Supporting Information

Multicomponent Radziszewski Emulsion Polymerization Towards Macroporous Poly(ionic liquid)s Catalysts.

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EXPERIMENTAL SECTION.

Materials. Formaldehyde (aqueous solution 37 w%), glyoxal (aqueous solution 40 w%), vinyl acetate (VAc) (> 99 %), caffeic acid (98 %) and tris(2-aminoethyl)amine (TREN) (96 %) were purchased from sigma-aldrich (Belgium). Acetic acid glacial (> 99 %), Methanol (MeOH, > 99.9 %), cyclohexane (> 99.9 %), dimethylsulfoxide (DMSO, 99.5 %)) and tetrahydrofuran (THF, 99.9 %) were purchased from VWR. Benzyl alcohol (99 %) was purchased from TCI Europe and deuterated solvents from Eurisotop. Jeffamine-T403® was kindly provided by HUNTSMAN. Pluronics PEF68 was purchased from ICI Surfactants. All chemicals and solvents were used without purification with a few exceptions. DMSO and THF used in the transesterification and decarboxylation reactions were dried on molecular sieves and stored under inert atmosphere (Argon). Benzyl alcohol and VAc which were dried under calcium hydride, purified by distillation under reduced pressure and degassed by freeze-drying cycle under vacuum.

Characterizations. ^{13}C CP MAS NMR spectra were recorded with 4-mm zirconia rotors spinning at 10 kHz on a Bruker Avance III HD spectrometer (B0=9.04 T) working at the Larmor frequency of 100.62 MHz. Cross polarization experiments were performed with a delay time of 2 s and a contact time of 2 ms. ^{1}H NMR spectra were recorded at 298 K with a Bruker Avance III HD spectrometer (B0=9.04 T) (400 MHz) and treated with MestraNova software. IR spectra were recorded on ThermoFischer Sientic Nicolet IS5 equipped with an ATR ID5 module using a diamond crystal (650 cm-1 - 4000 cm-1). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q1000 DSC, using hermetic aluminium pans, indium standard for calibration, nitrogen as the purge gas, a sample weight of ~5 mg. The sample was dried at 90 °C during 20 minutes under flux of nitrogen. Then, the sample was cooled down to -80 °C at 20 °C/min cooling rate, followed by an isotherm at −80 °C for 2 min and heating up to 120 °C at 10 °C/min heating rate. These cycles were repeated twice. The fourth cycle (last heating from -80 to 120 °C) were analyzed and reported in table S1. TGA analyses were carried out with a TGA 2 from Metler Toledo under nitrogen at a heating rate of 20°C /min from 30 °C to 600 °C with a sample weight between 5 and 10 mg. The solvent uptake (SU) values were determined by gravimetry and calculated as follows: SU (%) = ([Ww - Wd] / Wd) * 100, Ww and Wd correspond to the weight of the polymer wet and dry, respectively. The SU represents the entire solvent quantity in the materials which includes the swellability and the filling of the macropores. The SEM images of the polyHIPEs were collected with a Jeol JSM 804-A apparatus after metallization of the sample with Pt (30 nm) in order to estimate the size of cavities and pores. To analyze the porous structure of the materials, a critical point drying method was used to prepare the samples for electron microscopy. The polyHIPEs were fixed in a 3% glutaraldehyde solution (1h at room temperature), and were then washed in 0.1 M Soerensen's Phosphate Buffer for 15 min. Afterwards, they were dehydrated first through acetone solutions of 30%, 50%, 70% and 90%, with 10 min in each, and then through pure acetone 3 times for 10 min. The samples were transferred to a small wire-basket holder in a Balzers Critical Point Dryer and flooded with liquid CO_2. After 20 min CO_2 was slowly vented. Flooding and venting as above were repeated to purge all acetone. The samples were then fixed onto a silicon wafer substrate using a carbon glue and coated with a 6 nm AuPd conducting layer. FESEM measurements were performed on a Hitachi S4800 field emission scanning electron microscope.

Typical procedure for the synthesis of macroporous PILs. In a beaker, formaldehyde (37 wt% in water, 0.983 g, 12 mmol), glyoxal (40 wt% in water, 1.741 g, 12 mmol), acetic acid (2.160 g, 36 mmol), water (1.000 g) and the surfactant PEF68 (0.285 g, 4 w% of the total aqueous phase) were mixed together at 6 °C. At this temperature, tris(2-aminoethyl)amine (TREN) (1.168 g, 8 mmol) was added slowly under mechanical stirring (500 rpm) followed by dropwise addition of cyclohexane (15.94 g, 20.46 mL, 75 v% of the total emulsion). The resulting HIPE emulsion was casted into a polyethylene mold and cured at room temperature for 3 days. Finally, the $P_{TREN-OAc}$ monoliths produced accordingly were immersed in DMSO for washing and stored in this solvent.

In order to carry out the SEM analyses of the polyHIPEs in the dry state, DMSO was first exchanged for MeOH before drying the polyHIPEs under vacuum.

A similar procedure was repeated using Jeffamine-T403 (3.520 g, 8 mmol) instead of TREN, cyclohexane (21.86 g, 28.06 mL, 75 v% of the total emulsion) and PEF68 (0.410 g, 4 w% of the total aqueous phase).

