

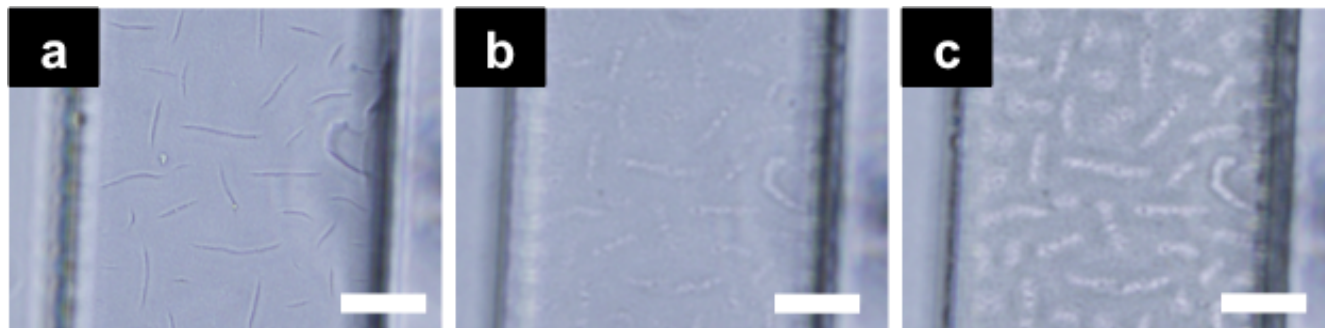
Supplementary Information

Reaction-diffusion reactions occur in a PMDS elastomer matrix and can modify its
topography

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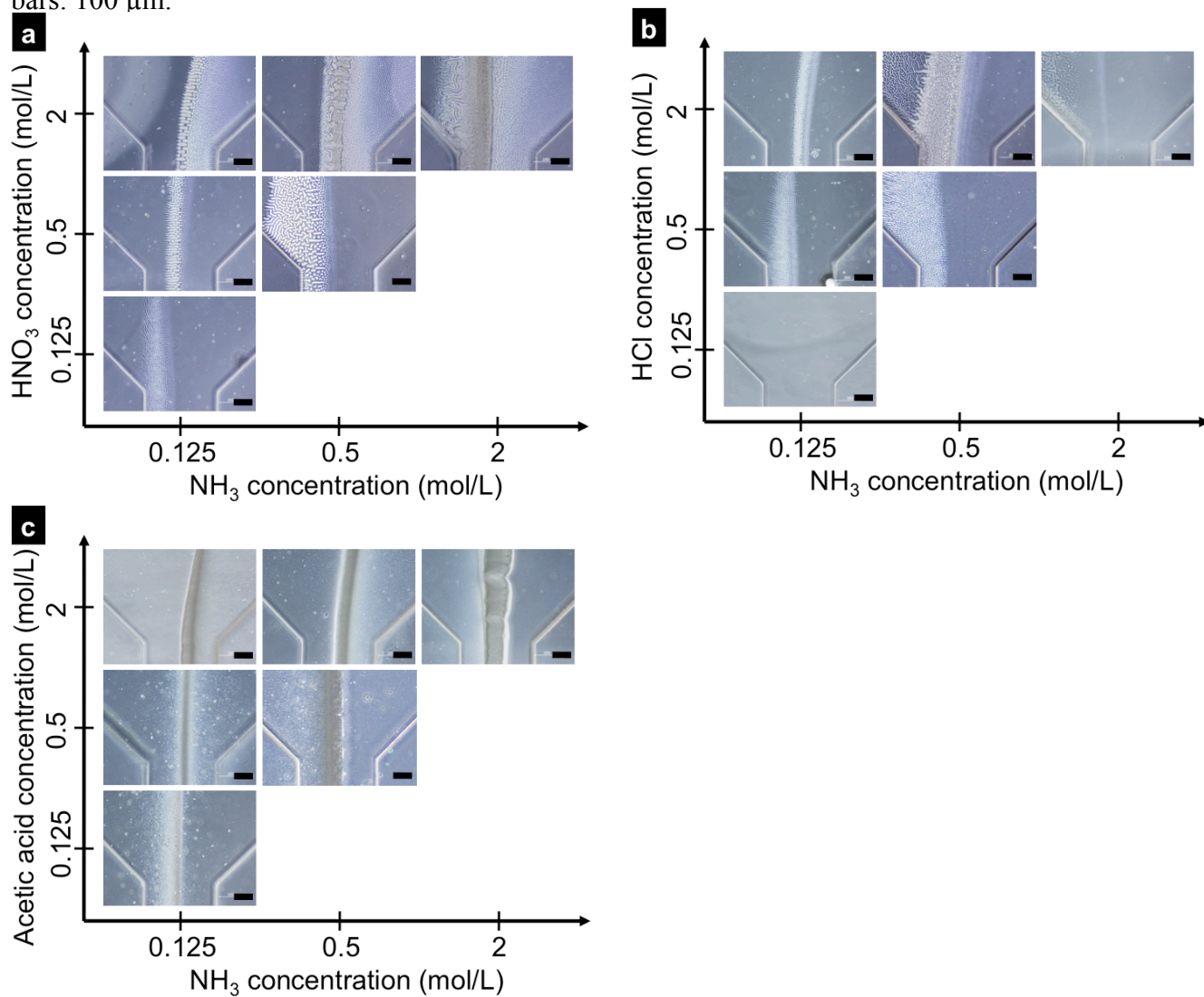
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Figure S1: Swelling of the wrinkles



