Electronic Supplementary Information

Deep-eutectic solvents as support in the nonaqueous synthesis of macroporous poly(HIPEs)

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Experimental Section

All reagents were used as received without any further purification. Methyl methacrylate (MMA) 99%, lauryl acrylate (LA) 90%, stearyl methacrylate (SMA) technical grade, ethylene glycol dimethacrylate (EGDMA) 98%, 1,4- butanediol diacrylate (BDA) technical grade, 2,2'-Azobis(2-methylpropionitrile) (AIBN), urea 99%, and choline chloride (ChCl) 98% were purchased from Sigma Aldrich. The nonionic surfactant, Cithrol® (Arlacel P135), a polyethylene glycol dipolyhydroxysterate ABA triblock copolymer used in cosmetics and creams, was generously contributed by Croda Ltd.

The continuous phase (20 vol %) was prepared by dissolving 2.0 mol% AIBN (as thermal initiator) with respect to the total concentration of C=C reactive groups in a 2:1 monomer (MMA, LA or SMA) to crosslinker (EGDMA if methacrylate or BDA if acrylate) molar ratio and surfactant mixture. The amount of surfactant used was 10 or 7 wt % with respect to the total weight of the emulsion. To prepare the internal nonaqueous DES phase (80 vol %), ChCl was oven dried at 90^{o}C. A 2:1 molar ratio of urea and ChCl were combined and oven heated to 60^{o}C until a clear viscous, homogeneous liquid was obtained. HIPEs were prepared by mixing both phases in an 8 mL glass vial and vortexing at 3200 rpm for at least 10 min. until a white homogenous emulsion was obtained. The emulsion did not flow upon the inversion of the vial. HIPEs were polymerized in an oven at 50^{o}C for 36 h. In addition, a SMA sample with 10 wt% surfactant was prepared at 50^{o}C in a low pressure oven (-67.7 kPa). All poly(HIPEs) were named according to the first letter of the monomer used and the amount of surfactant.

Poly(HIPEs) were frozen and extracted from their vials. The produced monoliths were washed in water, 40 times their original volume, at ambient temperature for 4 days and later in ethanol at 50^{o}C for an additional 3 h. The monoliths were dried at 90^{o}C in a low pressure oven (-67.7 kPa) for 24 h. and weighed.

Conversion was determined by dividing the mass of the dried monolith by its expected mass. Conversion was also determined using FTIR (Bruker Tensor 345 Alpha-P) by integrating the signal ascribed to C=C at 1635 cm^{-1} normalized to the C=O signal at 1715 cm^{-1} and comparing the polymer with its pure components. Similarly, the water washes (containing the DES's dissolved components) were freeze-dried. The resulting viscous liquid was weighed and placed in a capillary tube for ^{1}H-NMR analysis. The percentage of recovered DES was calculated by dividing the mass of recovered DES by its expected recovered mass.

The microstructures of DES-based emulsions were studied using confocal laser scanning microscopy (CLSM; Leica TCS SP2 spectral confocal microscope, equipped with Ar and He/Ne lasers of laser lines 458, 476, 488, 514, 543, and 633nm). To discern the placement of each component in the occurring phases, the monomer/crosslinker phase was marked with the fluorescent dye rhodamine 6G (Rh6G, 0.004 m).

The morphologies of all poly(HIPEs) were investigated by scanning electron microscopy (SEM; JSM 6610 LV) with an accelerating voltage of 10 kV. Samples were platinum coated for 240 seconds in an inert argon atmosphere at $1x10^{-5}$ mbar (Emmitech 550). The average pore and pore window diameters were calculated in sets of 50 using ImageJ analysis software. Additionally, the degree of pore openness was estimated using the equation proposed by Pulko and Krajnc (**Scheme S1**).[7a] Pore surface area of the extracted HIPEs was determined by N_2 physisorption-desorption analysis using an autosorb-1 (Quantochrome) porosimeter applying a Brunauer-Emmet-Teller (BET) model. Samples were equilibrated for 1 hr. at 150^{o}C prior to making measurements. Poly(HIPEs)' thermal stability was assessed by thermogravimetric analysis (TGA 2950 thermogravimetric analyzer) in an inert nitrogen atmosphere from 25^{o}C to 500 ^{o}C with a heating rate of 10^{o}C min^{-1}. TGA was carried out using 1 to 5 mg of sample in standard aluminum pans. Thermal analysis was performed using TA Universal Analysis software.

