

## SUPPORTING INFORMATION

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# Hydrogen bonded polymeric multilayer films assembled below and above the cloud point temperature

André B. da Fonseca Antunes,<sup>a</sup> Marijke Dierendonck,<sup>a</sup> Gertjan Vancoillie,<sup>b</sup> Jean Paul Remon,<sup>a</sup> Richard Hoogenboom<sup>\*b</sup> and Bruno De Geest<sup>\*a</sup>

### Materials and Methods

**Materials.** Mercaptosuccinic acid, branched PEI (25 kDa) and tannic acid were purchased from Sigma-Aldrich. Poly(2-(*n*-propyl)-2-oxazoline) with a DP of 100 was synthesized according to Hoogenboom et al. <sup>1</sup>. SEC analysis against PMMA standards showed a  $M_n=14$  kDa and  $\bar{D}=1.14$ . Gold coated quartz chips with a nominal resonance frequency of 10 MHz were purchased from International Crystal Manufacturing Co (ICM). Silicon AFM cantilevers with a nominal resonance frequency of 75 kHz and a spring constant of 3 N/m were obtained from Bruker. All water used in the experiments was of Milli-Q grade.

**Quartz Crystal Microbalance (QCM).** QCM measurements were performed on a Gamry eQCM equipped with an ALS flow cell. Gold coated quartz chips were first coated by 1h immersion in an aqueous solution of mercaptosuccinic acid (2 mg/mL) followed by extensive rinsing with water. Secondly, the quartz chip was immersed into an aqueous PEI solution (2 mg/mL) for 1h and again extensively washed with water and dried under a gentle nitrogen stream. Next, the chip was mounted into the flow cell and water was injected and the measurement was started and continued until a flat baseline was obtained. Then the measurement was restarted and after 100 sec 200  $\mu$ L of tannic acid (TA; 2 mg/mL in water) was injected. 100 sec later, 500  $\mu$ L of water was injected to remove the non-adsorbed TA. 100 sec later PnPropOx (2 mg/mL in water) was injected and after 100 sec again 500  $\mu$ L of water was injected. This procedure was repeated until a total of 10 TA/PnPropOx bilayers were deposited. Multilayer assembly below the  $T_{CP}$  of the PnPropOx was performed in a cold room thermostated at 15 °C while measurements at 45 °C were performed by placing the equipment and all solutions in an oven thermostated at 45 °C.

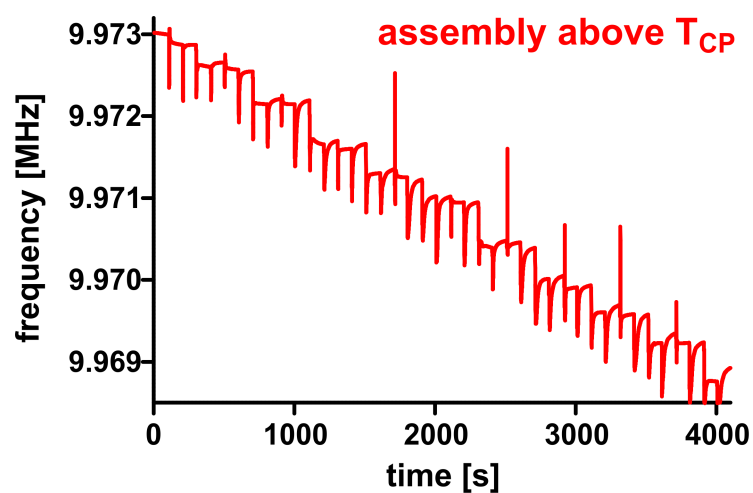
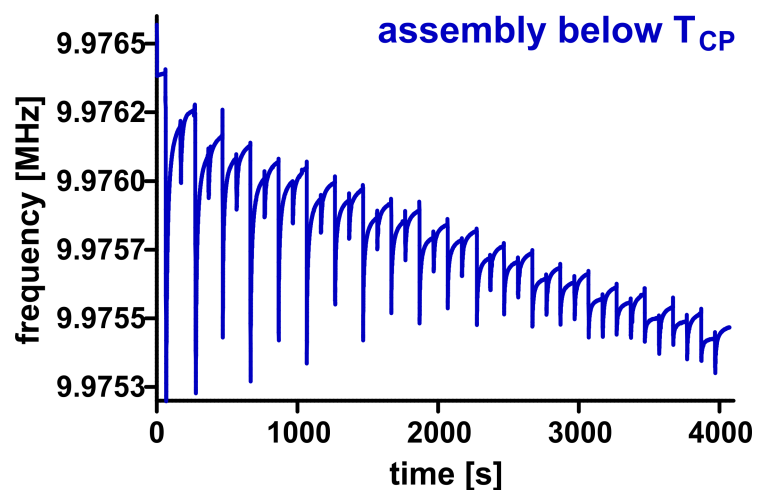
**UV VIS spectroscopy.** Quartz slides rinsed with piranha solution to render them more hydrophilic were coated with PEI followed by dip coating with alternating TA (2 mg/mL in water) and PnPropOx (2 mg/mL in water). After deposition of each bilayer, the absorption spectrum was recorded with a Shimadzu spectrophotometer.

