

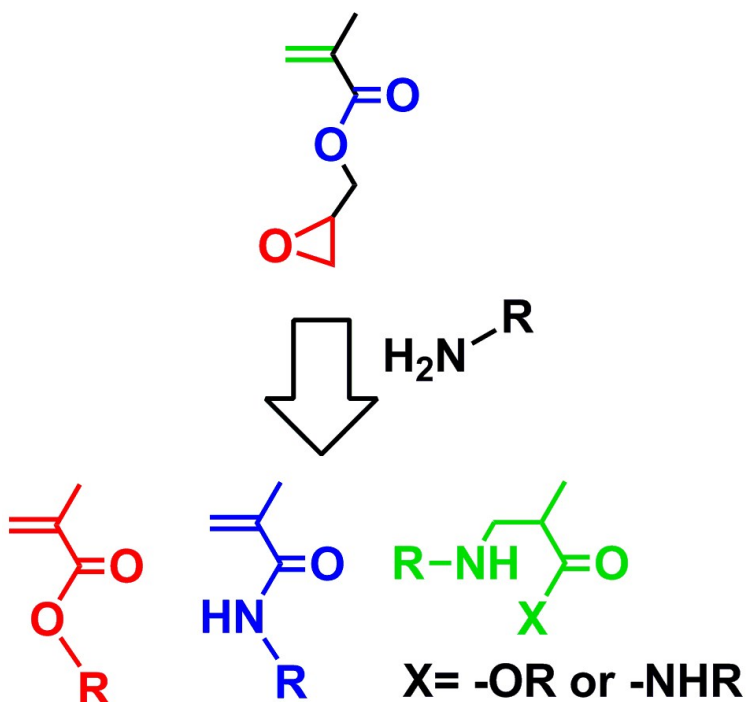
# Synthesis of Hydrogel PolyHIPEs from Functionalized Glycidyl Methacrylate

David Pahovnik,<sup>a</sup> Janja Majer,<sup>b</sup> Ema Žagar<sup>a</sup> and Sebastijan Kovačič<sup>\*a</sup>

<sup>a</sup> Department for Polymer Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia.

<sup>b</sup> University of Maribor, Faculty of Natural Sciences and Mathematics, Koroška 160, 2000 Maribor, Slovenia.

*Electronic Supplementary Information*



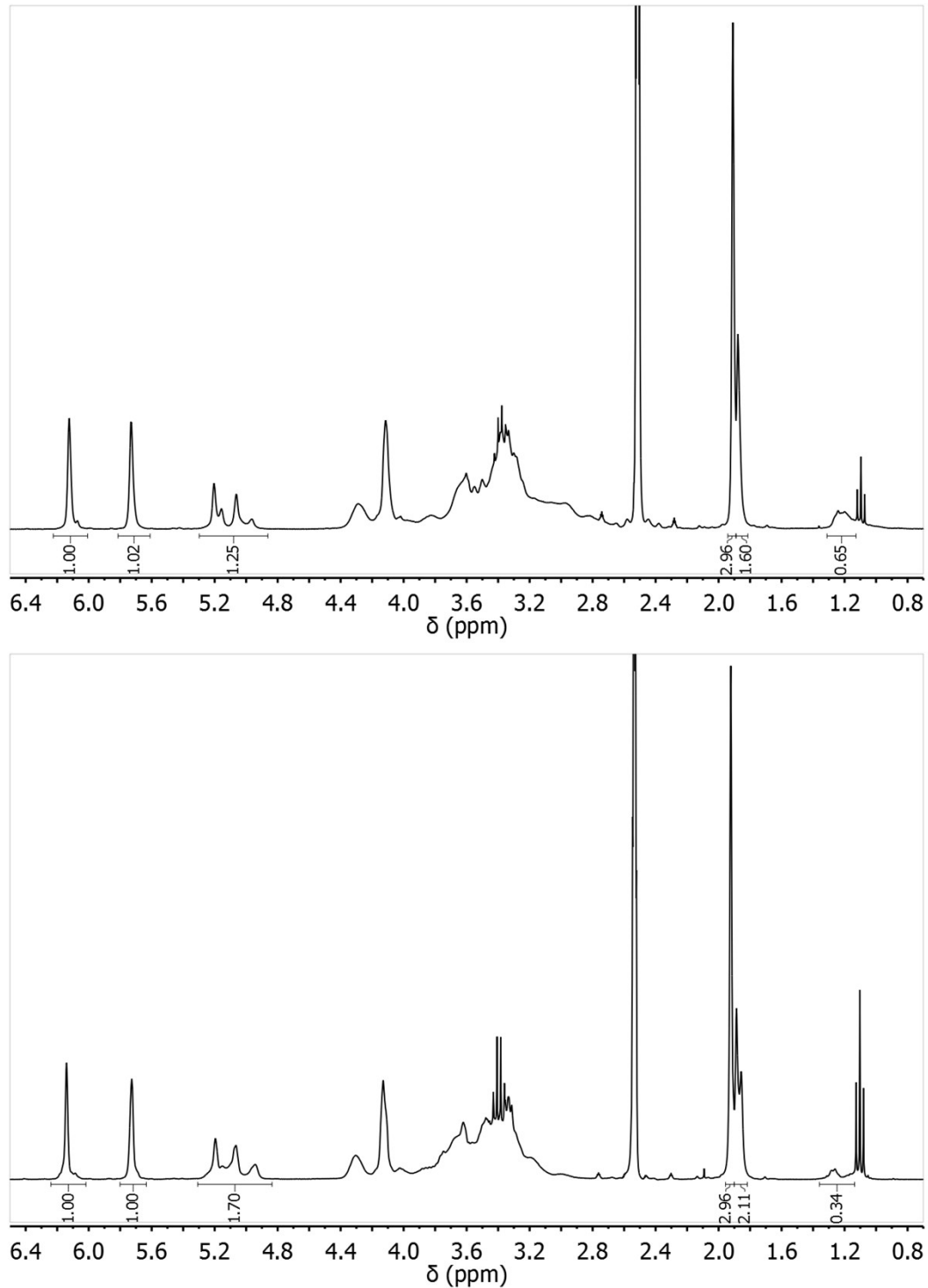
**Table S1** Recipes for O/W HIPEs.