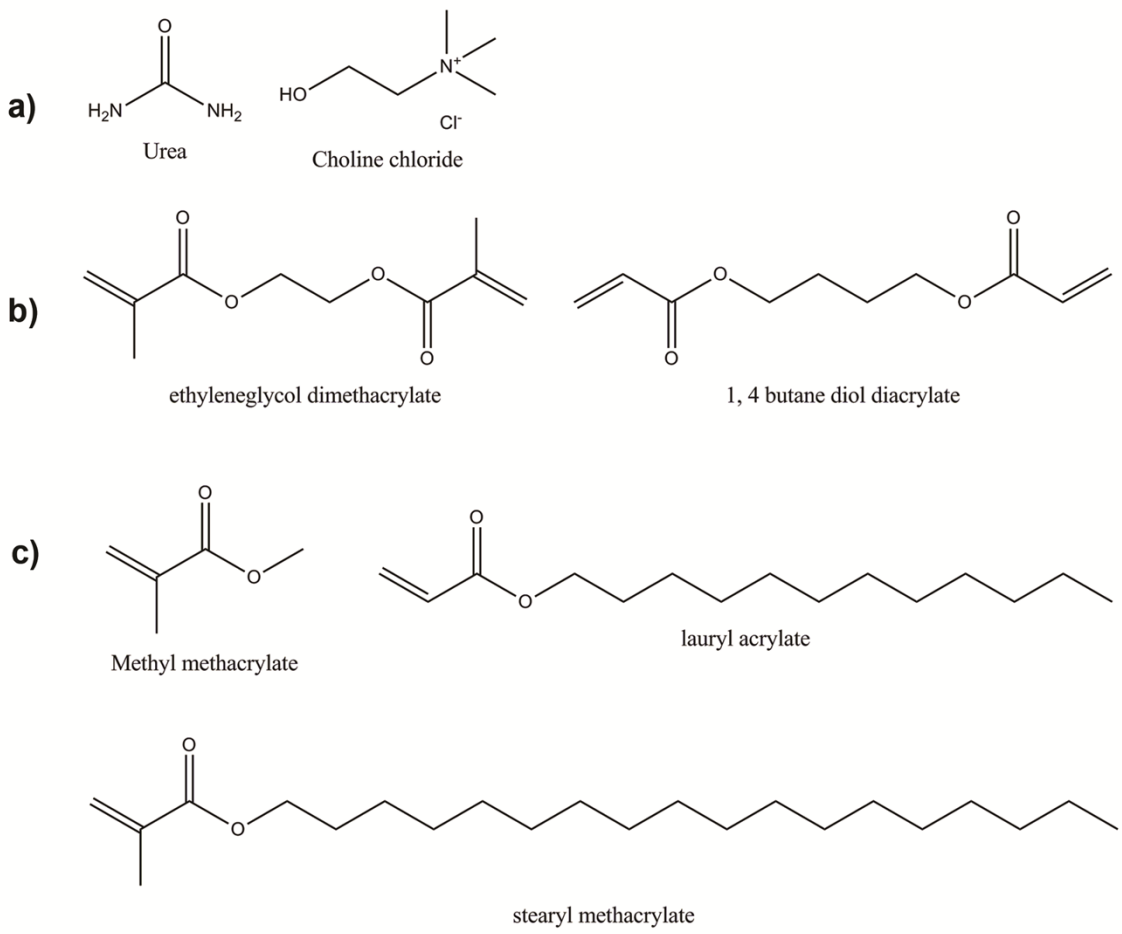
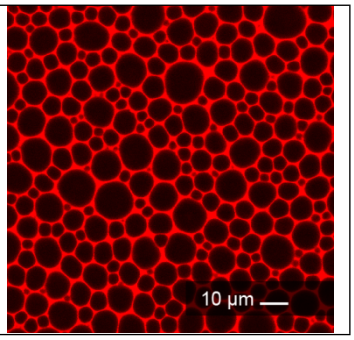


Figure S1. Structures of reagents: a) DES components b) cross-linkers and c) monomers used

Table S1. Confocal micrographs of HIPEs. Monomer/cross-linker labeled with fluorescent marker rhodamine 6G.

