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ARTICLE

Temperature and pH Responsive 3D Printed Scaffolds

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Synthesis and proof of copolymerization

FdMA was synthesized by reacting the hydroxy end groups of the F127 triblock with 2-Isocyanatoethyl methacrylate in a 1:2 molar ratio, as shown in Figure S1

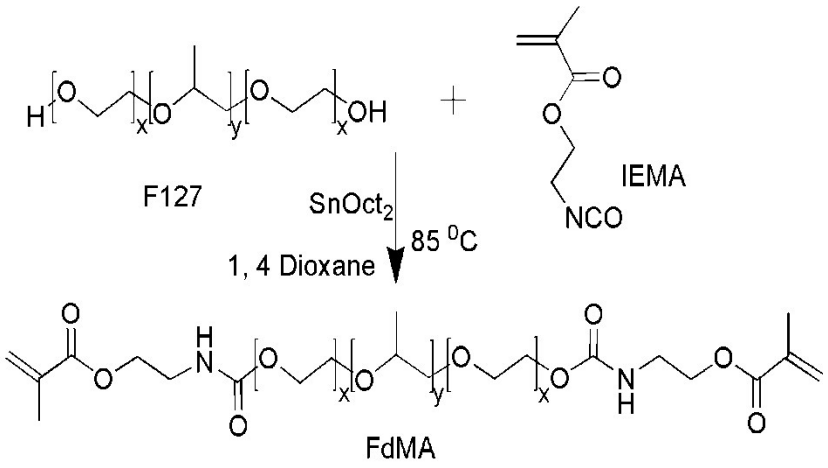

Figure S1. Synthesis scheme of FdMA.

The duplet peaks due to the unsaturated bond appeared at 5.62 ppm and 6.18 ppm, as shown in **Figure S2**, below. The introduction of the methacryloyl group allowed the identification of the peak corresponding to the last methylene unit of the PEO block, which was shifted downfield to 4.3 ppm.