	<b>p(GMA-TRIS)<sub>pre</sub></b> <b>polyHIPE</b>	<b>p(GMA-EDA)<sub>pre</sub></b> <b>polyHIPE</b>
<b>Aqueous External Phase, wt. %</b>		
H <sub>2</sub> O	19.59	19.28
monomer	7.25	7.02
MBAA	0.24	0.41
Triton X705	6.53	6.61
Total	33.62	31.32
<b>Organic Internal Phase, wt. %</b>		
Toluene	66.23	66.53
AIBN	0.15	0.15
Total	66.38	66.68

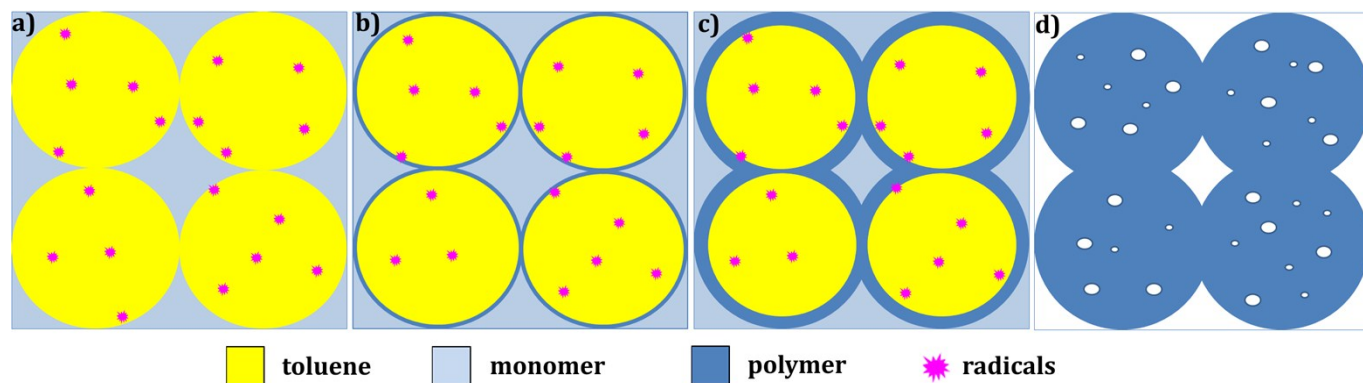
**Table S2** Recipe for W/O HIPE.