Typical procedure for anions exchange. In a 100 mL Erlenmeyer, the acetate-based polyHIPE (approximately 1 cm^3 of $P_{TREN-OAc}$ or $P_{JEFF-OAc}$) was immersed for three days under gentle stirring in a methanol solution (50 mL) containing the counter-ion salt in excess, i.e. NaBr (2.0 g, 19 mmol) or LiTFSI (2.0 g, 7 mmol). The samples were then immersed in pure MeOH for washing.

Typical procedure for transesterification. The acetate-based polyHIPE swollen by THF ($P_{\text{TREN-OAc}}$ or $P_{\text{JEFF-OAc}}$, 0.5 mmol of imidazolium, 10 mol% of imidazolium moieties compared to the BenzOH was placed under inert argon in a Schlenk tube followed by addition of dry and degassed reagents, namely THF (5 mL), VAc (0.6 mL, 534 mg, 6.2 mmol) and BenzOH (0.5 mL, 541 mg, 4.8 mmol). The reaction mixture was heated at 80 °C and stirred under inert atmosphere. The conversion was determined via ^{1}H NMR in deuterated chloroform by comparing the relative intensities of the methylene signals of benzyl acetate and benzyl alcohol at 5.1 ppm and 4.7 ppm, respectively.

$$Conversion = \frac{\int 5.1\, ppm}{\int 4.7\, ppm + \int 5.1\ ppm}$$

Typical procedure for caffeic acid decarboxylation. The acetate-based polyHIPE swollen by DMSO ($P_{\text{TREN-OAc}}$ or $P_{\text{JEFF-OAc}}$, 0.25 mmol of imidazolium, 50 mol% of imidazolium moieties compared to caffeic acid) was placed under inert argon in a Schlenk tube followed by addition of a degassed solution of caffeic acid in dry DMSO (5 mL, 0.1 M, 0.5 mmol). The reaction mixture was heated at 115 °C and stirred for 1 hour under inert atmosphere. The conversion was determined via ^{1}H NMR in deuterated DMSO by comparing the relative intensities of the olefinic methine hydrogen of vinyl catechol and caffeic acid at 6.2 ppm and 6.5 ppm, respectively.

$$Conversion = \frac{\int\ 6.20 +}{\int\ 6.20 + \int 6.50}$$

Recycling experiments. At the term of the decarboxylation reaction described above (115 °C, 50 mol% of imidazolium compared to caffeic acid), the reaction mixture was removed from the reaction vessel and the polyHIPE was washed with a fresh portion of DMSO under inert atmosphere before being reused as catalyst for the same decarboxylation reaction (same conditions). Four recycling steps were performed accordingly.