**Atomic Force Microscopy (AFM).** Silicon wafers were manually cleaved into rectangular pieces, cleaned with piranha (3:1 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>; Caution! Piranha is highly corrosive and should be handled with extreme care and should not be stored in closed containers). Similar to the quartz chips a precursor layer was applied by immersing the wafers for 1h in PEI (2 mg/mL in water), followed by extensive rinsing. Subsequently the silicon wafers were alternately dip-coated with TA (2 mg/mL in water) and PnPropOx (2 mg/mL in water), either at 15 °C or 45 °C. Between each step, the wafers

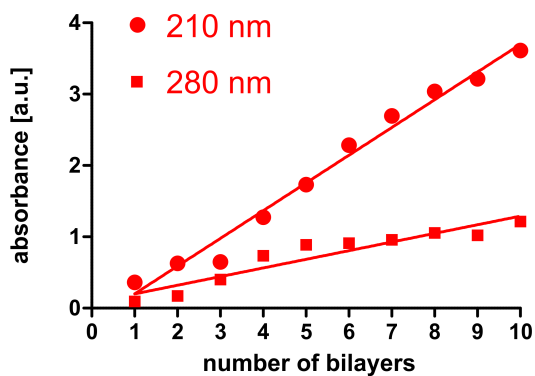
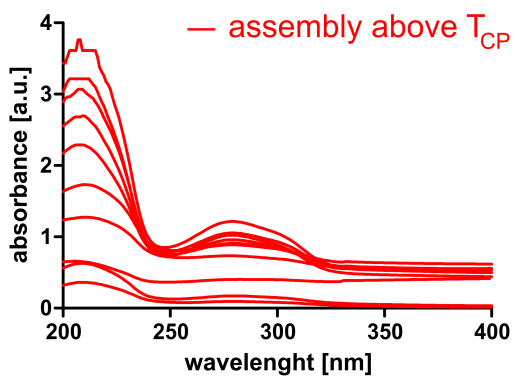
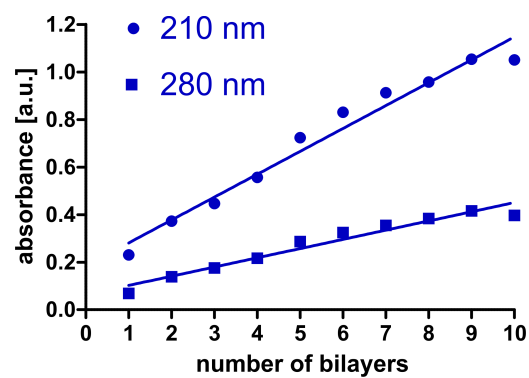
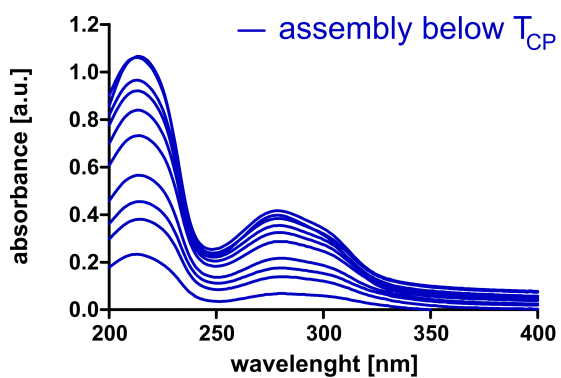
were extensively rinsed with water (at the same temperature as the TA and PnPropOx solutions) to remove non-adsorbed material. After the desired number of bilayers was reached, the coated wafers were dried under a gentle stream of nitrogen.