Methyl Methacrylate	**80% internal phase vol. 7 wt% surf.**	

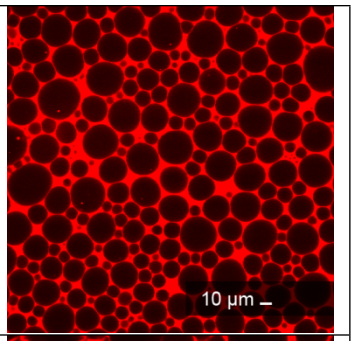
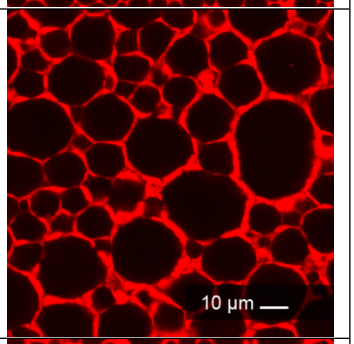
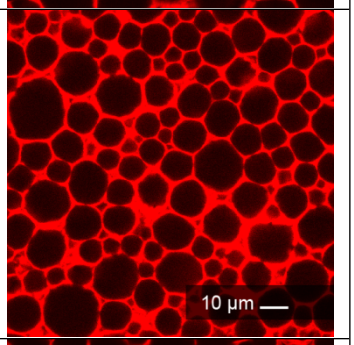
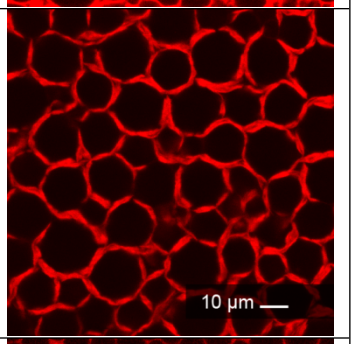
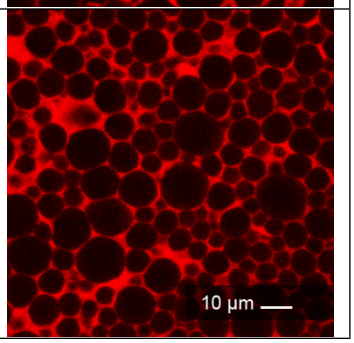
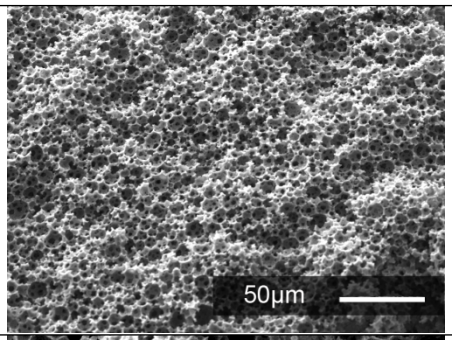
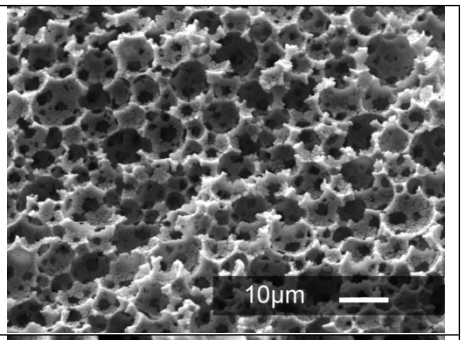
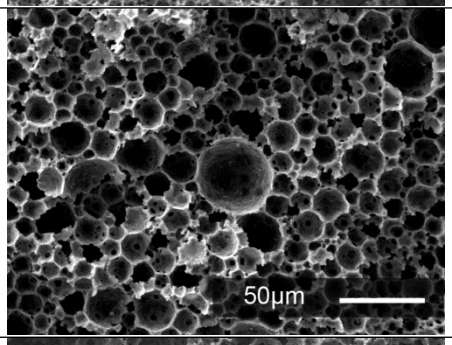
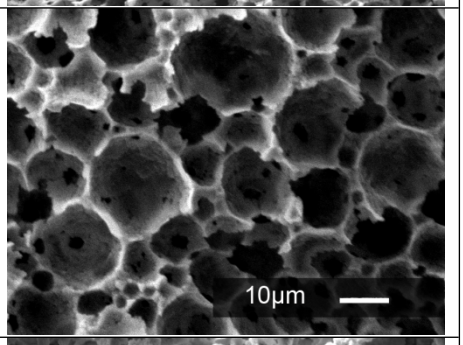
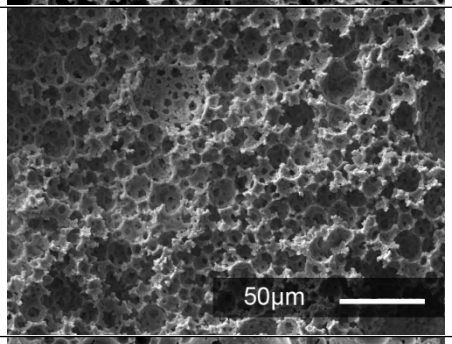
