Electronic Supplementary Information (ESI)

Convenient Method for Surface Modification by Patching a Freestanding Anti-Biofouling Nanosheet

Toshinori Fujie, Hiroki Haniuda, and Shinji Takeoka

Department of Life Science and Medical Bioscience, Graduate School of Advanced Science and Engineering, Waseda University (TWIns), 2-2 Wakamatsu-cho, Shinjuku-ku, Tokyo 162-8480, Japan.

Contents:

1. Synthesis of 2-bromo-2-methyl-propionic acid 2-hydroxy-ethyl ester

We followed the protocol described in a previous report.[s1] In brief; ethylene glycol (22.5 mL, 0.4 mol) was added to a 50 mL 3-neck round-bottom flask that had been purged with nitrogen. The flask was equipped with a magnetic stirrer bar and rubber septum. The flask was then cooled to 0^{o}C in an ice bath. 2-Bromoisobutyrylbromide (2 mL, 16.2 mmol) was slowly added dropwise to the stirring ethylene glycol. The reaction was stirred at 0^{o}C for 3 hours, quenched by addition of 10 mL H_2O and then extracted with $CHCl_3$ (3 x 10 mL). The combined organic extracts were dried over solid Na_2SO_4 and filtered. Any remaining $CHCl_3$ was removed by rotary evaporation. The subsequent product was obtained as a viscous colorless liquid (1.46 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ4.20 (t, 2H, J = 4.2 Hz), 3.76 (t, 2H, J = 3.7 Hz), 2.94 (s, 1H), 1.86 (s, 6H) **(Fig. S1a)**; ^{13}C NMR (500 MHz, $CDCl_3$): δ171.91, 67.30, 60.48, 55.85, 30.63 **(Fig. S1b)**.

