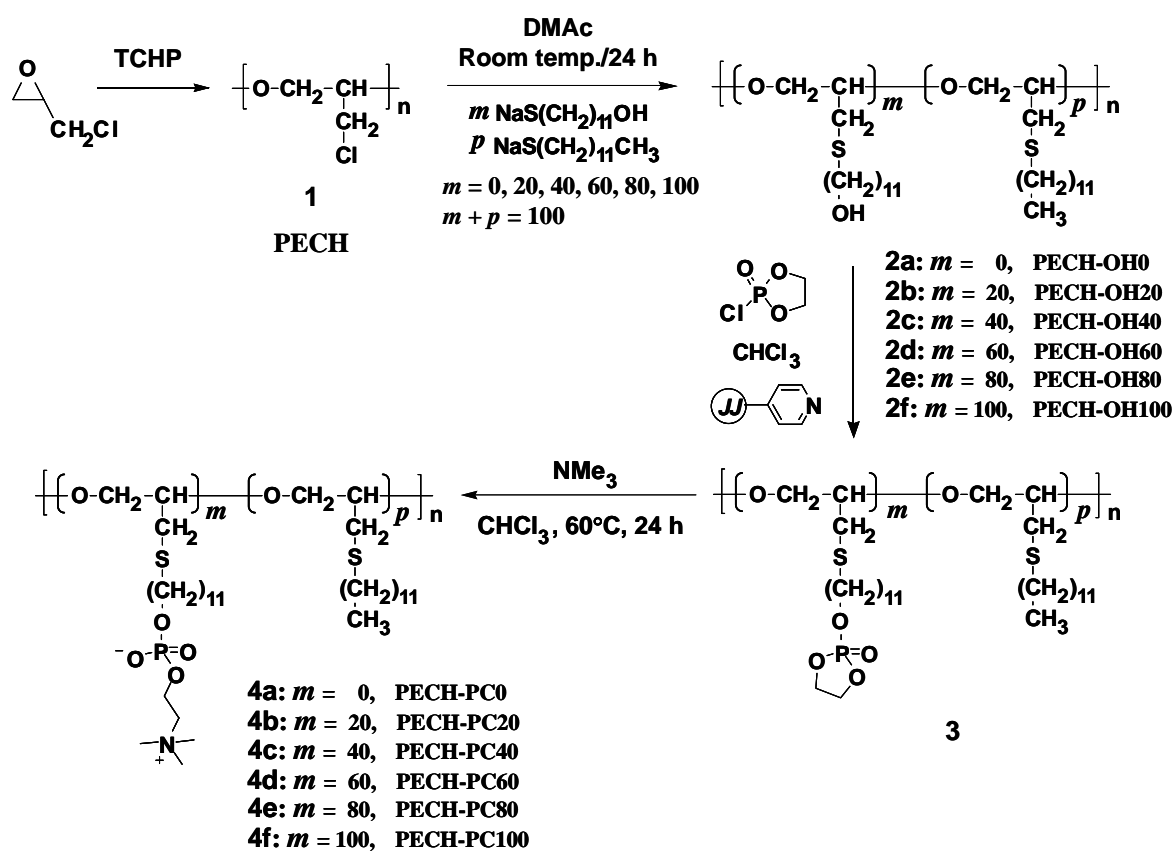
In the third step, 2-chloro-1,3,2-dioxaphospholane-2-oxide was incorporated into the 11-hydroxyundecylthio-bristle ends of the PECH-OH m polymers (**2b-2f**). For a typical synthetic example, the obtained polymer **2f** (1.3g, 5.02 mmol OH) and polypyridine (*JandaJel*TM, 1.67g, 8 mmol/g) in 20 mL chloroform were stirred at 0 °C for 30 min.³ Then, 2-Chloro-1,3,2-dioxaphospholane-2-oxide (0.506 mL, 5.52 mmol) was slowly added into the solution and stirred at room temperature for 6 h. The reaction mixture was filtered to remove polypyridine, giving the target product.

In the final step, the rings of the products obtained in the third step were opened, finally producing poly(oxy(11-phosphorylcholineundecylthiomethyl)ethylene-*ran*-oxy(*n*-dodecylthiomethyl)ethylene)s (PECH-PC m (**4b-4f**)). For a typical synthetic example, the product obtained from **2f** in the third step, as well as trimethylamine (0.982 mL, 10 mmol) in anhydrous CHCl₃ (5 mL) was added into the Smith Process VialsTM. The mixture was heated to 60 °C and stirred for 24

h. The reaction mixture was cooled, concentrated under reduced pressure and dried in vacuum. For the polymer product, the incorporation of phosphorylcholine moieties to the hydroxyl-terminated bristles was confirmed to be 100% by NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 4.26–4.15 (m, $\text{CH}_2\text{CH}_2\text{N}$), 4.06–4.03 (m, CH_2OP), 3.82–3.62(m, OCH_2 , OCH , CH_2N), 3.39(s, $(\text{CH}_3)\text{N}$), 2.70–2.50 (m, CH_2SCH_2), 1.67–1.27 (m, CH_2); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) = 79.55, 70.06, 68.57, 65.16, 63.38, 45.49, 39.64, 33.27, 30.77–29.95, 26.24; IR (in film): ν (cm^{-1}) = 3652–3133, 2925, 2852, 1724, 1456, 1253, 1037.

References

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Scheme S1. Synthetic route of the brush polymers with various numbers of bristle ends incorporating phosphorylcholine moieties, PECH-PC m . The ^1H NMR spectroscopy analysis of the synthesized brush polymers found that the proportion of 11-phosphorylcholine-undecylthiomethyl bristle is 0 mole % for PECH-PC0, 16 mole % for PECH-PC20, 38 mole % for PECH-PC40, 57 mole % for PECH-PC60, 78 mole % for PECH-PC80, and 100 mole % for PECH-PC100.