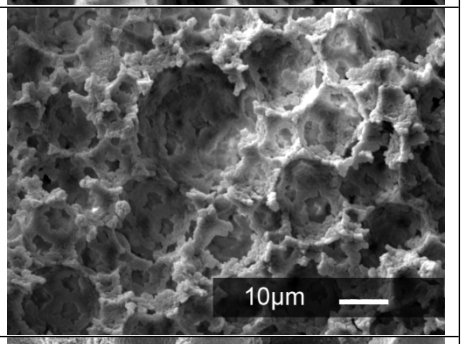
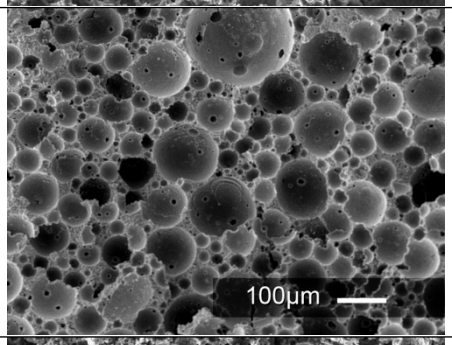
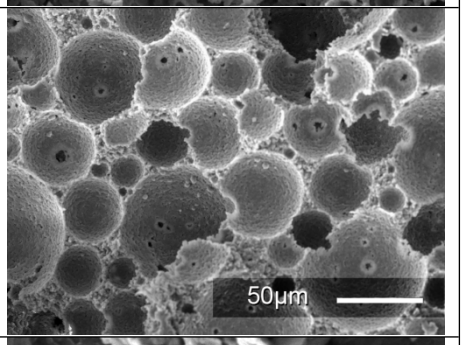
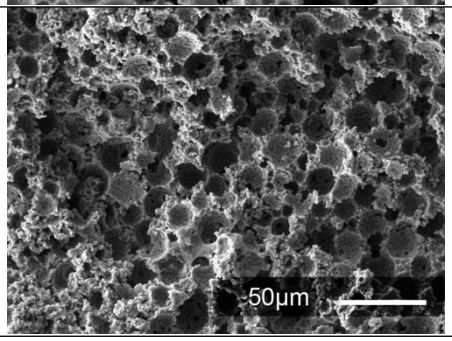
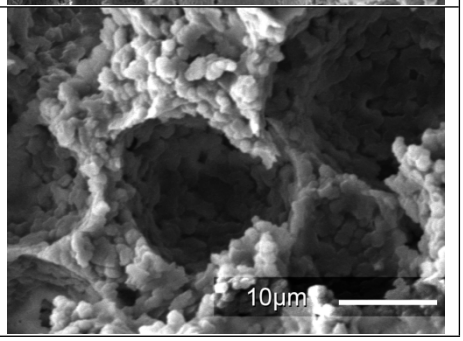
	80% internal phase vol. 10 wt% surf.	
Lauryl Acrylate	**80% internal phase vol. 7 wt% surf.**	
	80% internal phase vol. 10 wt% surf.	
Stearyl Methacrylate	**80% internal phase vol. 7 wt% surf.**	
	80% internal phase vol. 10 wt% surf.	