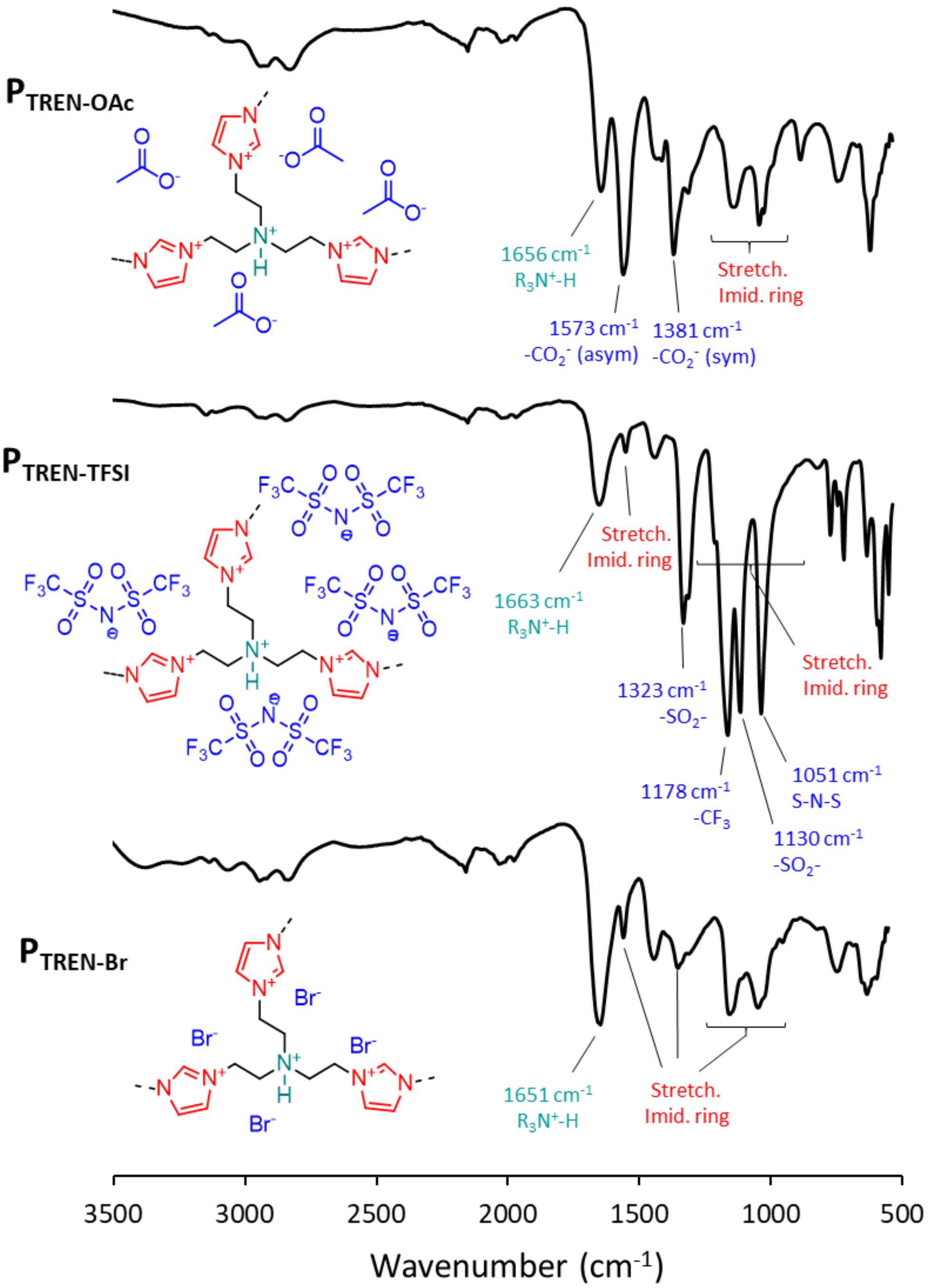

Figure S1. Infrared spectra (ATR) of P_{TREN} with acetate, TFSI and bromide as counterions.

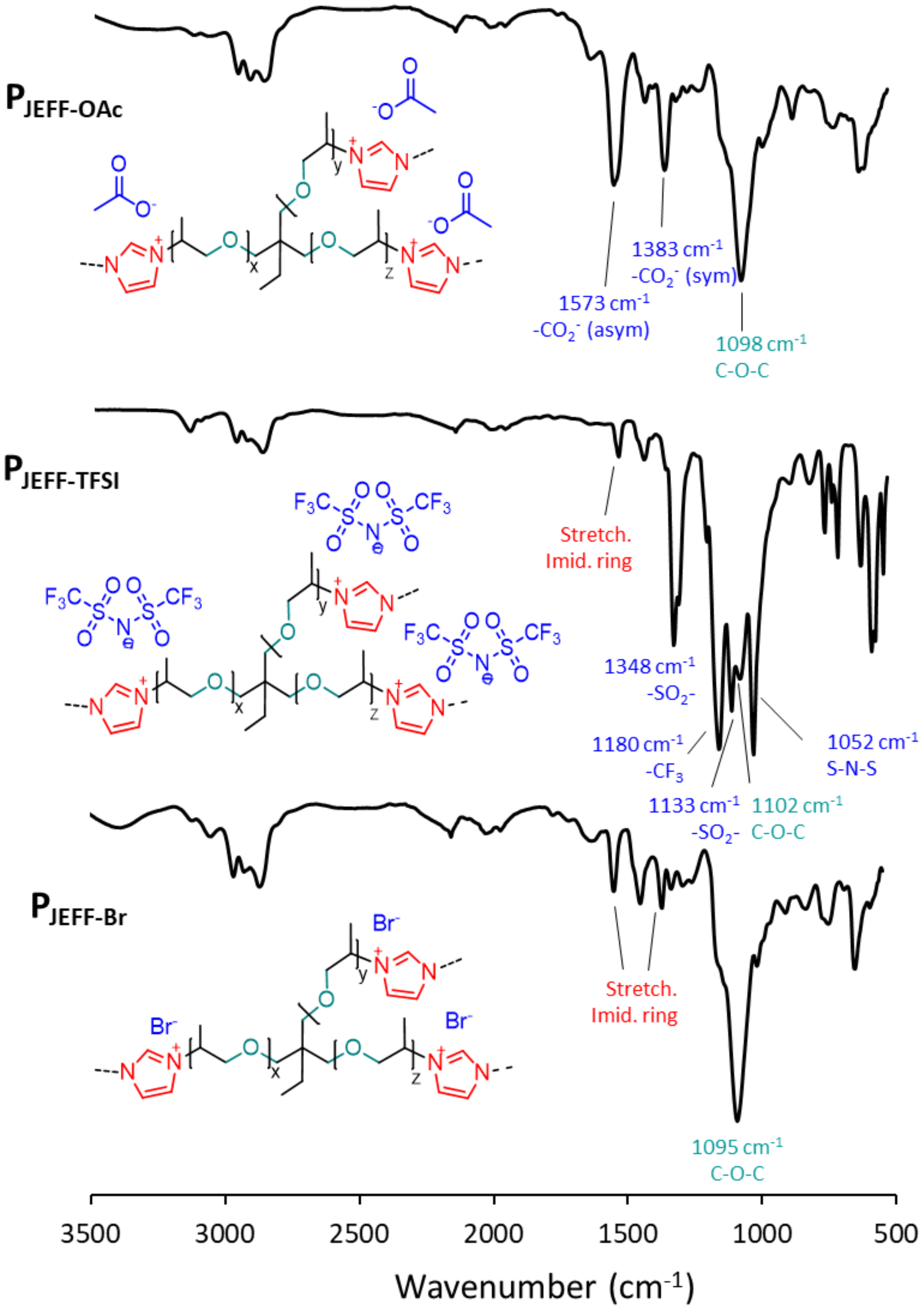

Figure S2. Infrared spectra (ATR) of P_{JEFF} with acetate, TFSI and bromide as counterions.