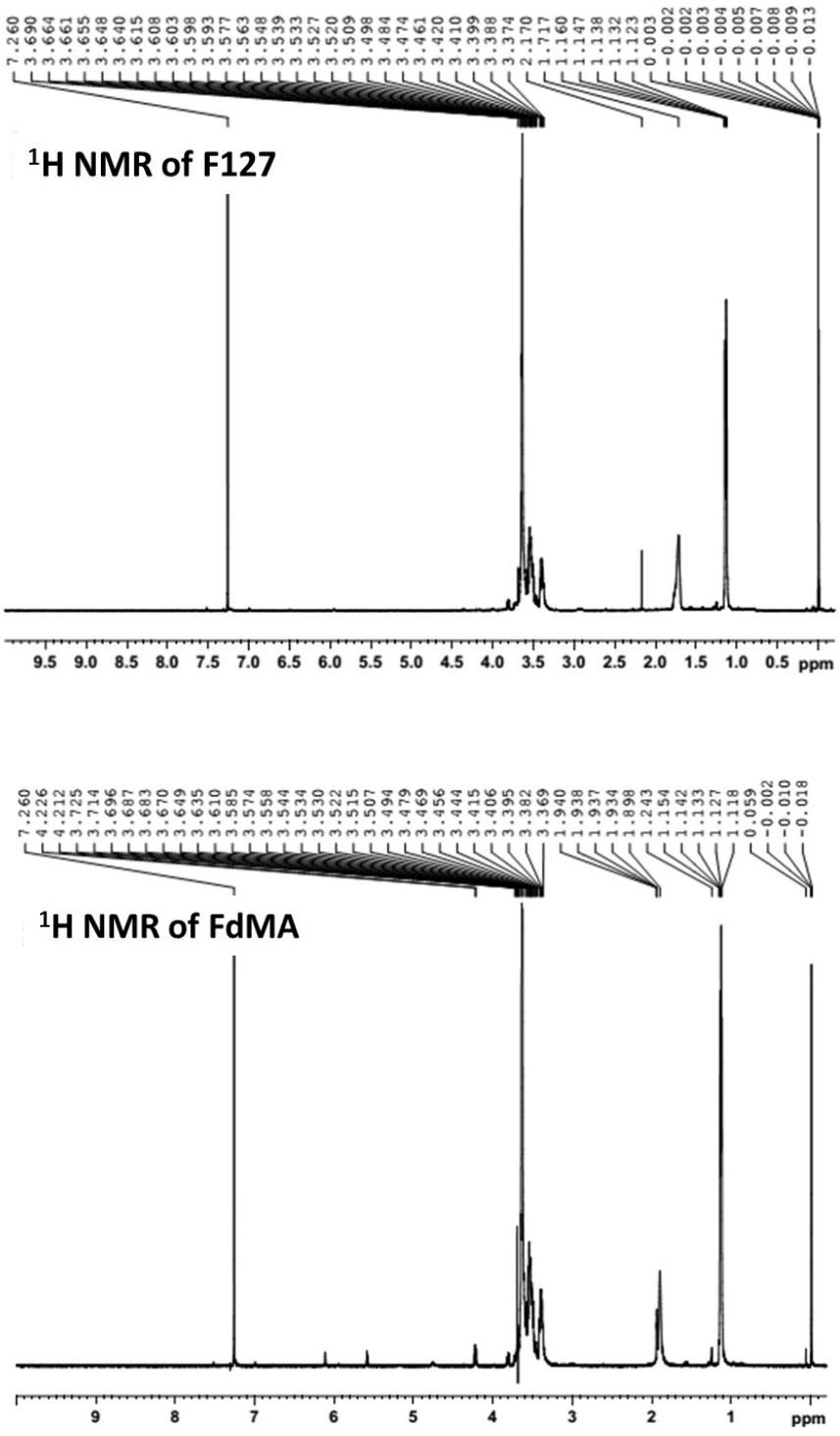

Figure S2. ^{1}H-NMR spectra of F127 and FdMA.

Thus, the integration of the vinyl protons and the above mentioned methylene group allowed the quantification of the functionalization yield, indicating that the functionalization was complete, or in other words, that two C=C bonds were introduced in each triblock chain.

FTIR spectroscopy was performed to provide additional proves of both the reaction of F127 with IEMA and the copolymerization of the resulting FdMA with acrylic acid. F127 showed its characteristic peaks (see **Figure S3**), most importantly, the large and sharp ether peak at 1109 cm^{-1}. FdMA showed peaks at 1720 and 1635 cm^{-1}, corresponding to the carbonyl vibration of the ester group and to the vinyl double bond, respectively.

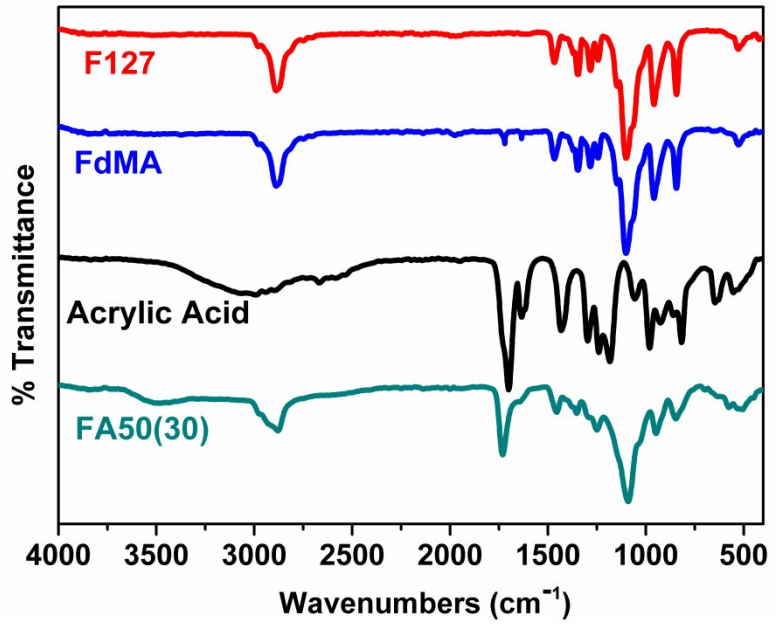

Figure S3. FTIR spectra of F127, FdMA, acrylic acid FA50(30) hydrogel.