	<b>p(GMA)</b> <b>polyHIPE</b>
<b>Organic External Phase, wt. %</b>	
GMA	15.35
EGDMA	2.36
L121	3.95
Total	21.66
<b>Aqueous Internal Phase, wt. %</b>	
H <sub>2</sub> O	77.93
APS	0.34
TMEDA	0.08
Total	78.34

## NMR characterization



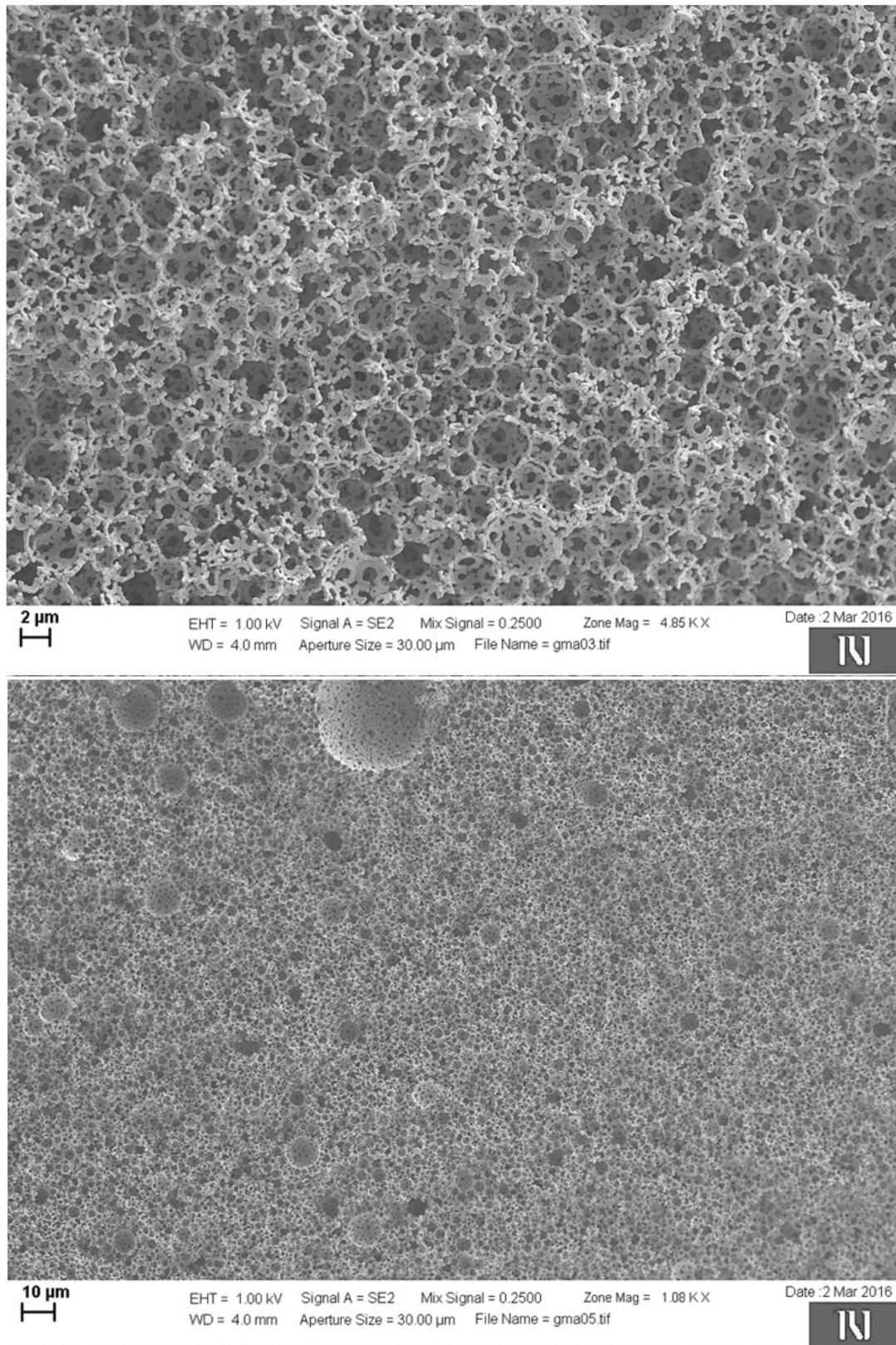
**Figure S1.**  $^1\text{H}$  NMR spectra of TRIS (top) and EDA (bottom) modified GMA. Ratio between the extents of individual reactions was calculated from the integrals of the signals for the double bond of methacrylate and methacrylamide groups, and the methyl group of  $\beta$ -aminoester.