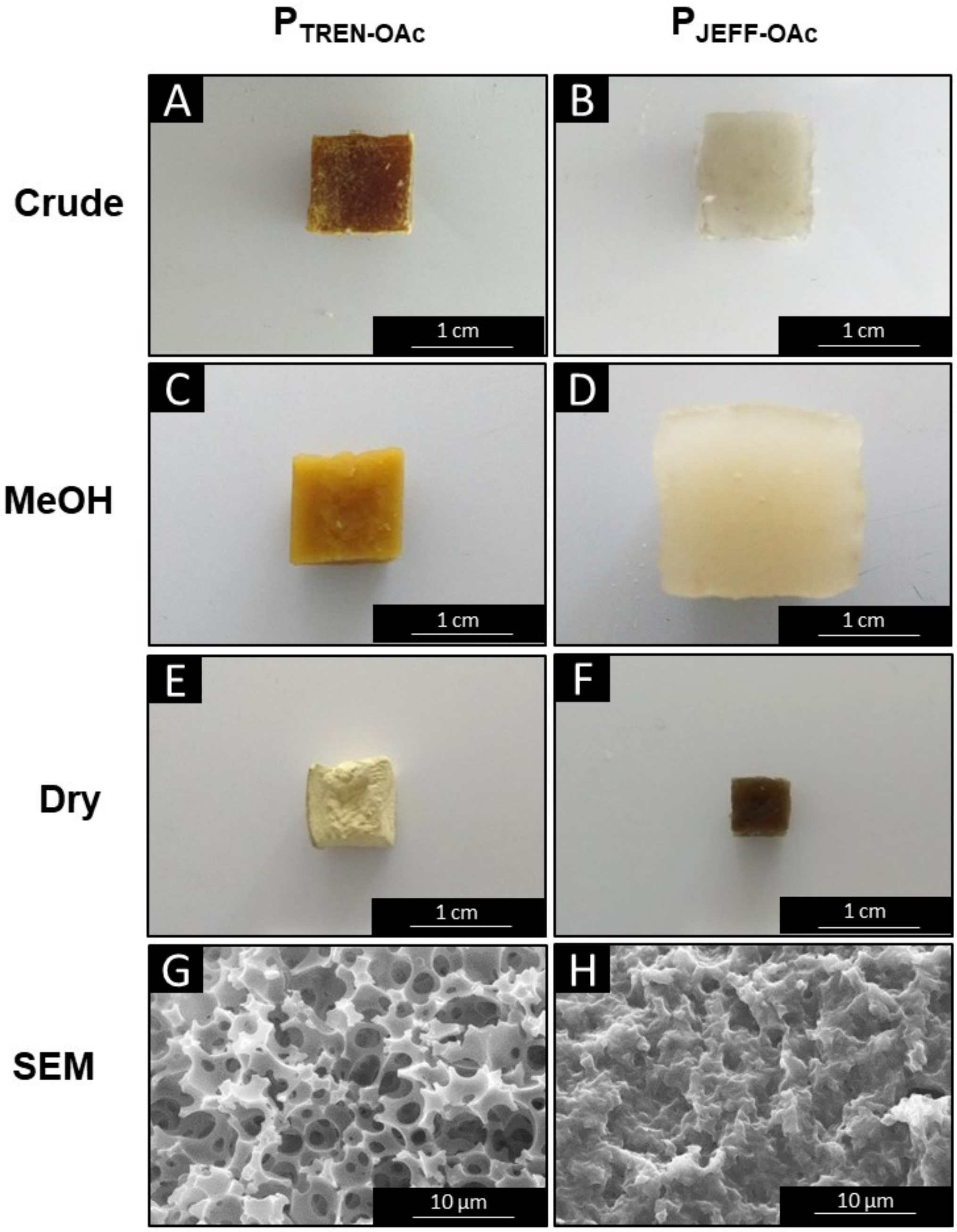

Figure S3. Pictures of the crude $P_{TREN\text{-}OAc}$ (A) and $P_{JEFF\text{-}OAc}$ (B) samples after curing. Images of the same $P_{TREN\text{-}OAc}$ (C) and $P_{JEFF\text{-}OAc}$ (D) samples swollen in MeOH. Pictures of the same $P_{TREN\text{-}OAc}$ (E) and $P_{JEFF\text{-}OAc}$ (F) samples dried under vacuum at 50 °C as well as the corresponding SEM images ($P_{TREN\text{-}OAc}$ (G) and $P_{JEFF\text{-}OAc}$ (H)).