These findings demonstrate the occurrence of the reaction between the hydroxyl group of F127 and IEMA, and the generation of FdMA. The key peak of acrylic acid due to the C=O of its carboxylic group can be readily seen at 1700 cm^{-1}. Once crosslinked, the gel was thoroughly rinsed in water, a step that would solubilize the water soluble polyacrylic acid that did not copolymerize with FdMA. Peaks due to F127, its 1109 cm^{-1} large ether group, and acrylic acid's typical C=O stretching vibration at 1735 cm^{-1}, were observed in the copolymer. Furthermore the vinyl double present in FdMA at 1635 cm^{-1}, disappeared following crosslinking.

Morphology study

The HR-SEM micrographs of freeze-dried FA0 and FA50 hydrogels, fully hydrated at pH 2.0 and pH7.4 at 6 °C and at 37 °C, are shown in **Figure S4**. As anticipated, lacking acrylic acid, FA0 exhibits only reverse thermo-responsiveness, with the FdMA matrix being denser above its LCST transition (at 37 °C), when compared to 6 °C, while no difference

was observed, when changing the pH, from 2.0 to 7.4. In striking contrast, FA50 displayed dual responsiveness, with both temperature and pH affecting the behavior of the hydrogel. As also seen when studying the water absorption of the different gels (see Figure 2), the effect of pH is markedly larger than that of temperature, as demonstrated by the highly porous structures generated at pH 7.4, contrasting to the compact structure at pH 2.0.

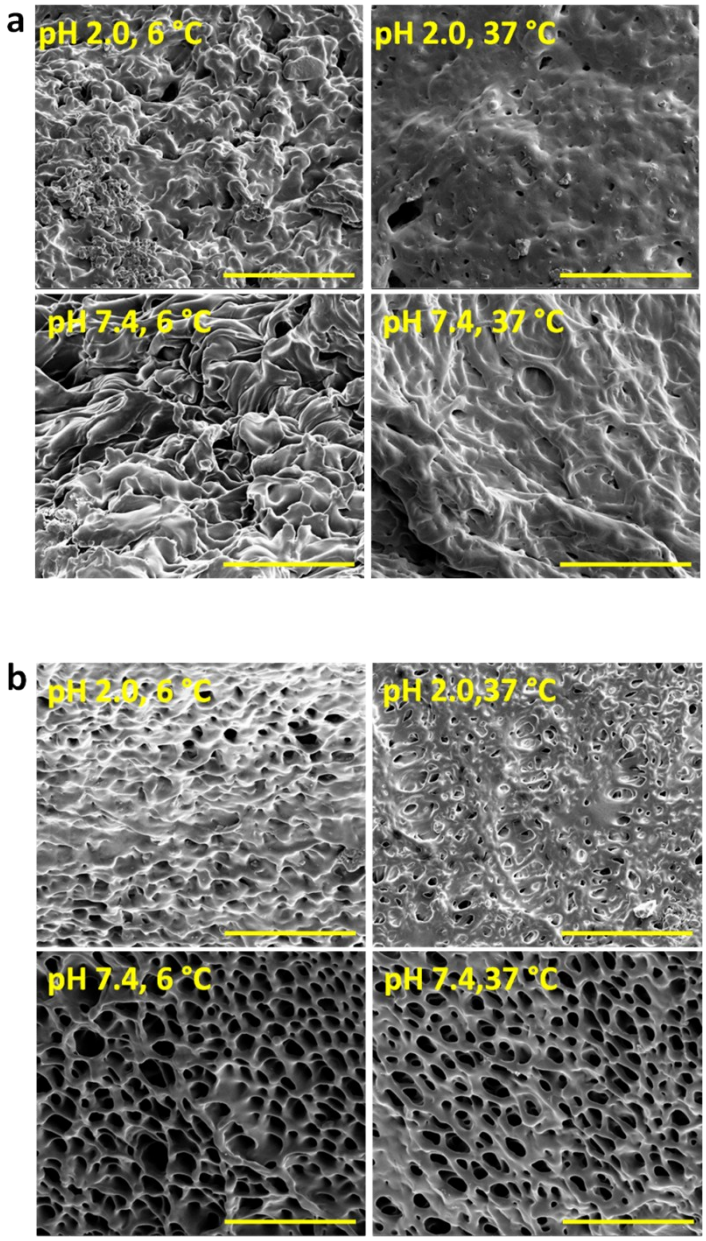

Figure S4. SEM micrographs of (a) FA0 and (b) FA50 hydrogels at different conditions.

Mag: x4,000. Scale bar: 30 μm.