AFM measurements were performed on a Bruker Innova operated in tapping mode in air. Images were recorded with a scan size of respectively  $5 \times 5 \mu\text{m}$  and  $50 \times 50 \mu\text{m}$ . At least three different images from different samples were recorded and representative images were selected.

### Raw QCM data

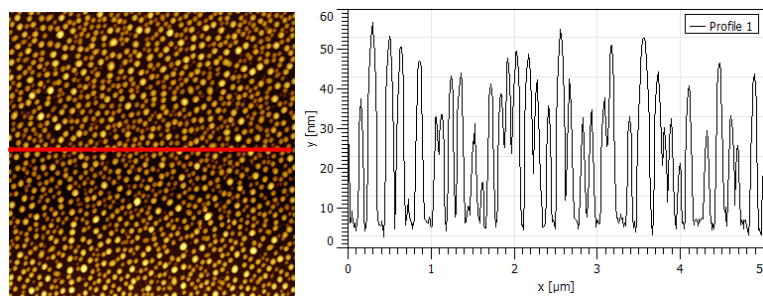


### LbL assembly on quartz slides monitored by UV-VIS

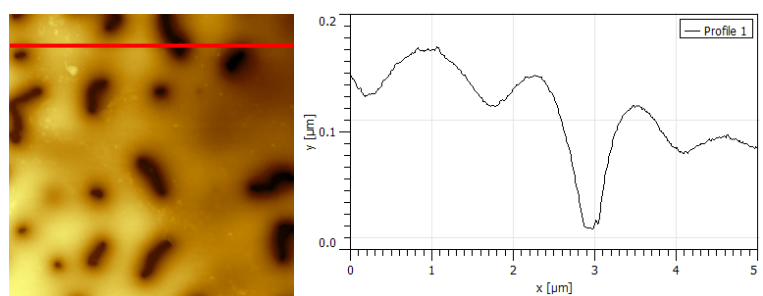


## Cross-sectional profiles of TA/PnPropOx films above the $T_{CP}$ of PnPropOx

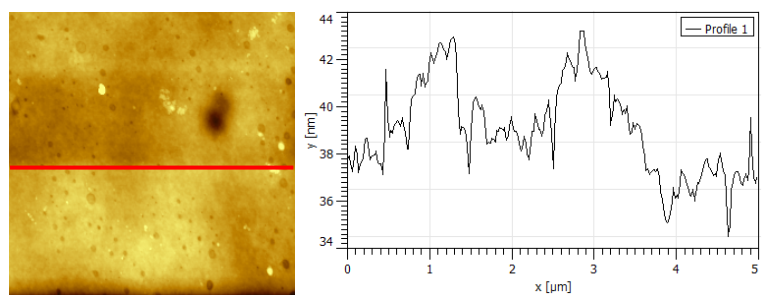
1 bilayer TA/PnPropOx assembled at 45 °C



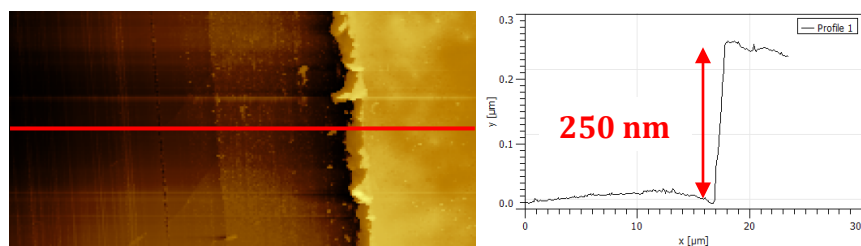
5 bilayers TA/PnPropOx assembled at 45 °C



