Supplementary Information

Visualization and characterization of interfacial polymerization layer formation

Yali Zhang[a], Nieck E. Benes[b], Rob G.H. Lammertink[a]*

[a]Soft Matter, Fluidics and Interfaces, [b]Inorganic Membranes, Department of Science and Technology, Mesa+ Institute for Nanotechnology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands

*E-mail: r.g.h.lammertink@utwente.nl

SI.1
Microchips fabrication

Both anodic bonding and thermal bonding have been employed for the microchips fabrication in this work. The anodic bonding provides a strong and irreversible bonding strength for the microchips. The covered glass layer can be etched away by hydrofluoric acid solution (50%) for the SEM samples preparation. However, the decomposition of Si-O-Si bond in hydrofluoric acid make such method inapplicable for the SEM sampling of POSS-TMC films. Therefore, a thermal bonded chip was utilized for the POSS-TMC film formation and its SEM sample preparation. Such method creates sufficient bonding strength to accomplish the experiment of film formation and allows a mechanical separation of the chips afterwards. The microchips fabrication by both the anodic bonding and thermal bonding processes, including their recycling procedures are described here,

Anodic bonded chips

- *Chips fabrication:*
  1) Fabricating microchannel and vale holes on a silicon wafer (diameter=10 cm, thickness =380 μm) by coupling the processes of standard photolithography with deep reactive ion etching.
  2) Cleaning both the glass and silicon wafers by immersing the wafers in 99% nitric acid for 20 min. Rinsing by DI water.
  3) Pre-bond the glass and silicon wafers by placing the glass wafer above the silicon wafer.
  4) Anodic bonding by Anodic bonder EV-501.
  5) Dicing into single chips in the size of 2 cm x 1.5 cm.

6) Hydrophobization and IP formation.

- *SEM samples preparation.*
  1) Seal the vale holes on the silicon slide by dicing foils.
  2) Etching away the glass slide by immersing the chip in hydrofluoric acid (50%) for 70 min. Rinsing by DI water.
  3) SEM imaging.

- *Recycling of the chips (without SEM sample preparation):*
  1) Etching away the complete glass slide by immersing the chip in hydrofluoric acid (50%) for 80 min. Rinsing by DI water.
  2) Cleaning the survived silicon slides by immersing the slide in acetone for 1 h, piranha solution for 14 min, nitric acid (99%) for 20 min.
  3) Immerse silicon slides in Hydrofluoric acid (1%) for 30 s.
  4) Dicing a glass wafer into slides in the same size as the silicon slides.
  5) Cleaning the glass slides in 99% Nitric acid for 20 min
  6) Pre-bonding followed by anodic bonding.
  7) Hydrophobization.

Thermal bonded chips

- *Chips fabrication:*
  1) Fabricating the microchannels and vale holes on the silicon wafers (diameter=10 cm, thickness =380 μm) by coupling the standard photolithography with deep reactive ion etching.
  2) Cleaning both the glass and silicon wafers by immersing the wafers in 99% nitric acid for 20 min. Rinsing by DI water.
  3) Pre-bond the glass and silicon wafers by placing the glass wafer above the silicon wafer.
  4) Placing the pre-bonded wafers in the furnace 400 °C for 4 h.
  5) Dicing into single chips in the size of 2 cm x 1.5 cm.
  6) Hydrophobization and IP formation
- *SEM samples preparation.*
  1) Separating the chip by applying mechanical force on the bonding edge.
  2) SEM imaging the POSS-TMC films formed in the microchannel.
- *Recycling of the chips(without SEM sample preparation)::*
  1) Cleaning the opened slides by immersing them in acetone for 1 h, piranha solution for 14 min, nitric acid (99%) for 20 min.
  2) Immerse silicon slides in Hydrofluoric acid (1%) for 30 s.
  3) Pre-bonding followed by thermal bonding
  4) Hydrophobization and IP formation.

Supplementary Information

SI.2

Interface control and pillar configurations

As described in the section 2.2, we attempted to create a stationary Aqu-Org interface for the IP films formation by process controlling. On one hand, the organic phase was introduced into the channel by providing the lowest feeding pressure after a stationary Aqu-G interface was generated. On the other hand, all the connections were opened to atmosphere pressure the moment the Aqu-Org interface was formed. As such, the formation process in terms of the reaction location and film growth rate were only reaction and diffusion controlled. Once the reaction started, the Aqu-Org interface was replaced by Aqu-film-Org interfaces. As a result of the film adhesion onto the channel wall, the initial position of the formed films can be localized till the end of the reaction, as indicated by the SEM images in Fig. SI(1). Therefore, the thickness of the film in time can be defined by the derivations of the L- film interfaces from this initial position.

