Supporting Information

Microfluidic studies of polymer adsorption in flow

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1. Fabrication of the MF device by thermoembossing

A 1 mm-thick polycarbonate (PC) sheet was placed on top of the SU-8/Cu master. A square polished copper plate with dimensions 7.6 × 7.6 cm and the thickness of 1 mm was placed on top of the PC sheet, with the polished side against it. Several copper plates and a piece of stainless steel plate were placed underneath the SU-8/Cu master, and a sheet of the temperature-resistant silicone rubber (Mcmaster-Carr 378 T22) was placed between them, in order to redistribute potential pressure imbalances. After the press was heated up to 175 ℃, the PS sheet, the master, and the metal and silicone plates were placed for 5 min in a vacuum chamber between the top and bottom platens. A required embossing pressure of 400 lb was imposed for 2 min at 175 ℃. The heater was turned off and the system was cooled under press to 140 ℃. The pressure was reduced, the vacuum chamber was opened, and the imprinted PC sheet was de-embossed. A drill press was used to make the inlet and outlet holes on the PC sheet.

Next, a PC film was embossed using a stainless steel template, which had a protruded feature with the diameter of 1.8 mm and a height of 175 μm in the middle, mimicking the dimensions of the ATR diamond crystal. The embossing protocol was the same as described above, however the heating temperature of 200 ℃ and the cooling temperature of 80 ℃ were used. After embossing, a 1200 grit sand paper and a polishing pad were used to sand and polish the PC film to ensure a clean and proper fit to the ATR diamond crystal. After polishing, the film contained a hole at the top of the crystal feature, which, after bonding, allowed the ATR crystal access to the liquid flowing through the MF channel. Finally, the PC sheet and PC film were bonded under the temperature of 143 ℃ and pressure of 200 lb for 5 min and subsequently, cooled to 80 ℃ to obtain the MF device.

2. Recipes for the preparation of buffer solutions

To prepare 100 mL of 0.1 mol/L phosphate buffer (pKa1=2.15, pH = 2), 0.98 g of phosphoric acid were dissolved in 100 mL of deionized water. In addition, 0.305 g NaCl were added to maintain a total ionic strength at 100 mol/m^3. To prepare 100 mL of 0.1 mol/L phosphate buffer at pH =2 with the higher ionic strength of 1000 mol/m^3, 0.98 g phosphoric acid and 5.56 g NaCl were added to 100 mL of deionized water. To prepare 100 ml of 0.1 mol/L Tris buffer (pKa=8.06, pH=8), 1.211 g of Tris base were dissolved in 100 mL of deionized water and 0.235 g NaCl were added to maintain a total ionic strength of 100 mol/m^3. To prepare 100 mL of 0.1 mol/L Tris buffer at pH = 8 with the ionic strength of 1000 mol/m^3, 5.491 g NaCl were added to 100 mL of deionized water. To prepare 100 mL of 0.1 mol/L piperidine buffer (pKa=11.12, pH=11), 0.851 g of piperidine were dissolved in 100 mL of deionized water and 0.216 g NaCl were added to maintain a total ionic strength of 100 mol/m^3. To prepare 100 mL of 0.1 mol/L piperidine buffer at pH = 11 with the ionic strength of 1000 mol/m^3, 5.472 g NaCl were added to 100 mL of deionized water.

3. LbL film preparation and film thickness measurement

To prepare alternating adsorbed layers of polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH) using a static "dipping" method, a substrate (1cm x 1cm silicon wafer) was treated by oxygen plasma for 5 min and immersed into a PAA solution (2 mg/mL) for 5 min at room temperature, rinsed with water (pH=7.0), immersed into a PAH solution (2 mg/mL), incubated for 5 min at room temperature, and rinsed with deionized water (pH=7.0). This dip-wash-dip process was repeated 5 times.[1]

To form the same multilayer film under flow conditions, the surface of silicon wafer treated by oxygen plasma for 5 min was covered by a microchannel with dimensions of 0.4 mm (width) x 0.1 mm (height) x 10 mm (length).[2] A 2mg/mL PAH solution was purged for 5 min through the microchannel using a syringe pump. The channel was washed with deionized water (pH=7.0) for 5 min. Then, a 2 mg/mL PAA solution was injected in the channel for 5 min. This process was repeated for 5 times, with washing steps between polymer solution injection. The flow rates of the polymer solutions and water were 1.0 mL/hr. Ten layers were built on the silicon wafer

To measure the thickness of the PAA/PAH LbL film, a small piece of the film was peeled off the silicon surface, rinsed with water and air dried for 10 s. The thickness of the film was measured using surface profilometer (Dektak XT, Bruker). For each film, five locations were randomly selected on the film to measure film thickness and an average thickness was calculated. Measurements on the films were completed in less than one hour to avoid any thickness change due to the film dehydration. There was no noticeable change of film thickness in two hours at room temperature.

4. Adsorption of polystyrene sulfonate at pH=2

Adsorption experiments were carried out with PSS solution at polymer concentration 8 mg/mL at pH=2 and C_{NaCl}=1.0 M. The IR spectra shown in Fig. S1 were acquired after 25 min injection of polymer solution in the MF device (solid line) and after 25 min washing (dotted line), respectively. The dotted line clearly shows the characteristic peaks of PSS, which indicates that the PSS strongly adsorbs to the ATR-crystal surface.

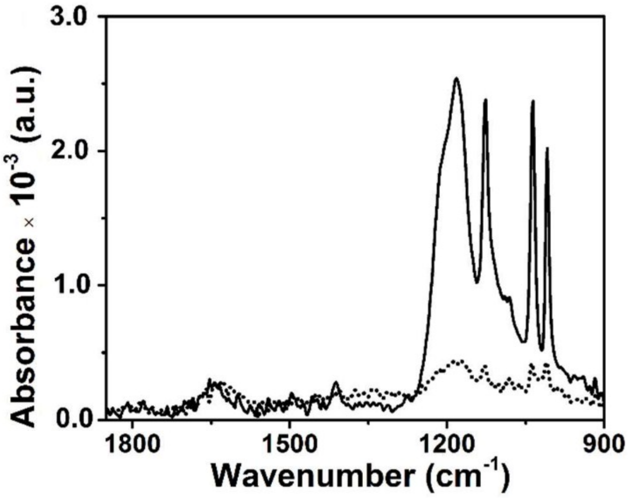

Fig. 1. Infrared spectroscopy characterization of adsorption of PSS from its solution in phosphate buffer solution at pH 2 with 1.0 M C_{NaCl}. Polymer concentration is 8 mg/mL. A pure buffer solution was introduced into the system after 25 min-long infusion of the polymer solution.

References

1. D. Yoo, S. S. Shiratori and M. F. Rubner, *Macromolecules*, 1998, **31**, 4309-4318.
2. S. A. Castleberry, W. Li, D. Deng, S. Mayner and P. T. Hammond, *ACS Nano*, 2014, **8**, 6580- 6589.