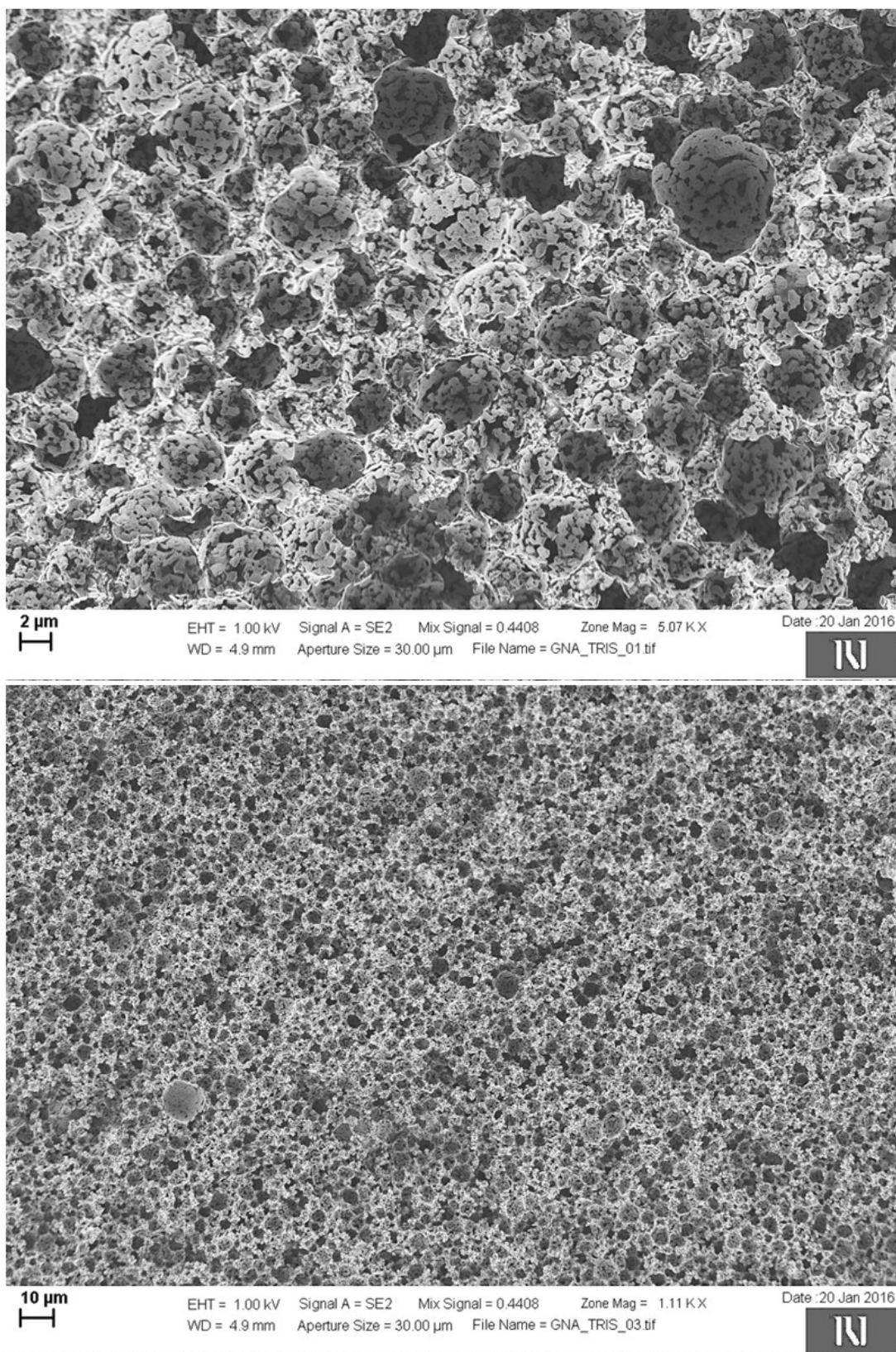
**Figure S2.** Schematic illustration of the polymerization path (a) interfacial initiation (b, c) polymeric film formation, and (d) structure after purification.