(a) Optical micrograph of a dried modified PDMS channel (11X repeated sequence of injections: NH_3 for 1 min, HNO_3 for 5 min). (b) Optical micrograph of the same channel 20 s after the addition of water. (c) Optical micrograph of the same channel 130 s after the addition of water. Scale bars: 50 μm .

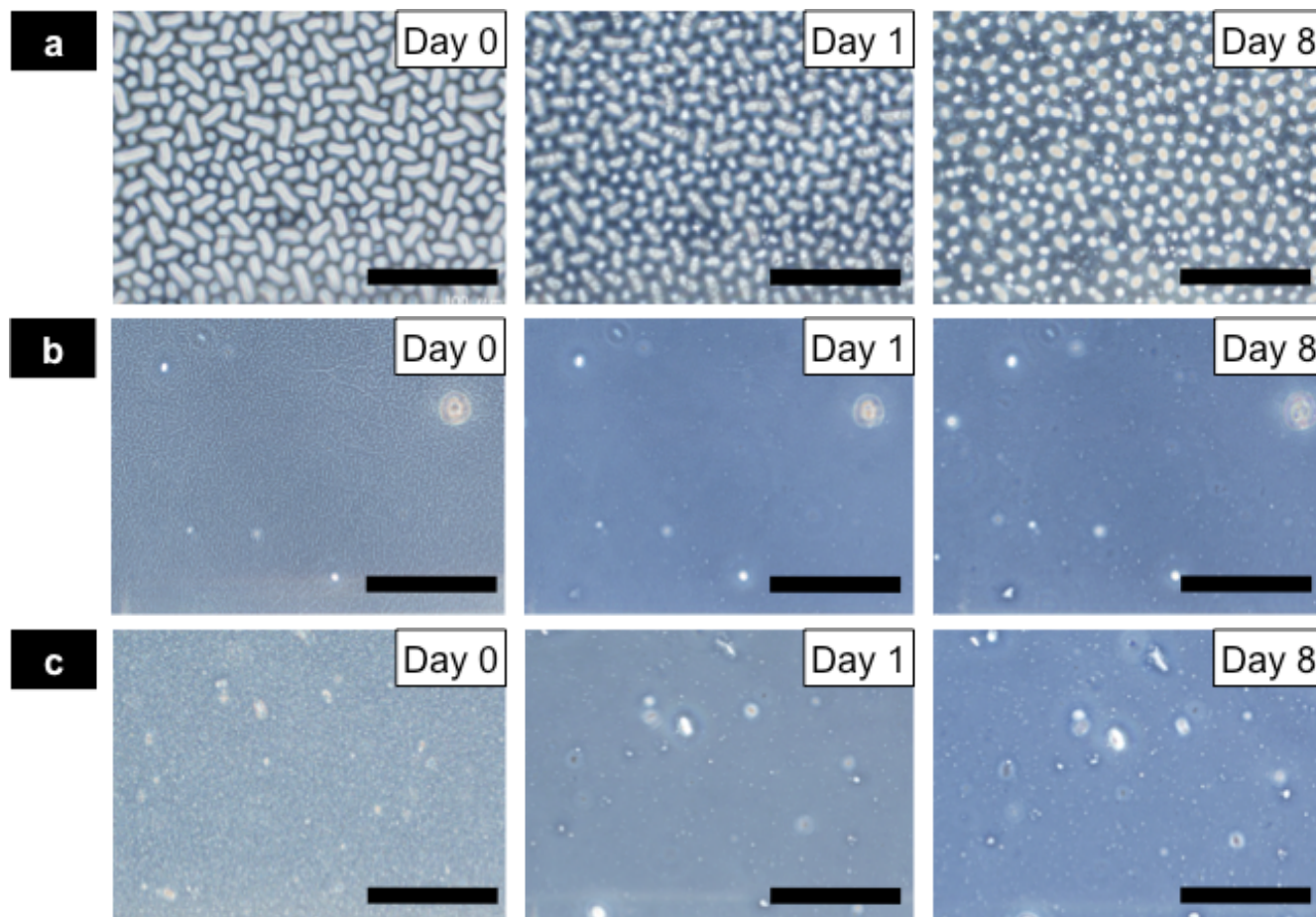
Figure S2: Effect of various combinations of acid and ammonia concentrations on the topography of a PDMS microdevice with side-by-side reagent flow. The device geometry and the flow parameters are the same as described in Figure 3a. The devices were filled with water before the photograph was taken. The acid used in these reactions is (a) HNO_3 . (b) HCl . (c) CH_3COOH . Scale bars: 100 μm .