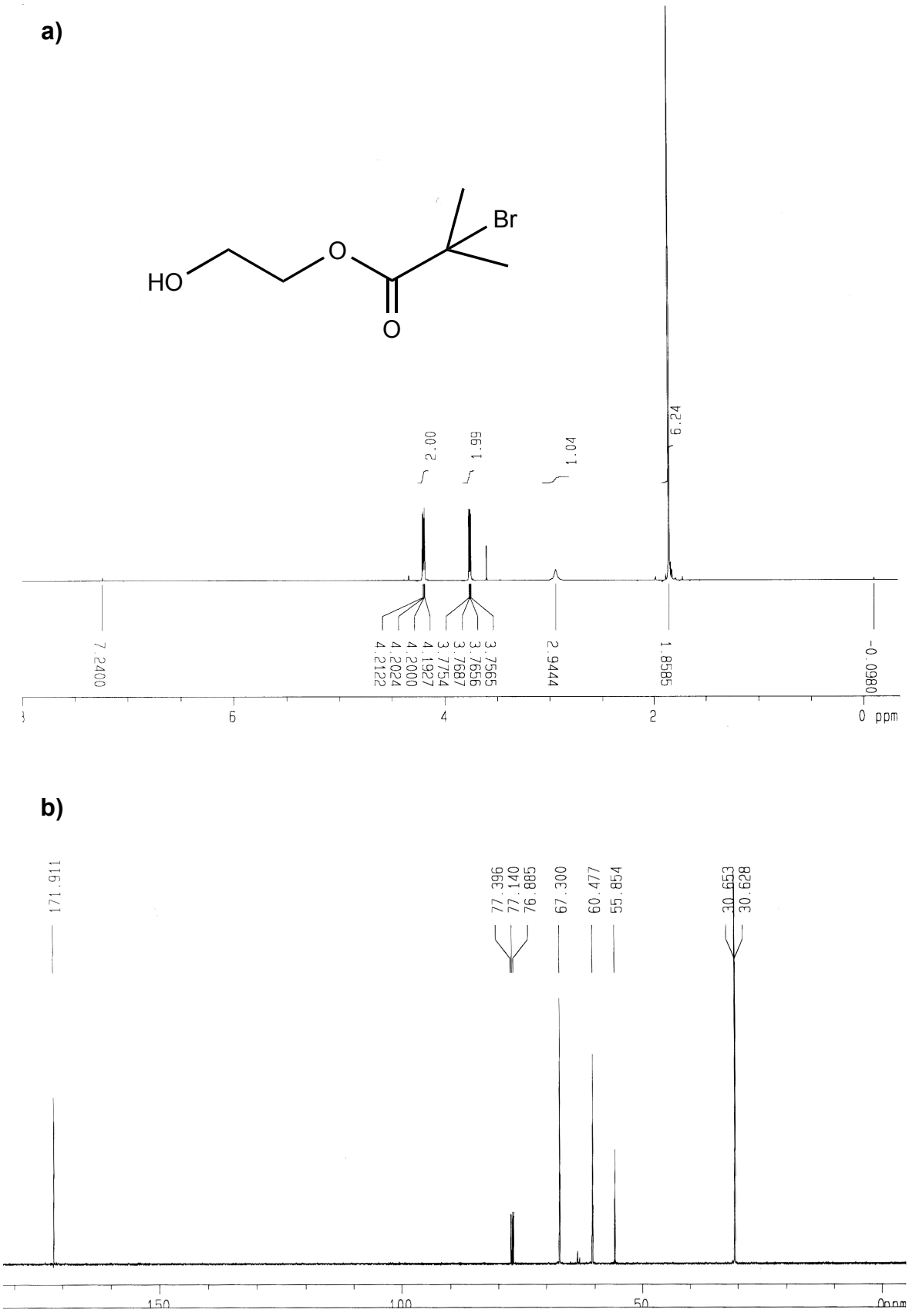

Fig. S1 (a) ^{1}H and (b) ^{13}C NMR of 2-bromo-2-methyl-propionic acid 2-hydroxy-ethyl ester.

2. Synthesis of anionic macroinitiator

PAA (1.5 g, 20.8 *unit* mmol) dissolved in dimethylformamide (DMF) (10 mL) and dimethyl amino pyridine (15 mg, 0.123 mmol) dissolved in CH_2Cl_2 (3 mL) were mixed in a 50 mL 3-neck round-bottom flask at r.t. The 2-bromo-2-methyl-propionic acid 2-hydroxy-ethyl ester (1 g, 4.76 mmol) dissolved in CH_2Cl_2 (3 mL) was added dropwise to the reaction mixture. The flask was then cooled to 0^oC in an ice bath. Dicyclohexyl dimethylcarbodiimide (982 mg, 4.76 mmol) dissolved in $CHCl_3$ (12 mL) was then added dropwise at 0^oC. The reaction was stirred at r.t., and aliquots periodically collected at 12, 132 and 164 hours. The product was then filtered and the subsequent liquid was precipitated in ether, which was filtered and extracted by acetone. The final product at 164 hrs was dried *in vacuo*, resulting in a white powder (475 mg, 40%). ^1H NMR (300 MHz, d-DMSO): δ4.18-4.24 (-C**H**$_2$, 4H), 2.16 (-C**H**-, 1H), 1.84 (-C**H**$_3$, 6H), 1.46-1.67 (-C**H**$_2$-, 4H), where the remaining peaks at δ3.34, 2.68 (-C**H**$_3$, 3H), 2.84 (-C**H**$_3$, 3H) and 2.46 (-C**H**$_3$, 6H) were assigned as H_2O, DMF and DMSO, respectively **(Fig. S2)**.