### Scanning Electron Microscopy (SEM) investigations

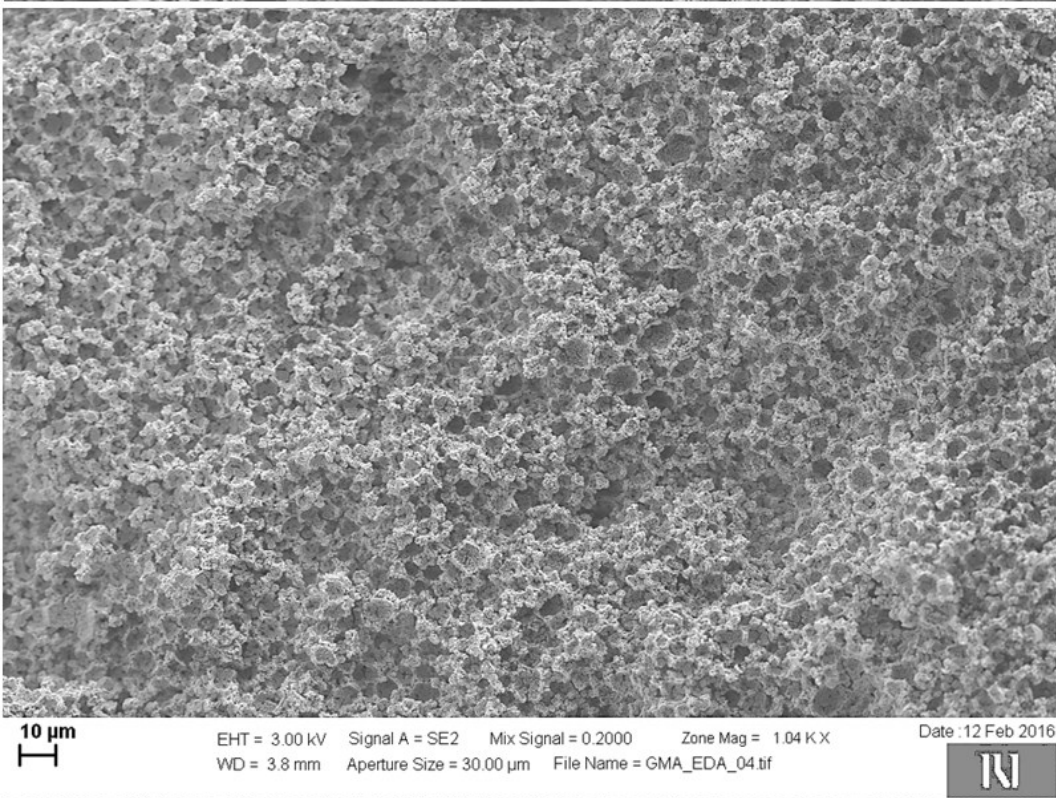
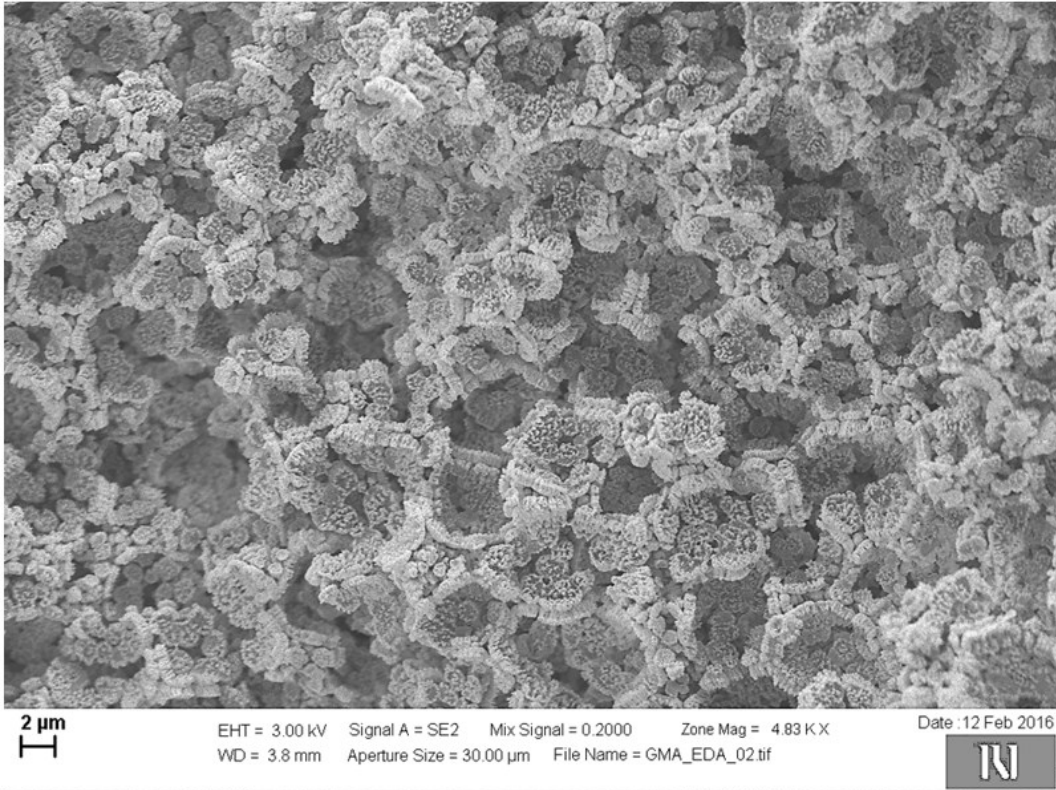
Morphology investigations of samples were performed by SEM. SEM images were taken on a Carl Zeiss, SUPRA 35 VP microscope, Germany. A piece of each sample was mounted on a carbon tab for better conductivity and a thin layer of gold was sputtered on the sample surface prior scanning analysis. An average void size was determined from SEM micrographs analysis after scanning. Therefore, the mean and the standard deviations were drawn by manual measurements of diameters from a population of at least 50 – 100 voids. To get a better estimation of the real void diameter, it was necessary to introduce a statistical correction. Multiplication of the observed void values from the SEM images by a statistical factor of  $2/3^{1/2}$  allows us better estimation of the real cavity diameters [A. Barbetta and N. R. Cameron, *Macromolecules*, 2004, **37**, 3188-3201].