Table S2. Scanning electron micrographs of polyHIPEs after DES removal.

Methyl Methacrylate	**80% internal phase vol. 7 wt% surf.**		
	80% internal phase vol. 10 wt% surf.		
Lauryl Acrylate	**80% internal phase vol. 7 wt% surf.**		
	80% internal phase vol. 10 wt% surf.		
Stearyl Methacrylate	**80% internal phase vol. 7 wt% surf.**		

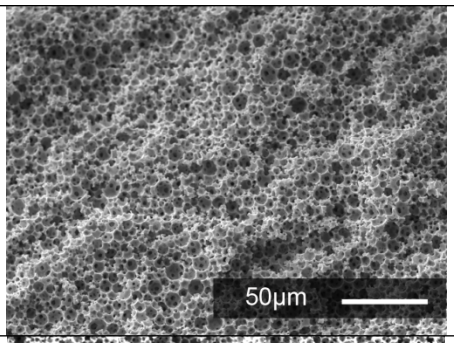
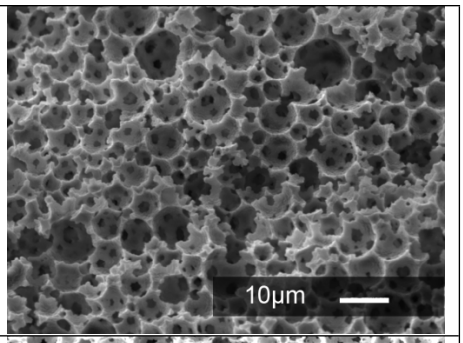
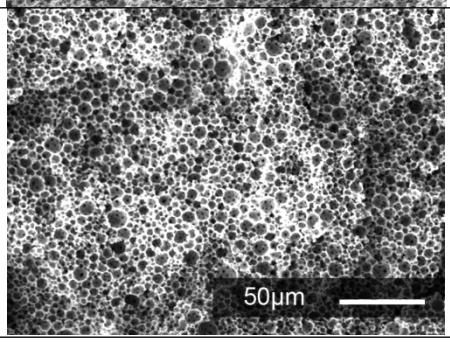
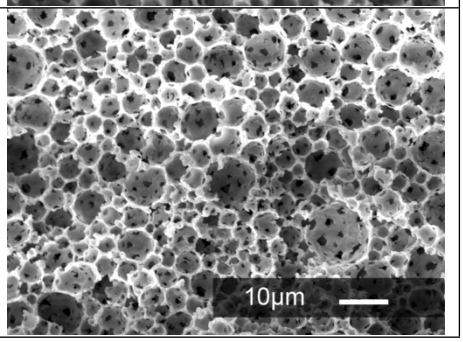
	80% internal phase vol. 10 wt% surf.		
Stearyl Methacrylate Vacuum	**80% internal phase vol. 10 wt% surf.**		

Table S3. Structural morphology of HIPEs and Poly(HIPEs)

PolyHIPE Sample	Specific Surface Area [$m^2\ g^{-1}$]	Confocal [μm]	SEM [μm]	Pore Window [μm]	Deg. of Openness [%]
pMMA10	nd[a)]	17.2±6.5	16.4±5.0	2.4±0.9	3.2
pMMA7	1.7	7.4±2.7	6.3±2.4	1.8±0.6	23.2
pLA10	nd[a)]	10.5±3.5	55.3±30	7.0±2.6	0.8
pLA7	1.0	13.1±6.4	14±4.6	2.8±1.2	10.1
pSMA10	4.3	6.9±2.5[b)]	5.8±2.0	1.4±0.6	2.8
pSMA10v	nd[a)]	-	5.7±2.5	2.1±1.2	6.2
pSMA7	nd[a)]	14.4±3.6	14.6±2.9	0.9±0.3	7.1

[a)] not determined. [b)] pSMA10 droplet measurement is representative of pSMA10v.

Scheme S1. PolyHIPE openness can be estimated using the following equation proposed by Pulko and Krajnc.[7]

$$O = \frac{Open\ surface\ of\ pore}{Surface\ area\ of\ pore\ window} = \frac{S_P}{S_W} \quad (1)$$

$$S_P = N \cdot \pi \cdot \left(\frac{d^2}{2}\right) \quad (2)$$

$$S_W = \pi \cdot D^2 \quad (3)$$

$$O = \frac{N \cdot \pi \cdot \left(\frac{d^2}{2}\right)}{\pi \cdot D^2} = \frac{N \cdot \left(\frac{d^2}{2}\right)}{D^2} = \frac{N \cdot d^2}{4 \cdot D^2} \quad (4)$$

$$N = \frac{4n}{\sqrt{3}} \quad (5)$$

Where:

O = PolyHIPE openness

N = Estimated average number of pore windows

n = average number of visible pore windows

d = average pore window diameter

D = average pore diameter

Figure S2. FTIR of PolyHIPEs and individual components (monomer and crosslinker) a) pMMA b) pLA c) pSMA Top shows shift of carbonyl and acrylic bands. Bottom shows decrease in acrylic peaks.