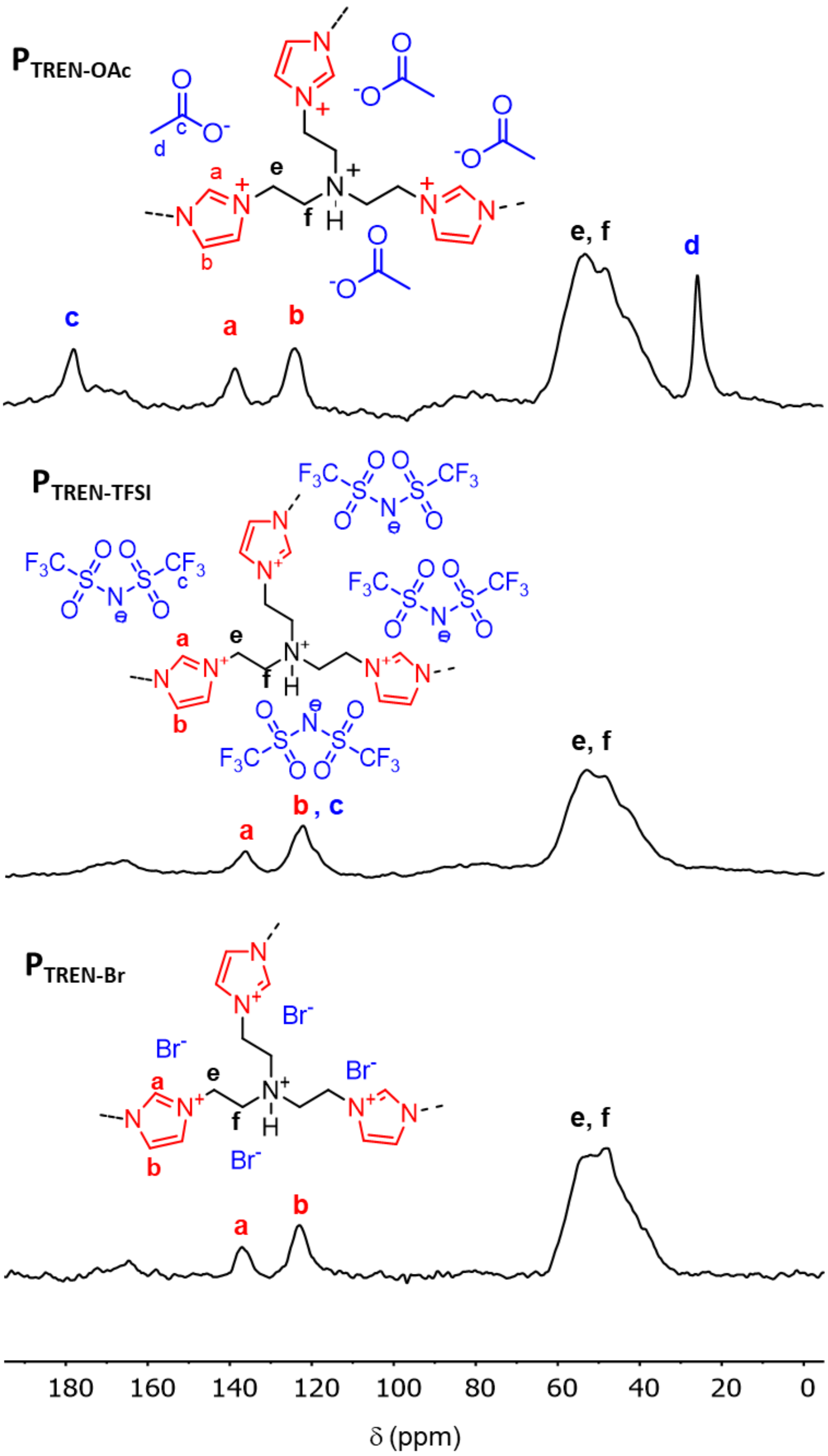

Figure S4. ^{13}C solid state NMR spectra of PTREN with acetate, TFSI and bromide as counterions.