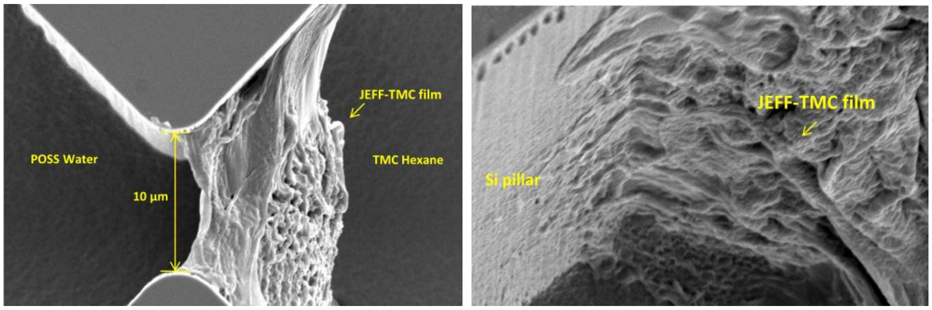


Fig. SI(1). SEM images of the JEFF-TMC films formed in the adjacent pillars.

We have designed more than 40 types of pillar structures in terms of pillar shape and pillar distance to optimize the L-L interface control and investigate their influence on the formed film morphologies. Some of the configurations with successful IP film formations are shown in Fig.SI(2)-(4). The pillar density (d, pillar length (horizontally) / pillar distance) is indicated in the images.

1. POSS

As can be seen, our designed pillar structures shows miner influence on the formed POSS film morphologies and thickness. POSS film establishes high homogeneities in terms of film thickness and morphology along all the pillar configurations (Fig. SI(2)). Observations of the film formation process can be problematic by the microscope when the pillar distance is shorter than 5 µm (d=2.5). Square pillars (Fig. SI(2), d=1) provides stable interface control. However, the cleaning flow after the reaction can easily break the films.

Supplementary Information

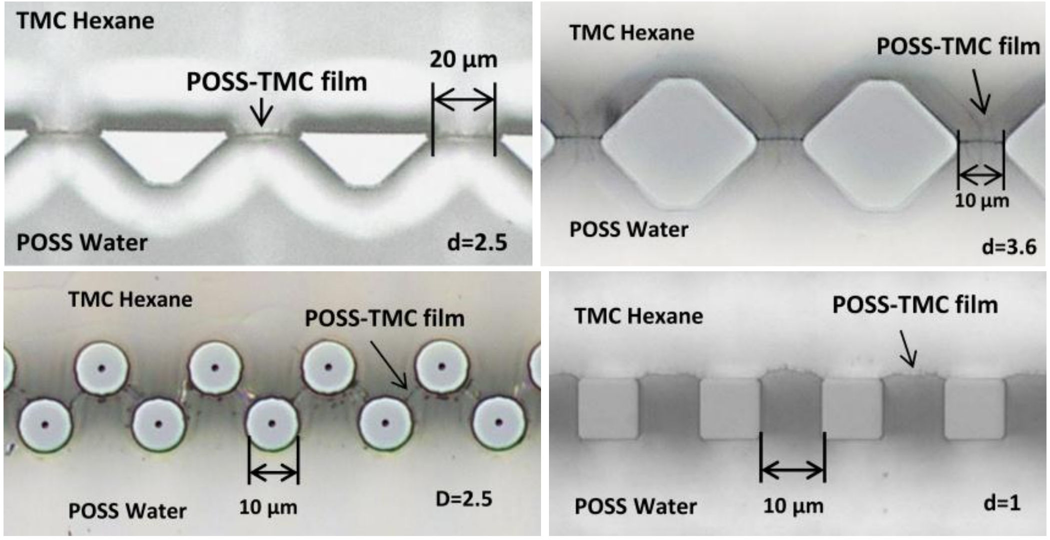
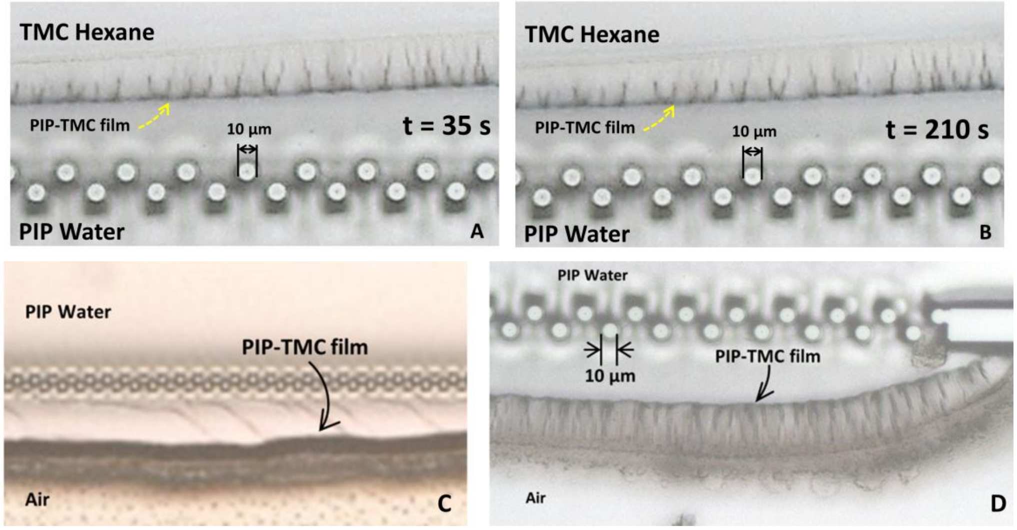


Fig. SI(2). POSS-TMC film formation in different pillar configurations.

