ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for

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Supporting Information for the Manuscript:

PVA Scaffolds with Tailored Morphologies for Drug Delivery and Controlled Release

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Figure S1: Optical microscope images of crystalline CFX needles in the PVA2-CFX5 (left) and PVA2-CFX10 (right) suspensions used for scaffolds preparation. Bar is 50 μm.

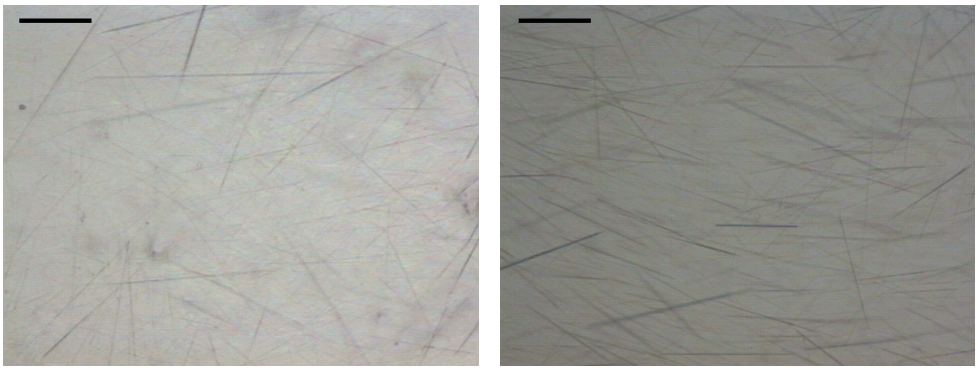


Figure S2: SEM micrographs of ISISA processed PVA2-CFX10 scaffolds at a freezing rate of 0.7 (left, bar is 50 μm) and 9 mm/min (right, bar is 20 μm).

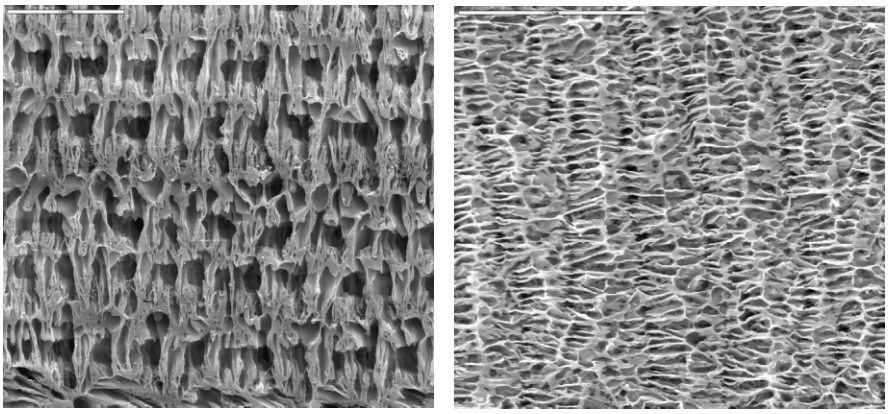
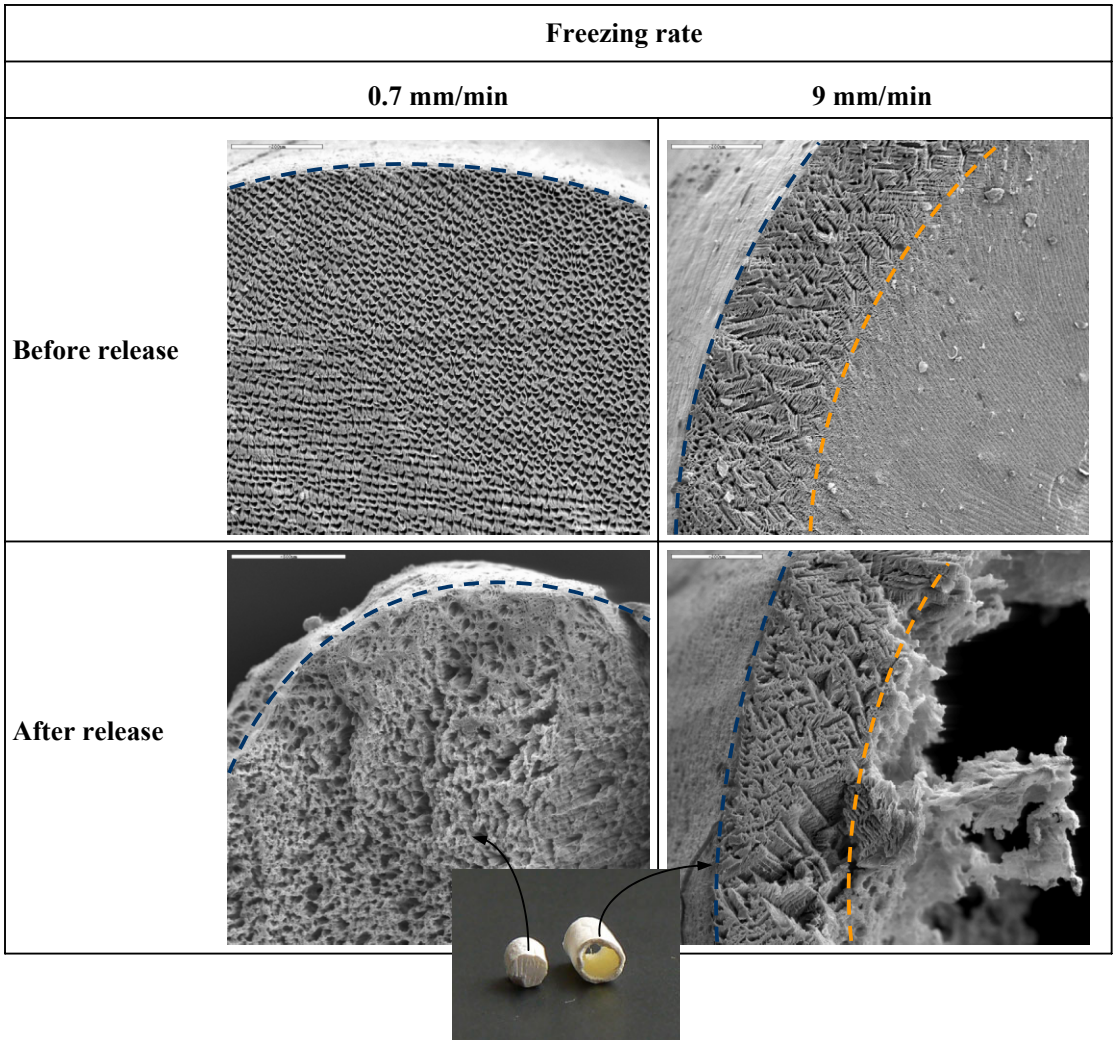