**Figure S3.** Scanning electron micrographs of p(GMA) polyHIPE morphology at higher (above) and lower (below) magnification.



**Figure S4.** Scanning electron micrographs of  $\text{p(GMA-TRIS)}_{\text{pre}}$  polyHIPE morphology at higher (above) and lower (below) magnification.



**Figure S5.** Scanning electron micrographs of  $\text{p(GMA-EDA)}_{\text{pre}}$  polyHIPE morphology at higher (above) and lower (below) magnification.

## Densities and Porosities.

The monomer, bulk polymer and bulk hydrogel densities were determined according to the literature procedure.<sup>1</sup>

GMA-TRIS<sub>pre</sub> or GMA-EDA<sub>pre</sub> densities: The dry pyknometer was conditioned at 20 °C in water bath until the equilibrium had been attained, dried and weighted ( $m_0$ ). Afterwards, it was filled with distilled water and placed in water bath (20 °C). After the equilibrium had been reached, the pyknometer was removed from the water bath, dried and weighted again ( $m_1$ ). Density of water at 20 °C was taken as 0.9982 g/cm<sup>3</sup> ( $\rho_w$ ). Following this procedure, the volume of the pyknometer was determined.

Then, the clean and dry pyknometer was filled with the sample, placed in water bath at 20 °C for at least half an hour to reach the equilibrium. The pyknometer was then removed from the bath, dried outside, and weighted ( $m_2$ ).

$$\text{Calculated density of the sample: } \rho = \frac{m_2 - m_0}{m_1 - m_0} \times \rho_w$$

p(GMA-TRIS)<sub>pre</sub> or p(GMA-EDA)<sub>pre</sub> polyHIPEs' densities: The densities ( $\rho_{PH}$ ) of polyHIPEs were determined by measuring the specimens mass and volume. The specimens were cubes of approximately 1 cm · 1 cm · 1 cm which were cut from the monolith using scalpel.

The polyHIPE's porosities were calculated using equations as published elsewhere:<sup>2</sup>

$$P_{PH-T} = 1 - \frac{\rho_{PH}}{\rho_P} \quad \text{Equation S1}$$

where  $P_{PH-T}$  is the total polyHIPE porosity,  $\rho_{PH}$  is the polyHIPE density, and  $\rho_P$  is the polymer density determined by pyknometer.

$$P_{bHG-T} = 1 - \frac{\rho_{bHG}}{\rho_P} \quad \text{Equation S2}$$

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<sup>1</sup> Adhesives – Determination of density, European Standard, EN 542:2003E

<sup>2</sup> M. Ovadia and M. S. Silverstein, *Polym. Int.*, 2016, **65**, 280–289.



where  $P_{\text{bHG-T}}$  is the total bulk hydrogel porosity, and  $\rho_{\text{bHG}}$  is the density of bulk hydrogel.

$$P_{\text{PH-V}} = P_{\text{PH-T}} - P_{\text{PH-HG}} = P_{\text{PH-T}} - \left( \frac{\rho_{\text{PH}}}{\rho_{\text{HG}}} \right) P_{\text{HG-T}} = 1 - \frac{\rho_{\text{PH}}}{\rho_{\text{HG}}} \quad \text{Equation S3}$$

where  $P_{\text{PH-V}}$  is the polyHIPE void structure,  $\rho_{\text{PH}}$  is the polyHIPE density and  $\rho_{\text{HG}}$  is the density of bulk hydrogel.

### Water uptake

The dry samples cubes of approximately 1 cm · 1 cm · 1 cm were immersed in 100 mL of distilled water. The equilibrium water uptake (WU) was determined as

$$WU = \frac{(m_{\text{wet}} - m_{\text{dry}})}{m_{\text{dry}}} \quad \text{Equation S4}$$

S4

where  $m_{\text{wet}}$  is the mass of the swollen sample, and  $m_{\text{dry}}$  is the mass of the dry sample.