2. PIP

During the formation process, PIP displays fast kinetics with TMC, which instantly shifts the interface from the initial position into the hexane phase (Fig SI.4(A)-(D). A ~20 µm thick film has been formed within 35 s and no growth in film density and thickness has been observed after that (Fig SI.4(A)-(B)). Such formation behavior implies a high preference of the formation location in the organic phase.

The formed PIP –TMC films are highly independent on the pillar configurations since the reaction instantly drives the film formation into the organic phase, in most of the cases (Fig. SI(3)). We have varied the PIP concentrations in water from 0.5 wt% to 2.5 wt%. The highest concentration of PIP solution drives the reaction into the organic phase the furthest and generates the thickest film. Only the lowest concentration can form films along the pillar-controlled interfaces.



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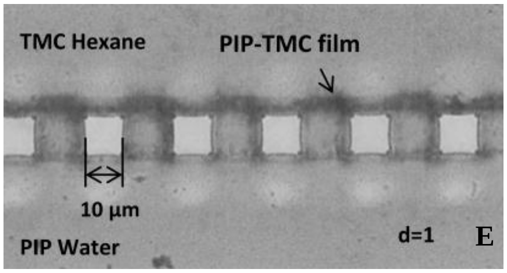

Fig SI(3). PIP films formed in variety concentrations.(A)-(B) 0.5 wt%. (C) 2.5 wt%. (D) 1 wt%. (E) 0.5 wt%. (A)-(B) PIP-TMC film formation at different time steps. d=1 for all the pillar structions.

3. JEFF

The formed JEFF-TMC film can be influenced by the pillar structures in some aspects (Fig. SI(4)). The appearance of the rough and irregular morphologies shows in all the pillar structures. Multi-layer morphologies in the organic sides have been frequently observed(B).

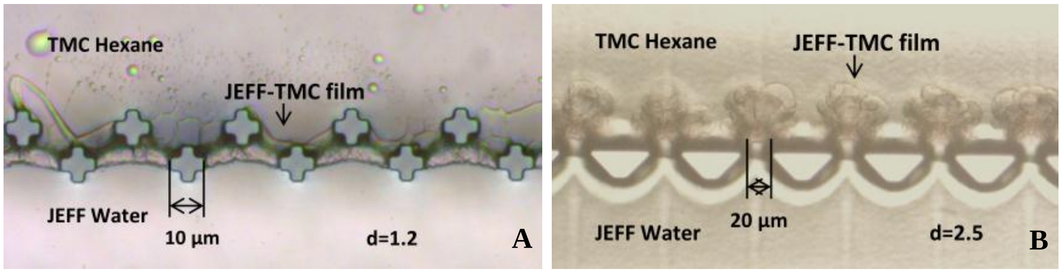

Fig. SI(4). JEFF-TMC film formation in different pillar configurations.

SI.3

Hexane permeability test by POSS-TMC films

The hexane permeability of POSS-TMC film has been tested in this study. We have firstly emptied the water-side channel by an air flow and then opened this channel to the atmosphere. After that, the other channel has been filled by hexane (Δh=350 mm) and its inlet and outlet have been blocked to maintain a certain pressure and prevent the evaporation of hexane. The system has been placed stationary for 17 h. We observed no difference in the hexane side channel but only a little wetting on the film-Air interface.

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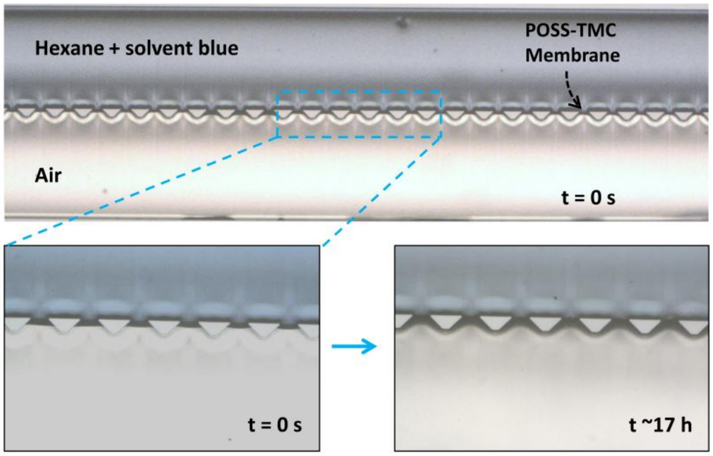

Fig. SI(5). Hexane permeability test by POSS-TMC film.