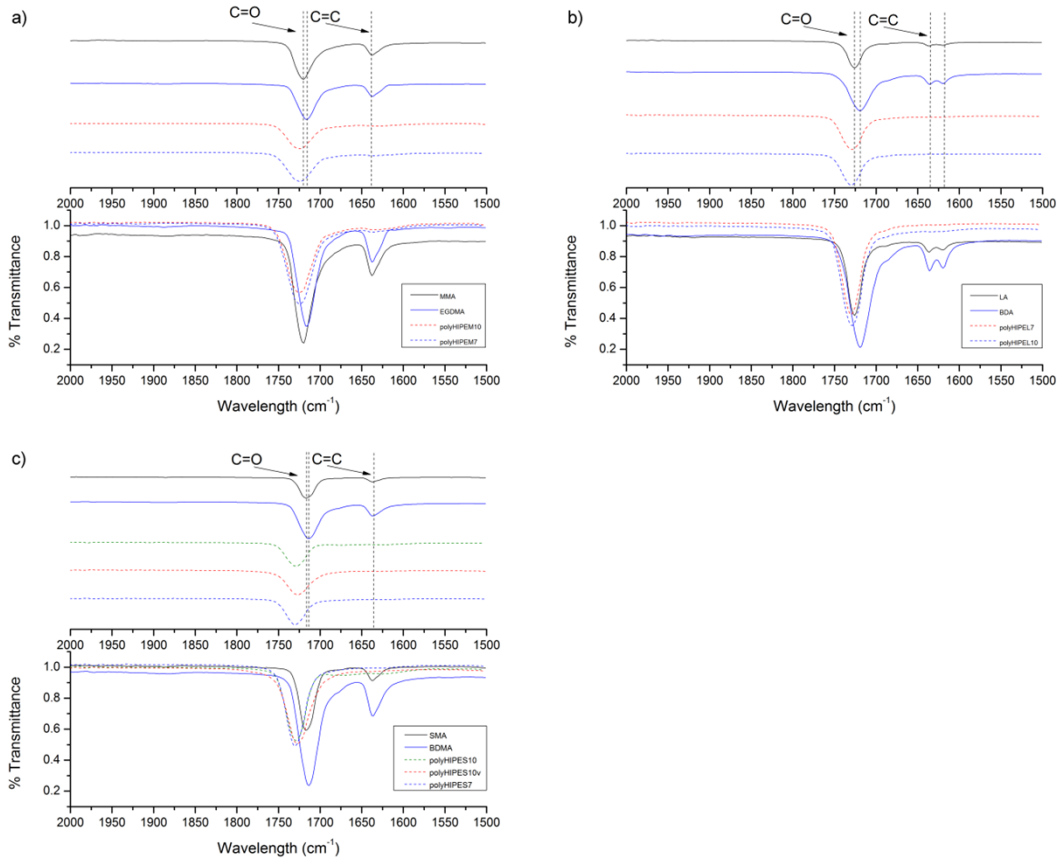
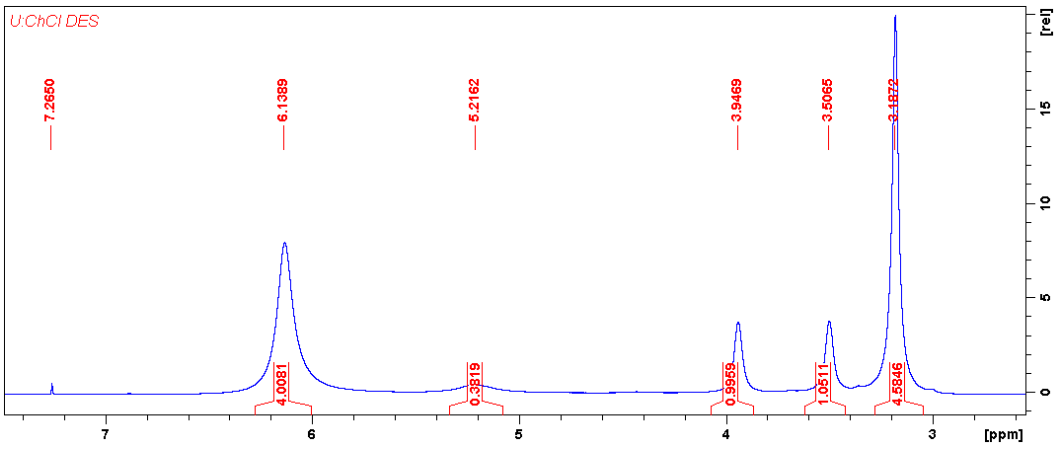