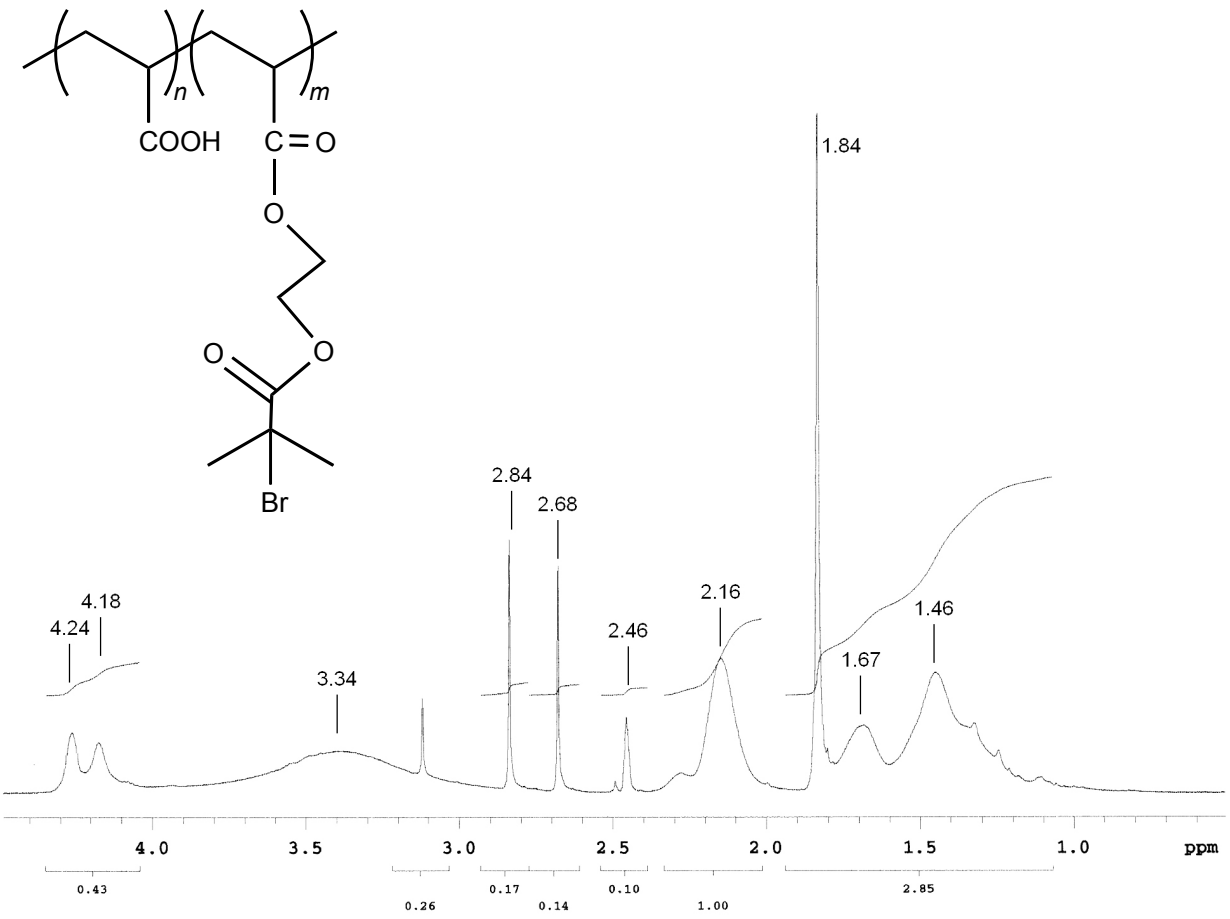

Fig. S2 ^{1}H NMR of anionic macroinitiator (164 hrs).

3. Degree of esterification in the macroinitiator

The degree of esterification at each time point in the reaction was determined by inclusion of a bromo initiator. The samples were then evaluated from integration of the broad methine peak around δ4.18-4.24 in Fig. S2.[s2] In this paper, the anionic macroinitiator at the 164-hour reaction time point was chosen as a building block of the LbL film, where 11% of carboxylic acid groups in the original PAA had been esterified with the hydroxide groups of the bromo initiator **(Fig. S3)**.