The water uptake can be attributed to different components, i.e. the water uptake in the polyHIPE voids ( $WU_{\text{PH-V}}$ ), the water uptake in the swollen hydrogel ( $WU_{\text{HG-T}}$ ), and the water uptake from the hydrogel swelling driven void expansion ( $WU_{\text{PH-VE}}$ ).<sup>2</sup>

$$WU_{\text{PH-V}} = P_{\text{PH-V}} \cdot \frac{\rho_{\text{w}}}{\rho_{\text{PH}}} \quad \text{Equation S5}$$

where  $WU_{\text{PH-V}}$  is the water uptake in the original void volume,  $P_{\text{PH-V}}$  is the polyHIPE void structure and  $\rho_{\text{w}}$  is the water density (taken as 1 g/cm<sup>3</sup>).

$$WU_{\text{PH-VE}} = WU_{\text{PH-T}} - WU_{\text{PH-V}} - WU_{\text{HG-T}} \quad \text{Equation S6}$$

S6

where  $WU_{\text{PH-VE}}$  is water uptake from the void expansion,  $WU_{\text{PH-T}}$  is equilibrium water uptake for the polyHIPE (measured),  $WU_{\text{PH-V}}$  is water uptake in the original void volume,  $WU_{\text{HG-T}}$  is water uptake for bulk hydrogel (measured).

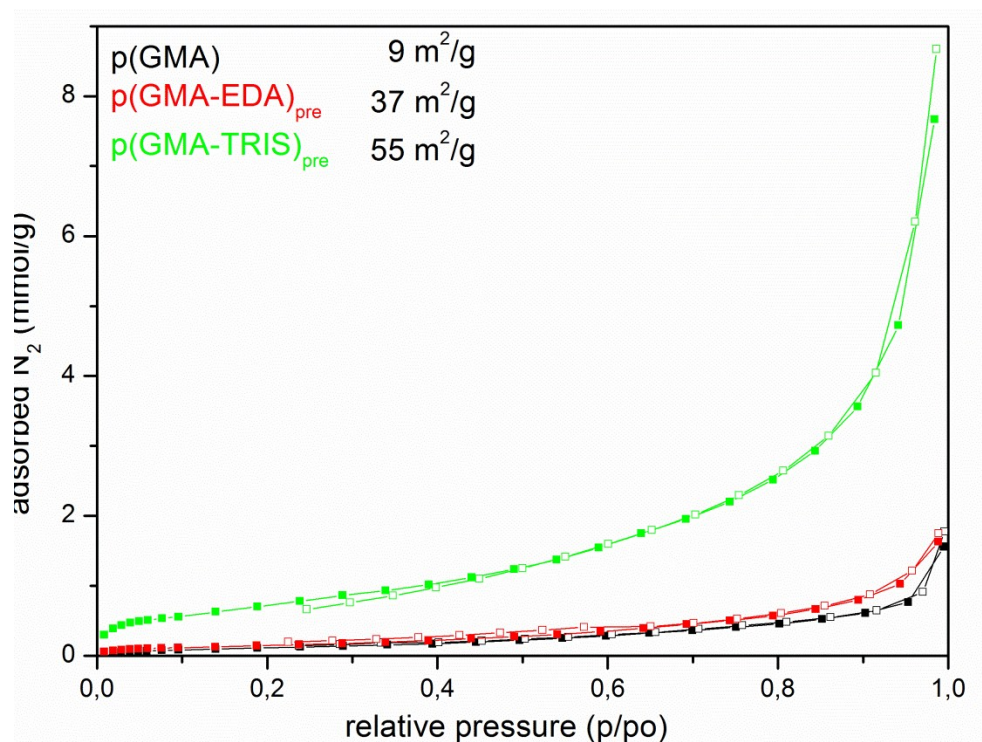
**Table S3.** Water-uptake properties of polyHIPEs.

	p(GMA-TRIS) <sub>pre</sub>	p(GMA-EDA) <sub>pre</sub>	p(GMA)
$WU_{\text{PH-T}}$ , g/g <sup>a</sup>	14.8	11.1	4.0
$WU_{\text{bHG-T}}$ , g/g <sup>b</sup>	7.3	3.0	0
$WU_{\text{PH-V}}$ , g/g <sup>c</sup>	5.0	3.9	3.8
$WU_{\text{PH-VE}}$ , g/g <sup>d</sup>	2.8	4.2	0.2

<sup>a</sup> total polyHIPE water uptake (measured); <sup>b</sup> bulk hydrogel total water uptake (measured); <sup>c</sup> water uptake in the original polyHIPE void volume; <sup>d</sup> water uptake from the polyHIPE void expansion

### Specific surface area

Nitrogen sorption measurements were performed on an IMI-100 manometric gas sorption analyzer (Hiden Isochema, Inc.) at 77 K in a range of relative pressure values from  $10^{-6}$  to 1. As-prepared samples were degassed at 150 °C for 16 h prior to measurements. The specific surface areas were determined by BET method based on the obtained sorption isotherms.