Figure S3. [1]H NMR of DES in a capillary tube A) pure DES B) recovered DES after water wash.

(A)



(B)

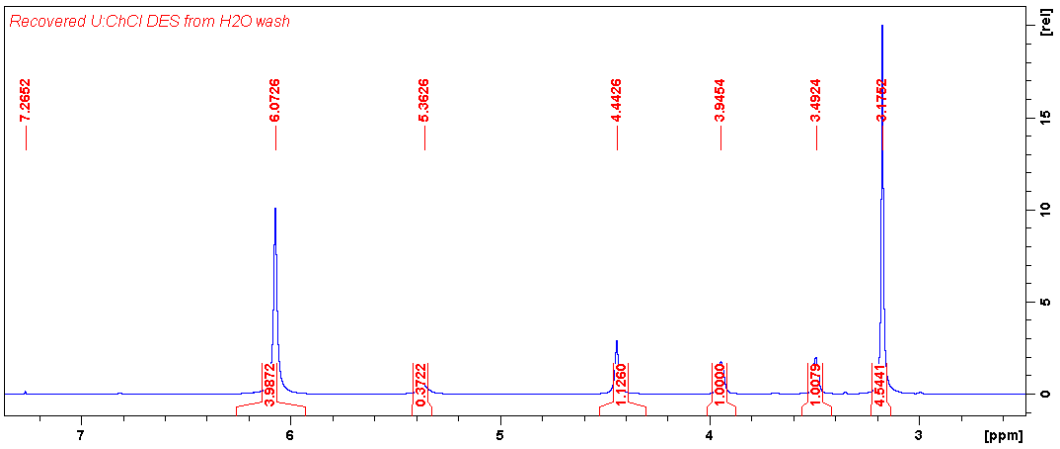


Table S4a. Summary of peak signals.

δ(ppm)						
	Urea	Water	Choline Chloride			
Sample	R-$(NH_2)_2$	H_2O	HO-	- CH_2 -	- CH_2 -	- $(CH_3)_3$
Pure DES	6.14	-	5.22	3.94	3.50	3.19
DES H_2O wash	6.07	4.44	5.36	3.95	3.49	3.18

Table S4b. Summary of integrals.

Integrals						
	Urea	Water	Choline Chloride			
Sample	R-(NH$_2$)$_2$	H$_2$O	HO-	- CH$_2$ -	- CH$_2$ -	- (CH$_3$)$_3$
Pure DES	8.04	-	0.76	2.00	2.10	9.14
DES H$_2$O wash	7.97	2.25	0.74	2.00	2.02	9.09

Figure S4. Nitrogen sorption/desorption isotherms for polyHIPEM7, polyHIPEL7, and polyHIPES10.

