Supporting Information for *Macromol. Rapid Commun*. **2007**, *28*, 1270.

First Cellulose Langmuir-Blodgett Films towards Photocurrent Generation Systems

Keita Sakakibara,* Yasuhiro Ogawa, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Experimental Procedures

Materials

Cellulose microcrystalline (Avicel®, DP = 114) was purchased from Merck. The other reagents were purchased from Nakarai Tesque Inc. (Kyoto, Japan) or Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Measurements

^{1}H and ^{13}C NMR spectra were recorded with a Varian Inova 300 FT-NMR (300 MHz) spectrometer in chloroform-*d* with tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively. The number averaged molecular weight of the polymer was obtained using gel permeation chromatography (GPC) in chloroform at 40 °C. Calibration curves were obtained with polystyrene standards (Shodex). A Shimadzu liquid chromatography injector (LC-10ATvp), a Shimadzu column oven (CTO-10Avp), a Shimadzu refractive index detector (RID-10A), a Shimadzu communication bus module (CBM-10A), a Shimadzu LC workstation (CLASS-LC10), and Shodex columns (KF802, KF802.5 and KF805) were used. The flow rate was 1.0 $mL \cdot min^{-1}$. The UV-vis spectra were measured with a Jasco V-560 spectrophotometer, using 75 × 25 × 1 mm quartz plates as a substrate.

Synthesis of 2,3-Di-O-stearoylcellulose

6-*O*-*p*-Methoxytritylcellulose (0.5 g), prepared from cellulose microcrystalline by a known method,[1,2] was dissolved in 10 mL of *N*,*N*-dimethylacetamide (DMA). The solution was treated with pyridine (1 mL, 11.5 mmol, 10 equivalents per AGU) and 4-(dimethylamino)pyridine (DMAP) (0.14 g, 1.15 mmol, 1 equivalent per AGU) at room temperature. Then, stearoyl chloride (3.49 g, 11.5 mmol, 10 equivalents per AGU) in 5 mL of DMA was added dropwise to the solution at 0 °C with constant stirring under a nitrogen atmosphere. The solution was stirred at 60 °C for 24 h. The mixture was poured into a large amount of methanol (MeOH) (300 mL). The precipitates were filtered off and washed thoroughly with MeOH under suction. The precipitates were dissolved in THF and then precipitated with MeOH (300 mL) for purification. Although this purification procedure was repeated three times, unreacted acid chloride was not completely removed. The final precipitation was used for the subsequent step without further purification.

The precipitate (0.7 g) was treated with concentrated HCl (2.5 mL) in THF (30 mL). The reaction mixture was stirred at room temperature overnight and refluxed for 4 h. The mixture was then poured into MeOH (500 mL). The product was isolated by filtration, washed with MeOH, and dried under a vacuum at 60 °C to give stearoylcellulose as a white solid in a yield of 91.4%. DS (calculated from elemental analysis) was 1.56, &Mdash;$_n$ (GPC) was 2.12 ×

10^4, &Mdash;$_{w}$ (GPC) was 3.71×10^4, &Mdash;$_{w}$/&Mdash;$_{n}$ (GPC) was 1.75 and DP_n (GPC) was 36.7.

^{1}H NMR of the acetylated compound ($CDCl_3$): $\delta = 0.88$ (3 × s, stearoyl $-CH_3$), 1.25 (broad-s, stearoyl $-CH_2-$), 1.51 (s, stearoyl $-CO-CH_2-CH_2-$), 1.84–2.46 (m, acetyl −H and stearoyl $-CO-CH_2-$), 3.52 (s, H^5), 3.68 (s, H^4), 4.04 (s, H^1), 4.37 (s, H^6), 4.80 (s, H^2), 5.08 (s, H^3). ^{13}C

^{13}C NMR of the acetylated compound ($CDCl_3$): $\delta = 100.5$ (C^1), 72.8, 71.7, 76.1, 71.4, 62.0 (C2, C3, C^4, C^5, C^6), 14.1 (stearoyl $-CH_3$), 20.5 (acetyl $-CH_3$), 22.6, 24.7, 29.0–29.5, 31.8 (stearoyl $-CH_2-$), 169.2, 169.6, 170.1 (acetyl −C=O), 171.8, 172.3, 172.9 (stearoyl −C=O).

IR (KBr): 3 450, 2 920, 2 851, 1 751, 1 468, 1 415, 1 379, 1 159, 1 117, 1 074, 914, 721 cm^{-1}.

Atomic Force Microscopy (AFM) Measurements

AFM images of a monolayer film deposited on a freshly cleaved mica substrate (15 × 7 mm) at a pressure of 10 $mN \cdot m^{-1}$ at 20 °C were obtained using a NV 2000 (Olympus). Measurements were carried out in tapping mode using a tetrahedral shaped silicon cantilever (AC240TS-C1, Olympus) with a spring constant of 2 $N \cdot m^{-1}$.

[1] J. A. C. Gómez, U.W.Erler, D.O.Klemm, *Macromol. Chem. Phys.* **1996**, *197*, 953.

[2] H. Kern, S. Choi, G. Wenz, J. Heinrich, L. Ehrhardt, P. Mischnick, P. Garidel, A. Blume, *Carbohydr. Res.* **2000**, *326*, 67.