**Figure S6.** N<sub>2</sub> sorption isotherms of p(GMA) polyHIPE (black), p(GMA-EDA)<sub>pre</sub> polyHIPE (red), and p(GMA-TRIS)<sub>pre</sub> polyHIPE (green).

## Elemental analysis

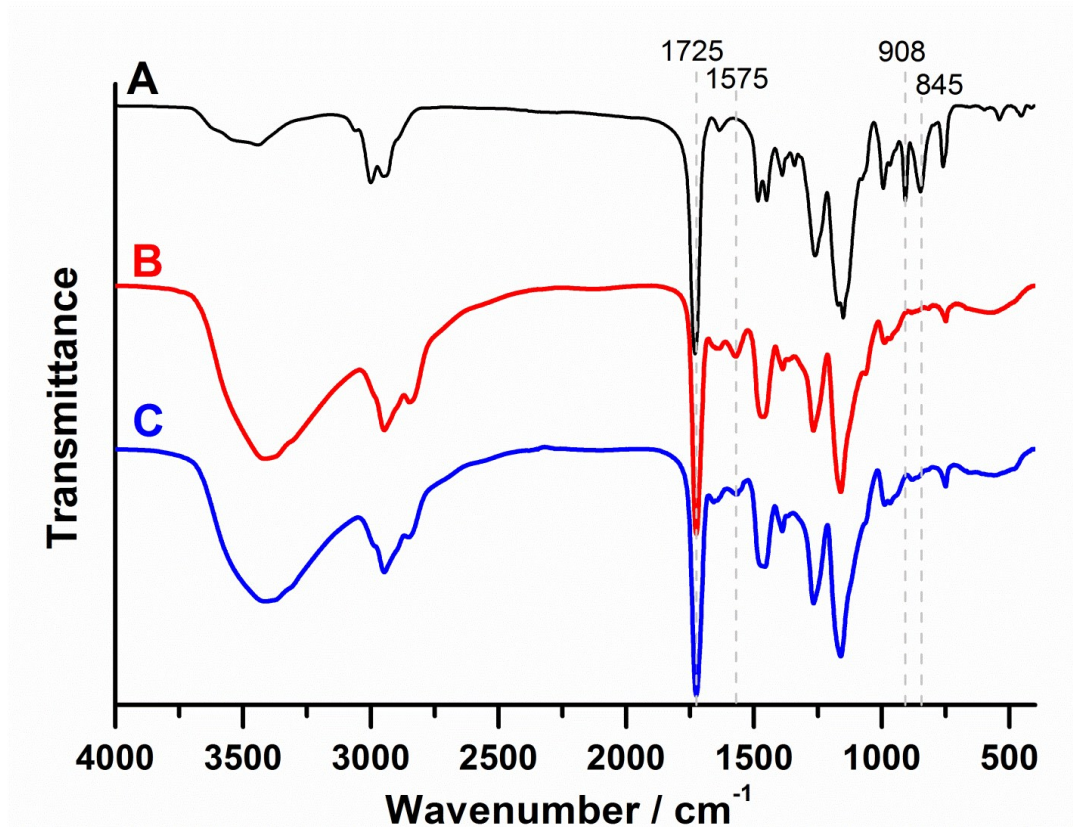
Elemental analysis was performed on an Elementar Vario EL III. The nitrogen content was calculated from elemental analysis data (Table S4).

**Table S4** Elemental analysis data.

PolyHIPE sample	N <sup>a</sup> [wt.%]	N <sup>b</sup> [wt.%]	Loading of N [mmol/g]	
			Calc.	Found
p(GMA-TRIS) <sub>pre</sub>	10.96	7.41	7.83	5.29
p(GMA-EDA) <sub>pre</sub>	10.01	6.43	7.14	5.10

<sup>a</sup> Calculated; <sup>b</sup> Found

## FTIR characterization



**Figure S7.** FT-IR spectra of A) p(GMA) polyHIPE , B) p(GMA-TRIS)<sub>post</sub> polyHIPE, and C) p(GMA-EDA)<sub>post</sub> polyHIPE.