Supplementary Information of the manuscript

# Tailor Made Deep-Eutectic Solvents Suitable for Frontal Polymerization

by

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## DEEP EUTECTIC SOLUTIONS CARACTERIZATION

<sup>1</sup>H NMR spectra were recorded in a Bruking spectrometer DRX-500 using CDCl<sub>3</sub> as external reference. Differential scanning calorimetry (DSC) was performed in a TA Instrument Model DSC-Q-100 system. The viscosity of the DES was measured with a Brookfield Digital Rheometer DV-III+ at 22°C.

**Figure S1.** Spectra of diluted (in  $D_2O$ ) AACCI-DES and MAACCI- DES samples. DES content ranged from 60 to 10 wt% in both AACCI-DES (top) and MAACCI- DES (bottom) samples.



**Table S1.** <sup>1</sup>H NMR spectroscopy data of non-diluted and diluted (in  $D_2O$ ) AACCI-DES samples. <sup>1</sup>H-NMR spectroscopy data of choline chloride (12 wt%) in  $D_2O$  solution is also included for comparison.

	δ(ppm)									
SAMPLE	HDO	AA				CCI				
		$\underline{H} - C - \underline{H} = C - \underline{H} - COOH$				$HO-C\underline{H}_2 - C\underline{H}_2 - N(C\underline{H}_3)_3$				
CCI	4.76					4.10	3.56	3.24		
AA*		6.52	5.96	6.14	12.0					
AACCI-DES		6.58	6.16	6.42		4.31	3.92	3.59		
AACCI-DES 60wt	5.41	6.48	6.09	6.26		4.19	3.69	3.37		
AACCI-DES 10wt	4.86	6.47	6.06	6.23		4.11	3.58	3.26		

\* Data from SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 03.01.2011)

The spectra of non-diluted samples (both AACCI-DES and MAACCI-DES) revealed that the characteristic signals of both choline chloride (mostly those assigned to  $CH_3$  and  $CH_2$  in position 1) and acrylic acid protons were downfield shifted (i.e., up to 0.36 ppm for chloline chloride) as compared to those obtained for choline chloride in D<sub>2</sub>O solution and for acrylic acid in CDCl<sub>3</sub> solution. Downfield chemical shifts were indicative of the formation of ion-hydrogen-bond-donor supramolecular complexes that characterize DES. The rupture of halide ion-hydrogen-bond-donor supramolecular complexes upon dilution is reflected in the upfield shift of some of the acrylic acid and choline chloride protons as compared to non-diluted DES, a feature indicative of the increased hydration of molecules. Therefore, in samples having 60 wt.% DES content, the interchange between acrylic acid and choline chloride protons to D<sub>2</sub>O is minor than in samples with 10 wt.% DES content. On the other hand, the chemical shift of the HDO signal further corroborated that the presence of halide ion-hydrogen-bond-donor supramolecular complexes is still significant in samples having 60 wt.% DES content. Further dilution yields the chemical upfield shift of the HDO signal (i.e. up to 0.55 ppm, from 5.41 (60 wt. %) to 4.86 ppm (10 wt. %)) as a consequence of complex rupture. Upfield shifts in HDO signals reflects the formation of hydrogen bond structures in water, a feature that is favored by the presence of free acrylic acid and choline chloride molecules (hence, non-forming ion pairs) in solution.

**Table S2.** <sup>1</sup>H NMR spectroscopy data of non-diluted and diluted (in D2O) MAACCI- DES samples. <sup>1</sup>H-NMR spectroscopy data of choline chloride (12 wt%) in  $D_2O$  solution is also included for comparison.

SAMPLE	δ(ppm)								
	HDO	MAA				CCI			
		$\underline{H} - C - \underline{H} = C - C\underline{H}_3 - COO\underline{H}$				$HO-C\underline{H}_2 - C\underline{H}_2 - (C\underline{H}_3)_3$			
CCI	4.76					4.10	3.56	3.24	
MAA*		6.26	5.68	1.96	11.3				
MAACCI-DES		6.22	5.77	2.03		4.25	3.90	3.56	
MAACCI-DES 60wt	5.46	6.19	5.72	1.96		4.23	3.73	3.40	
MAACCI-DES 10wt	4.87	6.16	5.77	1.95		4.11	3.58	3.26	

\* Data from SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 03.01.2011)

## ABOUT FONTAL POLYMERIZATION PROCESS

**Figure S2.** Pictures of the setup used to carry out frontal polymerization in DES.. reactor and the position of the thermocouples during a typical. It shows how In a typical run, the bottom end of the tube was immersed in an oil bath at 130°C whereas the upper end of the reactor remained open to atmospheric pressure. The non-immersed part of the reactor was covered with polyester foam for isolation. The picture also shows the position of the thermocouples at different heights of the reactor. The thermocouples located outside the reactor (T1-T4) provided the velocity of propagation of the front. There was one single thermocouple immersed into the reaction mixture to measure the temperature of the front. The position of this fifth thermocouple (at T4<sup>′</sup>, where we arbitrary decided the end of FP) was thus selected to avoid perturbations at the propagating front.



#### SWELLING BEHAVIOR OF THE HYDROGELS

**Table S3.** Small pieces of dry gel were swollen in buffer solutions at pH 2, 7 and 10 at room temperature until the equilibrium was reached. The concentration of all buffers was 0.2M.

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	BPO mol%	EGDMA mol%	Swelling ratio (%SR <sup>b</sup> ) at equilibrium				
			pH=2	pH=7	pH=10		
	0.2 <sup>a</sup>	0.35	536	5436	11537		
	0.2 <sup>a</sup>	0.7	454	4224	9730		
	0.2 <sup>a</sup>	1.4	274	733	с		
	0.2 <sup>a</sup>	2.8	209	712	с		
	0.1 <sup>a</sup>	0.7	394	3381	10093		
	0.4 <sup>a</sup>	0.7	397	3022	8161		

<sup>a</sup> AA:CCl in 1.6:1 mol ratio; <sup>b</sup> %SR = 100 \* ( swollen mass – dry mass) / dry mass; <sup>c</sup> the gels were fragmented and partially dissolved during their swollen process at this pH.

#### **GREEN PROCESS**

**Figure S3.** <sup>1</sup>H-NMR spectra of the residue recovered after washing the gels resulting from FP of AACCI-DES (left) and MAACCI-DES (right) and subsequent lyophilization. Spectra were recorded using  $D_2O$  as solvent and CDCl<sub>3</sub> as external reference. Signals corresponding to choline chloride were the only ones found in the spectra. These results revealed that choline chloride was fully recovered in every case. It is worthy to note that choline chloride recovery allowed its reusability in subsequent polymerization processes. This recyclability represents an additional advantage of the methodology reported herein since it may open interesting perspectives in industrial processes where sustainability is a remarkable issue.