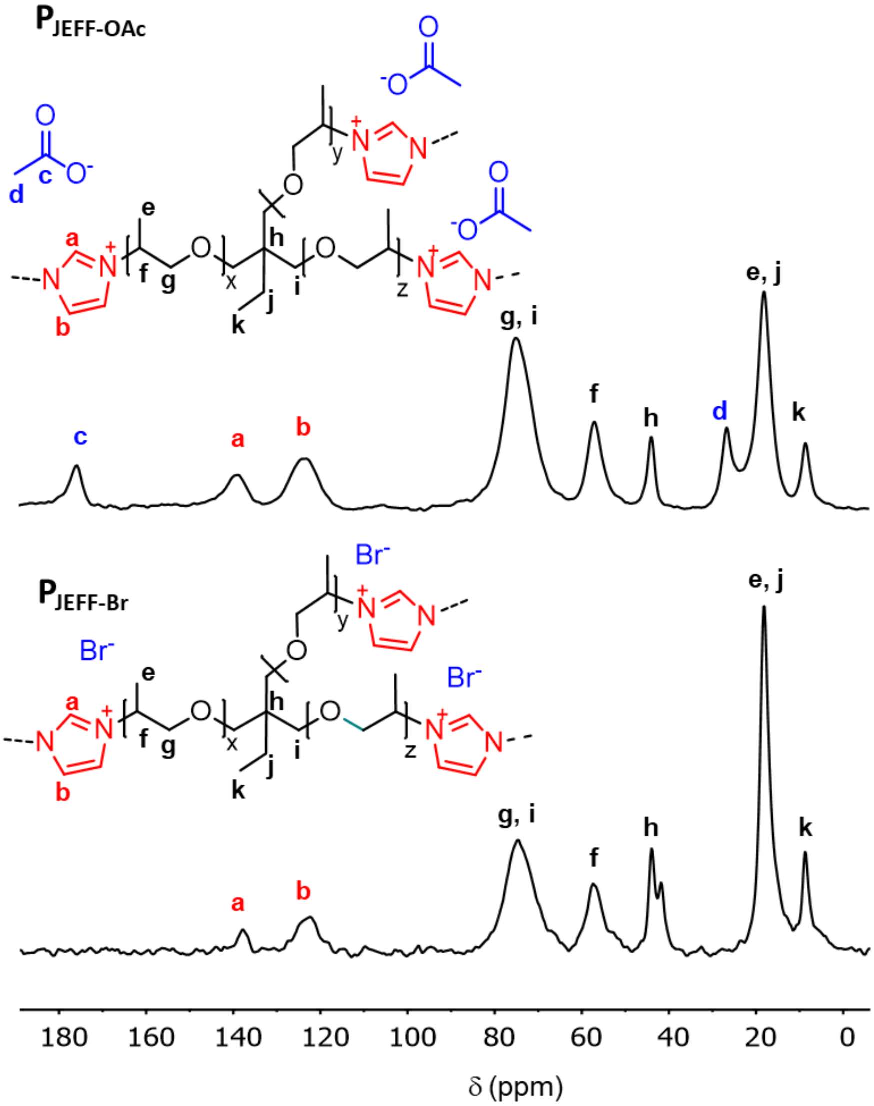

Figure S5. ^{13}C solid state NMR spectra of P_{JEFF} with acetate and bromide as counterions.

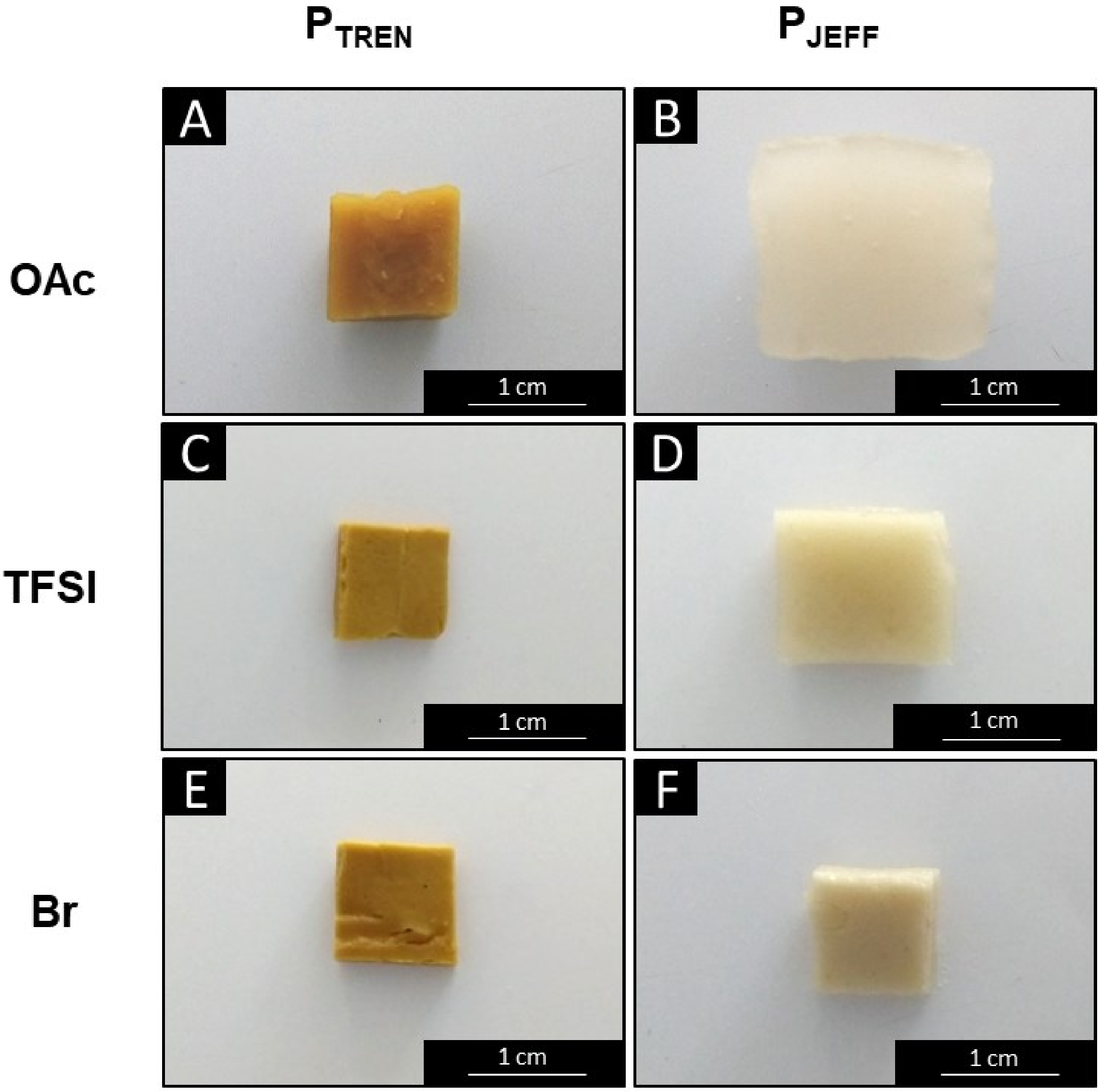

Figure S6. Pictures of polyHIPEs swollen in MeOH. $P_{TREN-OAc}$ (A), $P_{TREN-TFSI}$ (C), $P_{TREN-Br}$ (E) and $P_{JEFF-OAc}$ (B), $P_{JEFF-TFSI}$ (D), $P_{JEFF-Br}$ (F).

Table S1. Thermal properties of P_{TREN} and P_{JEFF} with different counterions.