Supplementary Data S1: Stability of topographical modifications

With the repeated alternate injection sequence protocol (Supplementary Figures S2), the most notable change in the modified surface occurs in the first 24 hours after fabrication as a result of the addition of hydrochloric and acetic acids. Wrinkles are barely visible in these figures, and the pores have almost disappeared. For nitric acid, the wrinkles are fainter, but λ is constant until 48 hours, after which the wrinkles begin to split (not shown). After these initial changes, the surface remains relatively constant after treatment with each acid for at least until one week after the fabrication.

Figure S3. Stability of topographical modifications vs. time after repeated (6X) alternate injection of the reagents (contact time: 5 min).

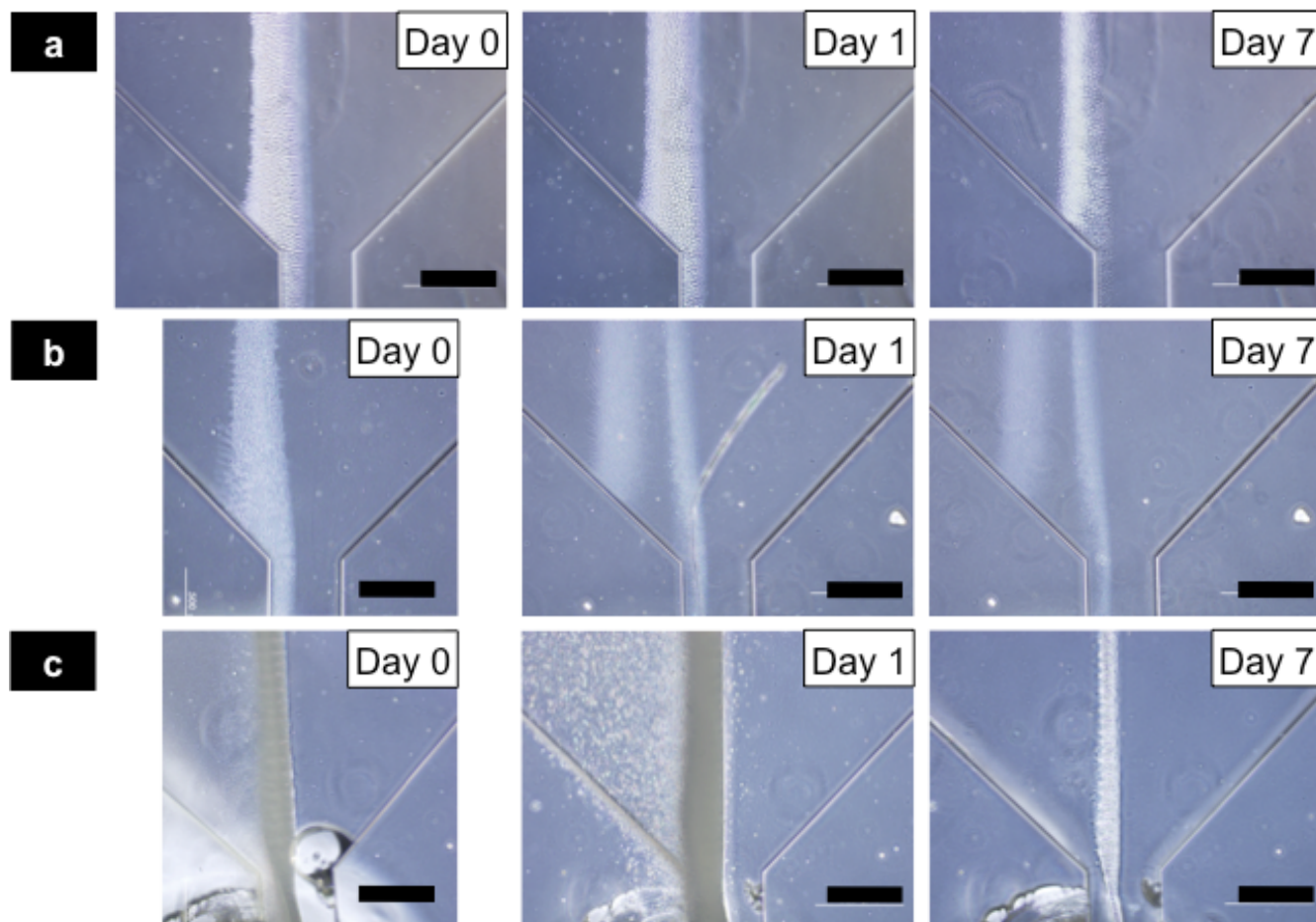


(a) HNO_3 (b) HCl (c) CH_3COOH . All devices were filled with water before the photograph was taken. Scale bars are 100 μm .

In the aforementioned injection protocol with side-by-side flow of the reagents (Supplementary Figures S3), the three acids show similar behavior in the first 24 hours: the area occupied by wrinkles and pores expanded slightly on the side opposite the ammonia stream. Specifically, the larger wrinkles obtained with HNO_3 were split into smaller ones; the long, straight wrinkles obtained with HCl are connected by smaller transverse wrinkles; for CH_3COOH , the pores appear to expand. For all acids, the small wrinkles/pores near the ammonia stream almost didn't change during this time period. Indeed, the wrinkles/pores appeared at this location first during experiments, meaning that these structures had more time to stabilize, compared to wrinkles and pores forming farther from the interface. After one week, the structures were still present but appeared fainter than they did initially because only larger