Figure S3: SEM micrographs of ISISA processed PVA2-CFX5 scaffolds at freezing rates of 0.7 (left column) and 9.1 mm/min (right column), before (top line) and after (lyophilized samples, bottom line) release experiments. Dash blue lines indicate the perimeter of cylindrical monoliths for better visualization. Dash orange lines indicate the border between the two distinguishable morphologies observed in PVA scaffolds prepared at freezing rates of 9.1 mm/min. Bars are 200 µm except for the micrograph situated at the left bottom corner that is 500 µm. The picture shows the lyophilized monoliths of PVA2 scaffolds prepared at freezing rates of 0.7 (left) and 9.1 mm/min (right) after release experiments



The SEM micrograph of cross sectioned PVA scaffolds prepared at freezing rates of 0.7 mm/min reveals a homogeneous microchannelled structure all over the entire sample (left upper corner). After release experiments (scaffolds overcome hydration and swelling), the SEM micrograph of lyophilized PVA scaffolds (left bottom corner) show the microchannelled structure basically intact with just some shape distortion of porosity.

The SEM micrograph of cross sectioned PVA scaffolds prepared at freezing rates of 9 mm/min reveals the formation of two distinguishable microchannelled structures; the external one of ~300 μm thickness at the periphery of the cylindrical monolith and the internal one forming a cylindrical core of 3.4 mm. Such heterogeneity is most likely consequence of the fast freezing rate, that does not allow the freezing temperature to stabilize all across the entire sample; i.e., the freezing temperature in the internal core of the cylindrical monolith is lower than at the periphery, which results is formation of small ice crystals (or eventually of amorphous ice) at the core and large ice crystals at the periphery. After release experiments, the SEM micrograph of lyophilized PVA scaffolds (right bottom corner) shows a noticeable loss of matter at the inner zones of the monolith. The matter at the periphery remains (as correspond to morphologies with large accumulation of matter between adjacent microchannels), forming a crown of ~300 μm thickness all around the external perimeter of the monolith.

Figure S4: SEM micrographs of a cross sectioned PVA2 scaffold ISISA processed at a freezing rate of 5.9 at the periphery (bar is 50 μm) of the sample. Dash red line indicates the perimeter of the cylindrical monolith. **Inset:** Detail of the microchanel structure (bar is 10 μm). Micrographs reveal the microchannelled structure is homogeneous all over the entire cross section of the sample. Bar is 50 μm.