Cation	**Anion**	**T_{OD} [a] (°C)**	**T_g (°C)**
P_{TREN}	Acetate	151	NA
	TFSI	274	NA
	Bromide	203	NA
P_{JEFF}	Acetate	172	27
	TFSI	347	-5
	Bromide	300	61

[a] Onset degradation temperature (T_{OD}) corresponding to a loss of 5 wt%.

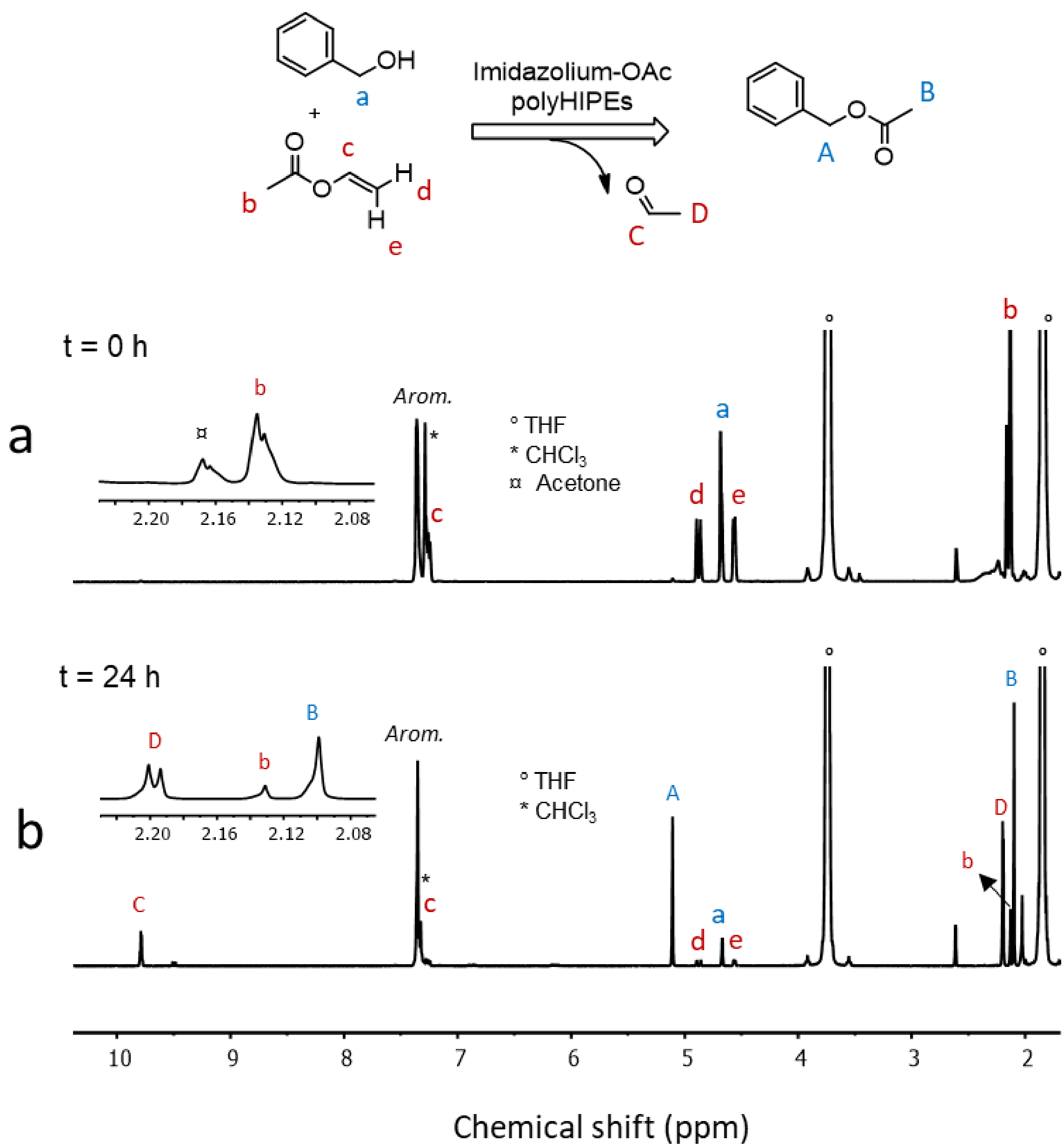

Figure S7. ^{1}H NMR spectra (in CDCl$_3$) for the transesterification reaction between of benzylic alcohol (0.5 mL) and vinyl acetate (0.6 mL) in dry THF (5 mL) in the presence of the P$_{\text{JEFF-OAC}}$ catalyst (193 mg, 10 mol%). a) spectrum of the initial reaction mixture at room temperature. b) Spectrum of the reaction mixture after 24 hours at 80 °C. (conversion = 83 %). For details, see Table 1.