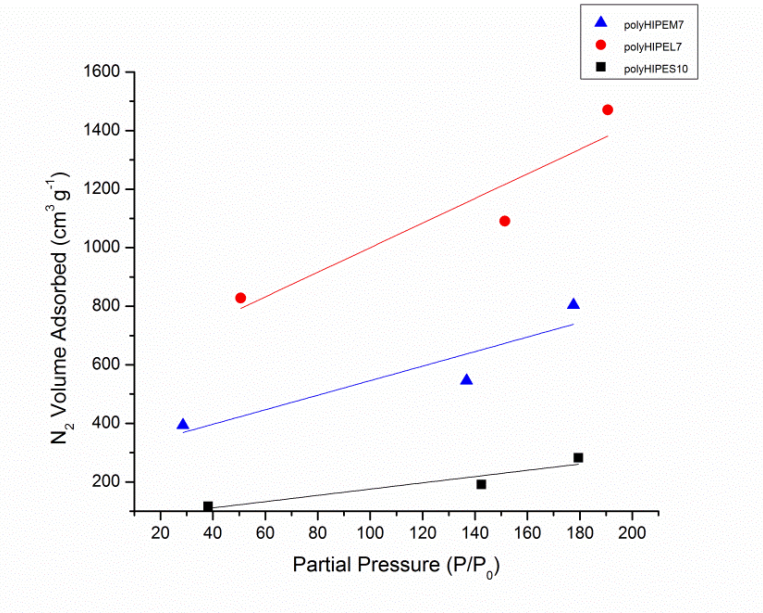


Figure S5. Thermogravimetric analysis of a) PolyHIPEM b) PolyHIPEL and c) polyHIPES.

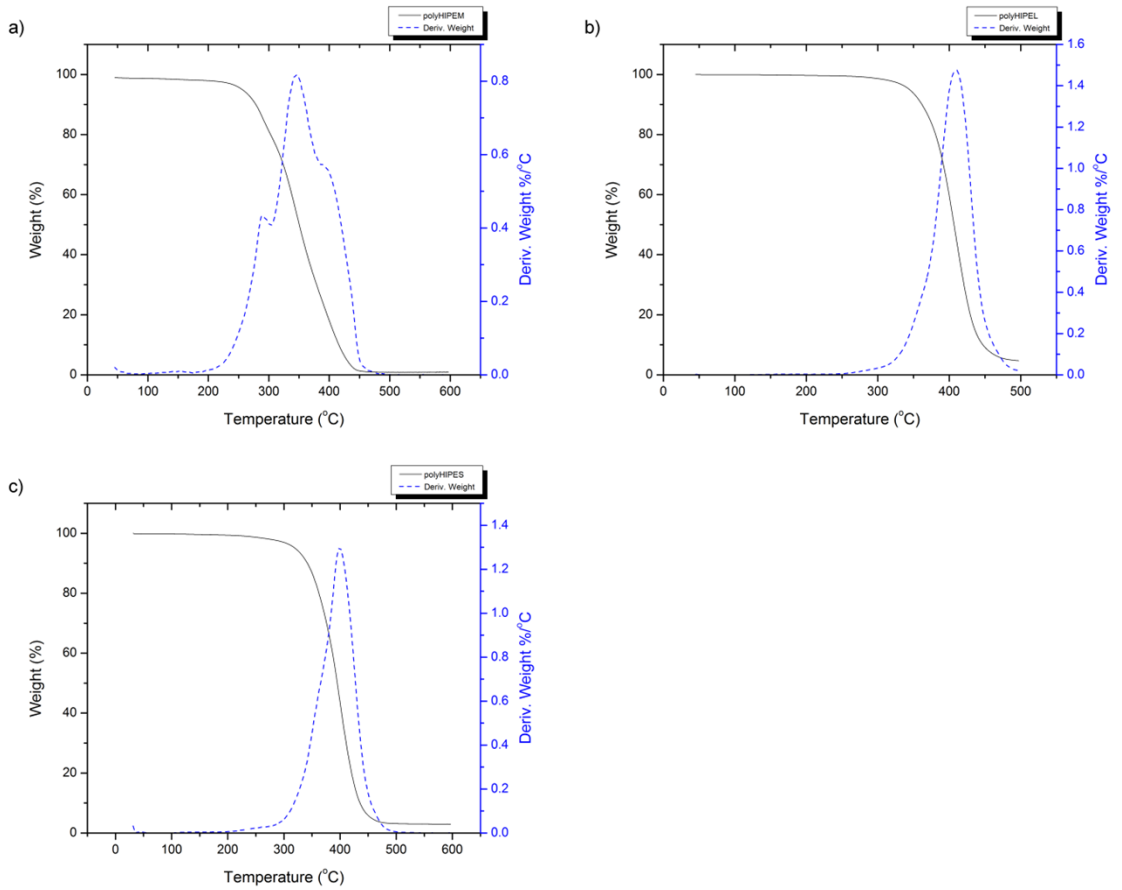


Table S5. Summary of thermal properties.

Sample	Mass of Sample [mg]	T_d 2% [°C]	T_d 5% [°C]	% H_2O Retained
pMMA7	1.43	225	260	0.16
pLA7	4.08	319	339	0.027
pSMA7	2.79	280	321	0.081