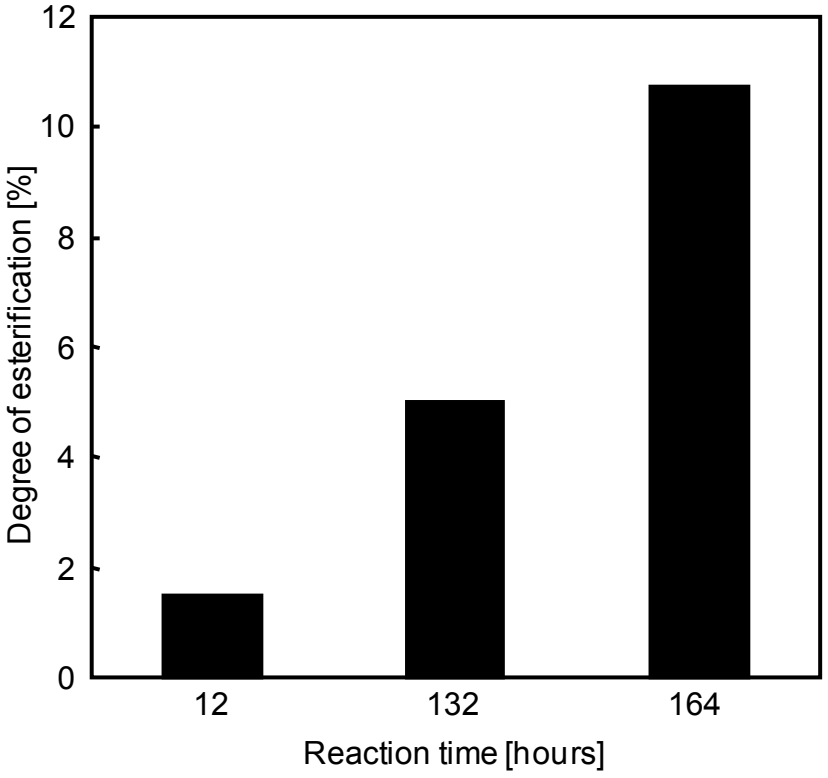

Fig. S3 Degree of esterification in the anionic macroinitiator.

4. Characterization of pMPC-nanosheet by FT/IR spectroscopy

Removal of the PVA supporting film pMPC-nanosheet was characterized by FT/IR spectroscopy (FT/IR-4000, JASCO Corp., Tokyo, Japan). The pMPC-nanosheet was prepared on a calcium fluoride (CaF_2) substrate, on which PVA was layered. Then, the bilayered film of pMPC-nanosheet and PVA supporting film was peeled from the CaF_2 substrate. After dissolution of PVA in D.I. water, the freestanding pMPC-nanosheet was collected on another CaF_2 substrate. The pMPC-nanosheets with respect to the individual steps ware analyzed by FT/IR spectroscopy, respectively. Spectra of the pMPC-nanosheets before deposition **(Fig. S4a)** and after removal of PVA **(Fig. S4b)** showed the similar vibration curve although spectrum of the pMPC-nanosheet with the PVA film remarkably showed a broad peak attributed to the hydroxyl groups of PVA (centered at 3300 cm^{-1}) **(Fig. S4c)**. Hence, it was clarified that the PVA film was removed only by water rinsing. The pMPC-nanosheet can be ubiquitously transferred with the supporting film method.

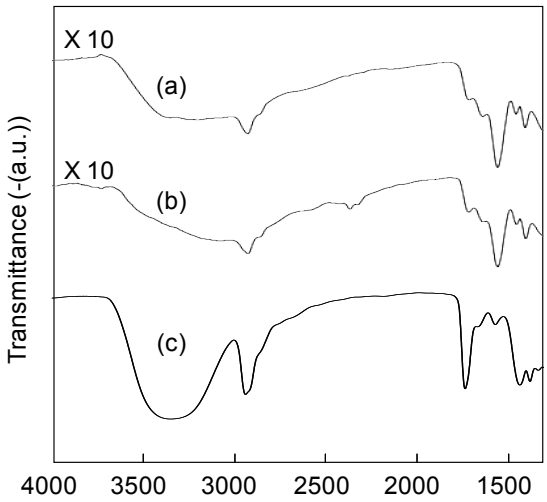

Fig. S4 FT/IR spectra of various pMPC-nanosheets: (a) pMPC-nanosheet on a CaF_2 substrate, (b) after removal of PVA and (c) after deposition of PVA (a.u.; arbitrary unit).

5. References

S1. M. A. White, J. A. Johnson, J. T. Koberstein and N. J. Turro, *J. Am. Chem. Soc.*, 2006, **128**, 11356.

S2. T. M. Fulghum, D. L. Patton and R. C. Advincula, *Langmuir*, 2006, **22**, 8397.