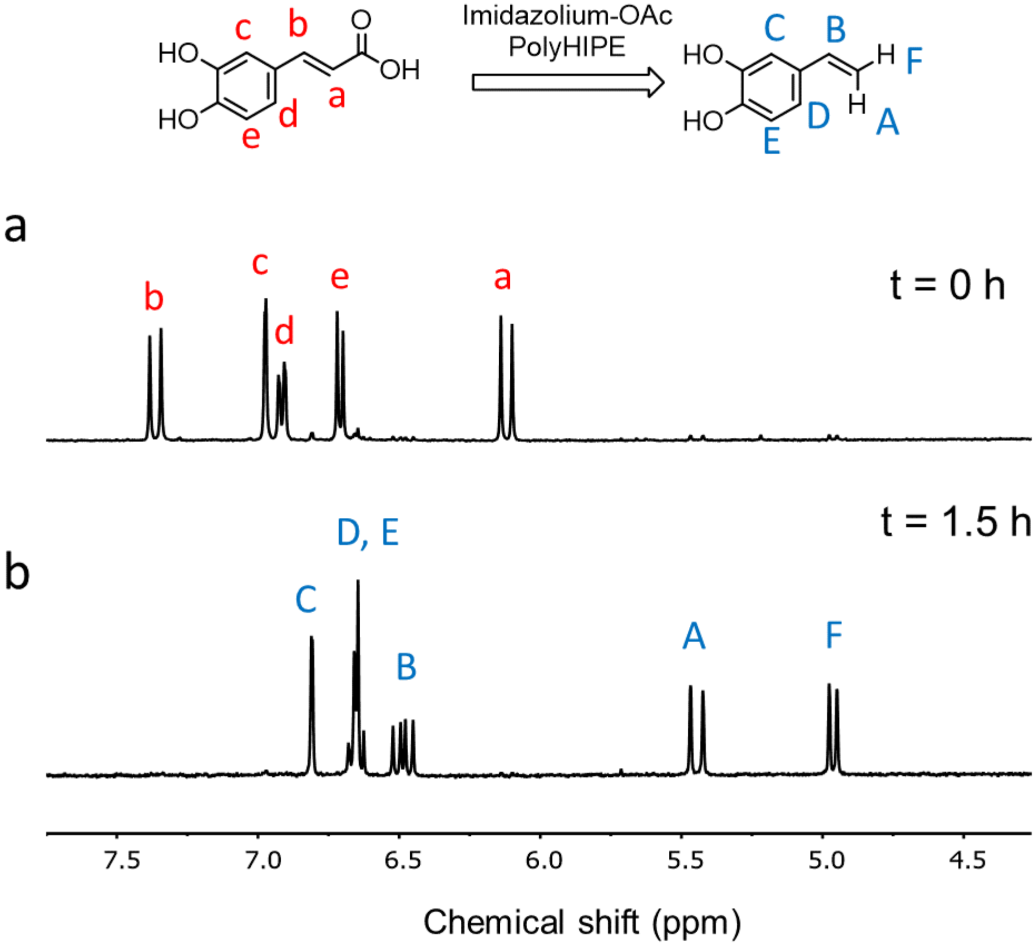

Figure S8. ^{1}H NMR spectra (in deuterated DMSO) for the decarboxylation reaction of caffeic acid (90 mg) in dry DMSO (5 mL) in presence of the $P_{JEFF\text{-}OAc}$ catalyst (97 mg, 50 mol%). a) Spectrum of the initial reaction mixture at room temperature. b) Spectrum of the reaction mixture after 90 minutes at 115 °C (conversion = 100 %). For details, see Table 1.

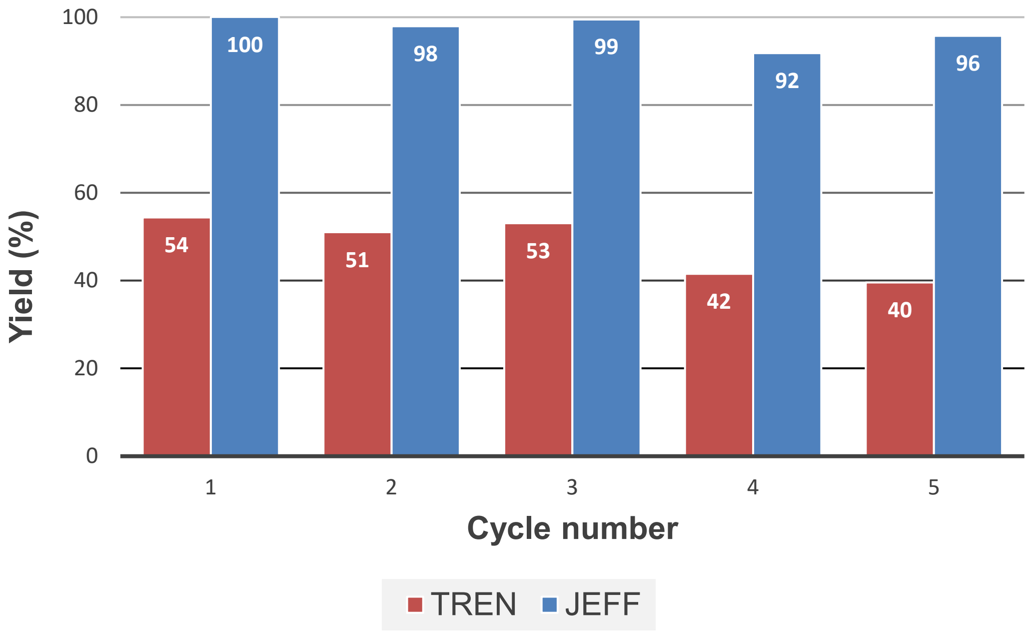

Figure S9. Recycling experiments carried out on the decarboxylation reaction catalyzed by $P_{JEFF-OAc}$ and $P_{TREN-OAc}$. The cycle was repeated five times for each catalyst.