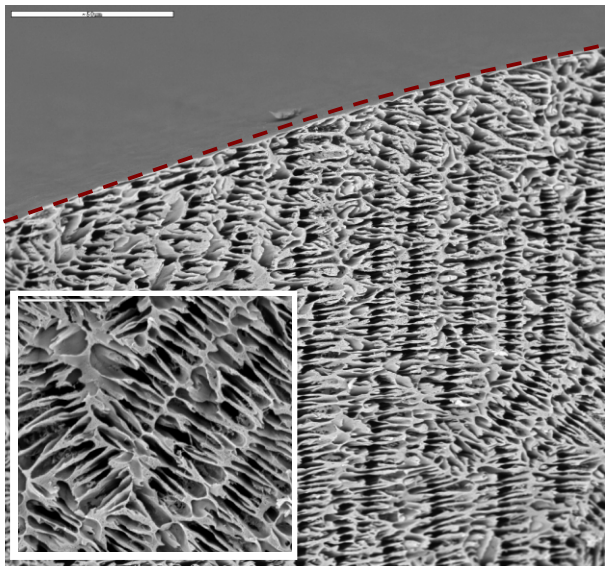


Figure S5: SEM micrographs of PVA3 and PVA4 scaffolds (7.8 wt. %) ISISA processed at a freezing rate of 0.7 mm/min. Bars are 5 μm.

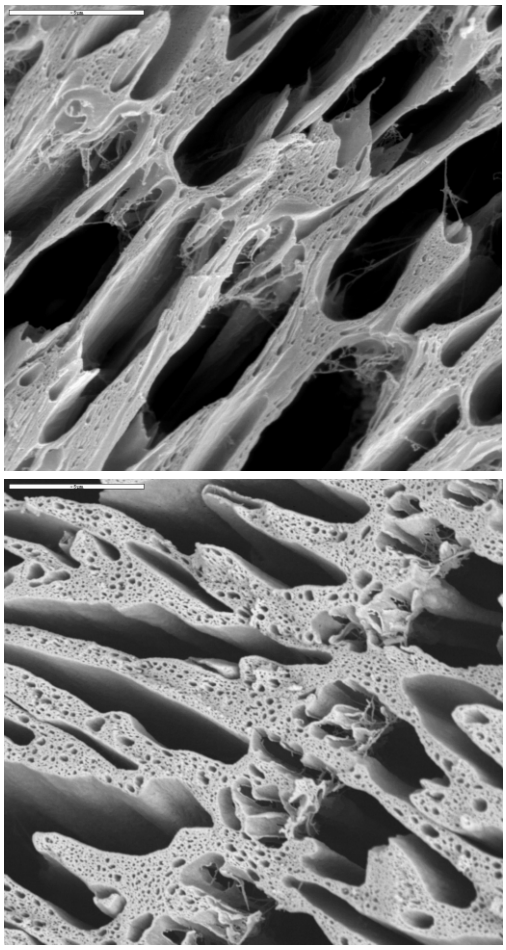


Figure S6: (a) DSC curves for PVA2 scaffolds ISISA processed at freezing rates of 0.7 (green), 2.7 (orange), 5.9 (blue) and 9.1 mm/min (red) and, **(b)** for PVA1 (magenta), PVA2 (blue), PVA3 (pink) and PVA4 (dark yellow) scaffolds ISISA processed at a freezing rate of 5.9 mm/min.