wavelengths were still visible and the scattered pores far from the interface disappeared. With acetic acid, it was also difficult to confirm whether the remaining structure was still composed of pores. After this point, the remaining wrinkles remained constant for many weeks/months, especially with the high λ obtained with long fabrication times and high concentrations of reagents (not shown).

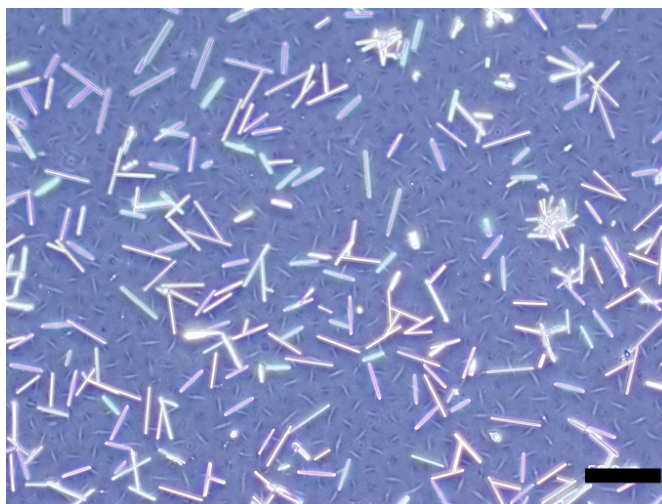
Figure S4. Stability of topographical modifications vs. time in the case of side-by-side reagent flow.



(a) HNO_3 (b) HCl (c) CH_3COOH . All devices were filled with water before the photograph was taken. Scale bars are 100 μm .

Furthermore, a noteworthy phenomenon was observed approximately 24 hours after the contact angle measurements for the samples prepared with HNO_3 (not observed on the surface modified with HCl or CH_3COOH): many rod-shaped microcrystal-like structures appeared on the surface (Supplementary Figure S4). These rod-shaped structures were relatively monodisperse and possessed a high aspect ratio, with a width measuring less than 1 μm and lengths ranging from 10 to 30 μm . These structures could be transferred to another substrate (like glass or silicon) by stamping and were very hygroscopic. This last observation and the fact that only ammonia and nitric acid were used suggest that the rods were probably composed of NH_4NO_3 . Nevertheless, the rods disappeared following a thorough rinse with water and were not observed in the microchannels, probably because of a more efficient rinsing step or because of different drying conditions in the channels. Time-lapse micrographs of the formation of the rods (Supplementary Figure S5) showed that they arose from below the surface. This suggests that some channels/pockets exist below the surface, where salt or reagents are trapped.

Figure S5. Rod-shaped structures appearing on the top of a modified open-surface.



Optical micrograph of structures on the surface of the PDMS modified by HNO_3 and used for contact angle measurement. Scale bar: 50 μm .

Figure S6. Time-lapse microphotography of the formation of rod-shaped salt crystals. Scale bars are 75 μm .