10 bilayers TA/PnPropOx assembled at 45 °C

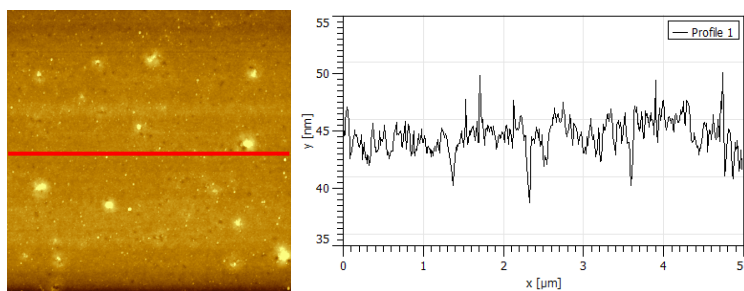


**Step height of a 10 bilayers TA/PnPropOx film assembled at 45 °C**

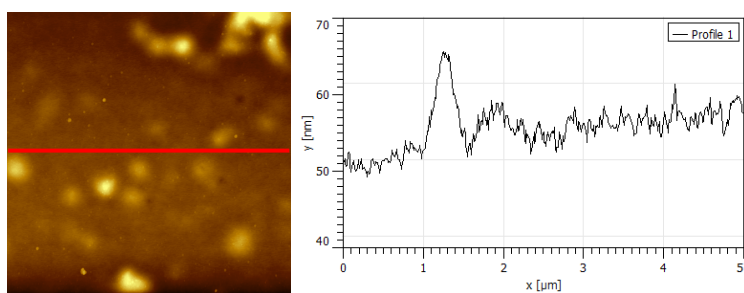


## Cross-sectional profiles of TA/PnPropOx films below the $T_{CP}$ of PnPropOx

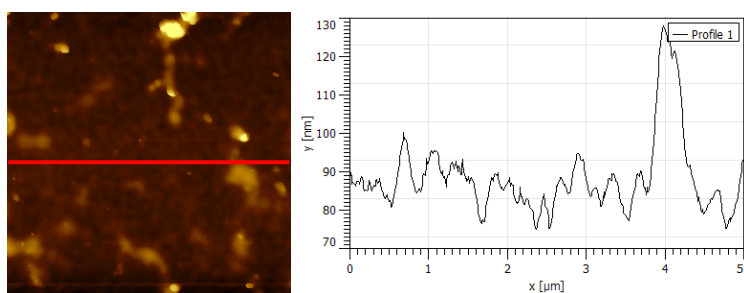
1 bilayer TA/PnPropOx assembled at 25 °C



5 bilayers TA/PnPropOx assembled at 25 °C

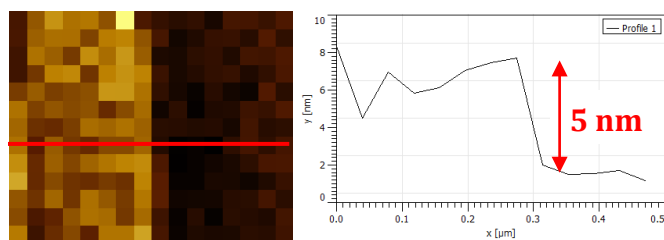


10 bilayers TA/PnPropOx assembled at 25 °C

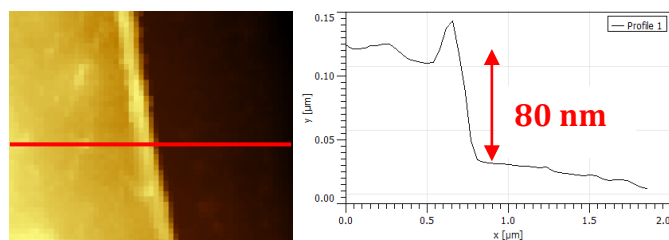


## **Step height of TA/PnPropOx films assembled at 25 °C**

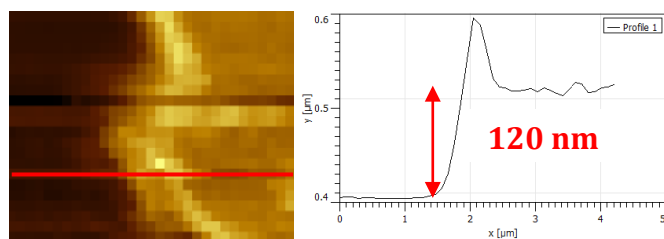
1 bilayer TA/PnPropOx assembled at 25 °C



5 bilayers TA/PnPropOx assembled at 25 °C



10 bilayers TA/PnPropOx assembled at 25 °C



- 1 Hoogenboom, R.; Thijs, H.M.L.; Jochems, M.J.H.C.; van Lankvelt, B.M.; Fijten, M.W.M.; Schubert, U.S. *Chem. Commun.* **2008**, 44, 5758.