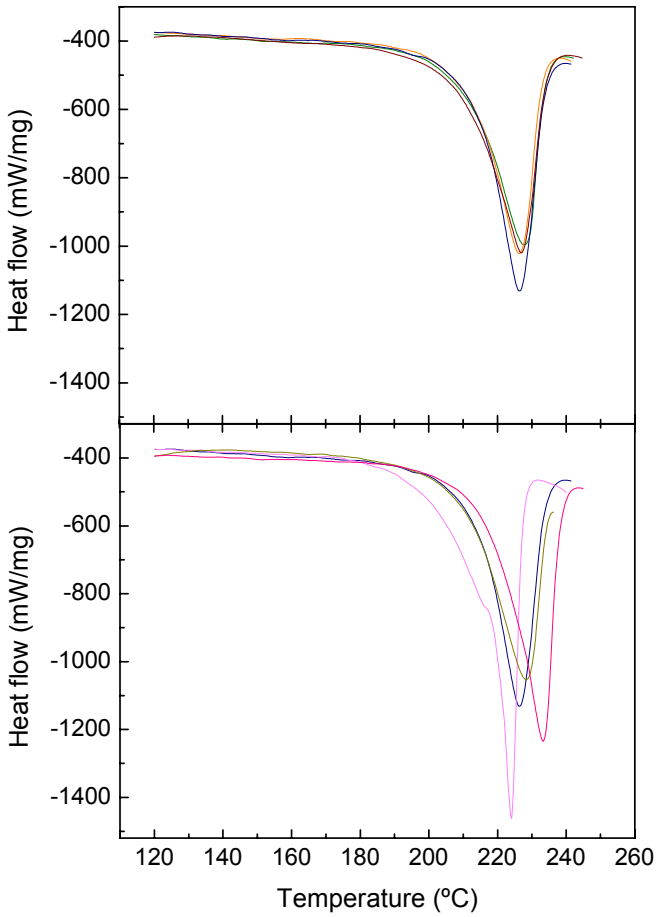


Figure S7: Representative XRD pattern of PVA1 scaffold ISISA processed at 0.7 mm/min. Scaffolds prepared from PVAs of different molecular weights (within the studied range, PVA1-PVA4) and ISISA processed at different freezing rates (within the studied range, 0.7-9.1 mm/min) do not exhibit significant differences.

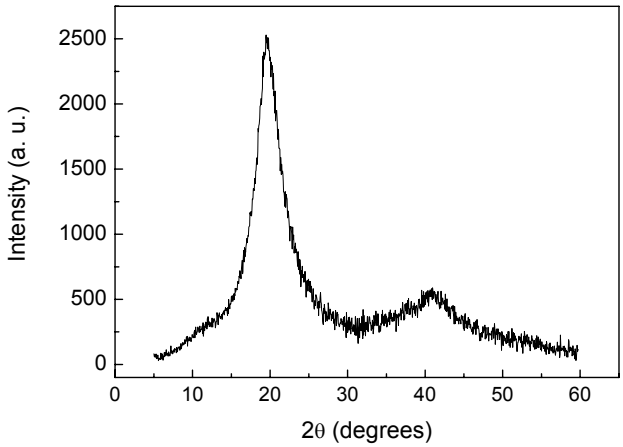


Figure S8: Kinetics of CFX release from PVA2 scaffolds ISISA processed at freezing rates of 0.7 (red squares), 2.7 (orange triangles), 5.9 (magenta inverted triangles) and 9.1 mm/min (blue circles), and PVA3 scaffolds prepared at freezing rates of 0.7 mm/min (green square). Experiments were conducted on PVA scaffolds containing 10 mg of CFX. Pictures show wet and lyophilized PVA2 scaffolds ISISA processed at 2.7 (right) and 5.9 (left) mm/min, after release experiments. In this case, the weight loss was ca. 43% and 52%, respectively. Such a remarkable weight loss does not result in full erosion of the internal core (because of their radial homogeneous morphology, see Figure S4), albeit it does in monolith deformation (mainly for the monolith ISISA processed at 5.9 mm/min).

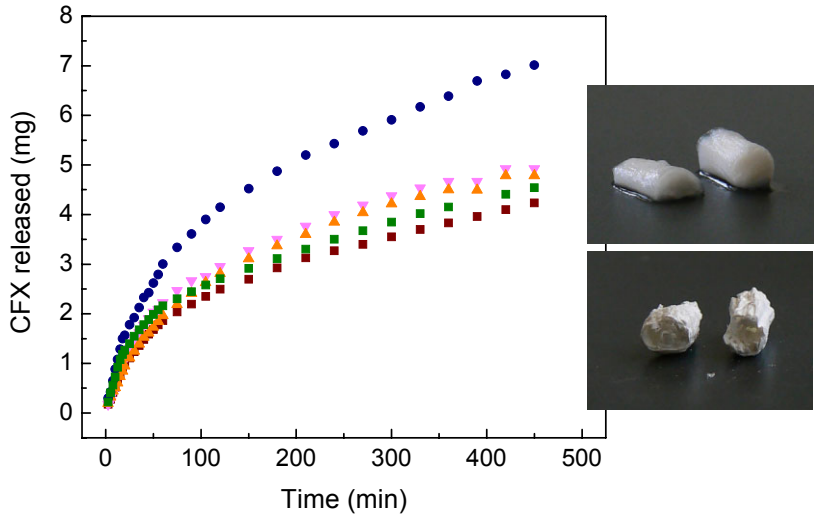


Figure S9: The flask at right hand shows that bacteria growth is fully inhibited (optical density of solution is negligible) by addition of very small pieces of PVA2-CFX monolith. In this case, the PVA2-CFX scaffolds need to release CFX into the solution for ca. 6 hours to reach the concentration that inhibits growth (MIC value). After release for 24 hours, this solution would reach a CFX concentration just 2-fold above MIC. The flask at left hand is that shown in Figure 7a (after release for 24 hours, this monolith would provide a CFX concentration 3000-fold above MIC in solution) and it is included for comparison. Red arrows point to PVA2-CFX monoliths (very small pieces in the right flask) used for the experiment.