Supporting information

Electrode-Modified Block CoPoly-Ionic Liquid Boosting the CO_2 Reduction toward CO in Water-based Media

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Experimental section

General methods

All chemicals were received from commercial sources and used as received. Styrene for synthesis, 4-vinylbenzyl chloride 90%, N,N-dimethylformamide 99.5%, imidazole 99%, 1-ethylimidazole >95%, 1-butylimidazole 98%, bis(trifluoromethane)sulfonimide lithium salt, Nafion© perfluorinated resin (10 µL of a 5 wt% solution in a mixture of lower aliphatic alcohols containing 5% water) and absolute ethanol were purchased from Sigma-Aldrich. Arkema provided the BlocBuilder® alkoxyamine and the nitroxide radical SG1. 1-ethyl-3-methylimidazolium tetrafluoroborate (>98%) was purchased from IOLITEC Ionic liquid Technologies GmbH.

Material characterization

The ^{1}H-NMR analyses were performed on a Bruker AVANCE spectrometer (1H frequency = 400 MHz). The quantitative spectra were acquired using a nutation pulse of 30°, 32 scans and a relaxation delay D1 of 5 sec. $CDCl_3$ and MeOD were used as solvents and purchased from Innova-chem. The chemical shift (ppm) has been calibrated based on the residual peak of the used solvent. Size-exclusion chromatography (SEC) with THF as eluent was used. It is equipped with 4 columns (Shodex KF801, 802.5, 804 and 806) of 8 × 300 mm and a pre-column (Shodex KF-G) of 4,6 × 8 mm. the analysis performed at 30 ˚C with 1 mL.min^{-1} THF flow. The detector is a viscosimeter Malvern VE3580. Thermogravimetric analyses were made on a TGA Q50 from 25 to 600 ˚C at 10 ˚C.min^{-1} with 10 min isotherm at 120 ˚C for solvents removal. Scanning electron microscope (SEM) images were recorded using SEM Hirox SH-3000 operating at 25 kV. The sample was previously metalized.

Synthesis of PS by Nitroxide-Mediated Polymerization (NMP)

The synthesis of the polystyrene first block was carried out using Nitroxide-Mediated Polymerization (NMP), a controlled radical polymerization (CRP).[1] Following this polymerization methodology, we used a commercially available alkoxyamine (BlocBuilder®) kindly provided by Arkema as an initiator for the radical polymerization and SG1 (4-(diethoxyphosphinyl)-2,2,5,5-tetramethyl-3-azahexane-N-oxyl) as a nitroxide controlling agent (Scheme S1). A PS small block was aimed. First, the styrene (96 mmol – 40 eq) and the BlocBuilder® alkoxyamine (2.4 mmol – 1 eq) were dissolved in 100 mL of DMF to have 1 M concentration of monomer, in a round-bottom flask of 150 mL. The flask was sealed with a septum, put in an ice bath, degassed for twenty minutes with nitrogen and immersed in an oil bath at 115 °C for 3h. The ^{1}H NMR spectrum of the crude product showed an approximate 22% monomer conversion (Figure S1 & Equation S1). The PS was purified

via three consecutive precipitations in MeOH and dried at 70 °C under vacuum. The purity of the polymer has been determined by ^{1}H NMR, showing no traces of monomer (Figure 2). The number average molar mass *Mn* was determined by Size Exclusion Chromatography (SEC) to be 2,000 g.mol^{-1}, *i.e.* corresponding to a degree of polymerization of around 16 units, with a low dispersity value $Đ$ of 1.08 (using conventional calibration from a polystyrene calibration curve).

Synthesis of PS-*b*-PVBC by NMP

The polymerization of the PVBC block, was then carried out using the initial PS as a macroinitiator (Scheme S2), adding free nitroxide (SG_1) to further control the reaction.

The dried powder of PS 2 kDa (0.045 mmol - 1 eq) was dissolved in 3.1 mL of dimethylformamide (DMF) overnight. After solubilizing the PS block, the 50 mL round bottom flask was placed in an ice bath. 4-vinylbenzylchloride (VBC) (36 mmol – 800 eq) and nitroxide radical (SG_1 solution, 0.0045 mmol, 0,1 eq) were added, the flask was sealed with a septum and the mixture was degassed for 20 minutes with nitrogen and immersed in an oil bath at 115 °C for 6 hours to reach a conversion of around 24% calculated from ^{1}H NMR analysis. The reaction was stopped and the resulting block copolymer was precipitated three times in methanol, filtered, and dried at 50 °C under vacuum. The resulting block copolymer (PS-*b*-PVBC) was analyzed by ^{1}H NMR and SEC in THF to determine its composition and molar mass. The purity after precipitation (in MeOH) was also assessed *via* ^{1}H NMR, which shows clear peaks of the polymer, as highlighted in Figure 2.

By comparing the signals between 6 and 7,5 ppm where 4 protons are attributed to the PVCB and 5 protons to the PS and the signal at 4,5 ppm of 2 protons of the PVBC (Figure 2 and S3), we can calculate a VBC/S molar ratio around 14. Given the PS degree of polymerization (Equation S3) of 16, the number of VBC units is then estimated to be around 220. A theoretical BCP molar mass of 35,500 g.mol^{-1}is calculated and which agrees with the experimental one of 29,000 g.mol^{-1} determined by SEC, calculated from conventional calibration from polystyrene samples. A quantitative reinitiating of the first PS block (Figure 2) is obtained but a dispersity $Đ$ of 1.8 was calculated for the PS-*b*-PVBC, which proves a relative low loss of control during the VBC polymerization, as reported in the literature.[2] This increase in the dispersity value $Đ$ does not bear any consequences for this work because no chain extension was then needed.

Functionalization of PS-*b*-PVBC with imidazole-based molecules

The nucleophilic substitution of the chloride in the copolymers was carried out using different imidazoles as nucleophiles. First of all, PS-*b*-PVBC (1 g – 0.034 mmol) was dissolved in 10 mL of DMF in a 50 mL round bottom flask. Separately, one of the imidazole-based molecules (imidazole,

1-ethylimidazole or 1-butylimidazole, molar ratio imidazole/vinyl benzyl chloride of 1) was dissolved in 10 mL of DMF and then added to the round bottom flask. The flask was sealed with a septum and the mixture was degassed for 20 minutes with nitrogen and immersed in an oil bath at 60 °C for 24 hours to reach complete substitution (verified by ^{1}H NMR). The reaction was stopped and the resulting functionalized block copolymer was purified three times *via* precipitation in ether, filtered, and dried at 50 °C under vacuum. The resulting block copolymer (PS-*b*-PVBIm) was analyzed by ^{1}H NMR to reveal the purity.

Counter-ion exchange

The Cl^- counter-ions present at the end of the PS-*b*-PVBIm synthesis was replaced by $TFSI^-$, by dissolving the 0.500 g of functionalized polymer in DMF and a two-fold excess (compared to the imidazole groups) of LiTFSI was added. The reaction was left to stir at room temperature for 3 days. The product was purified three times *via* precipitation in ether, filtered, and dried at 50 °C under vacuum.

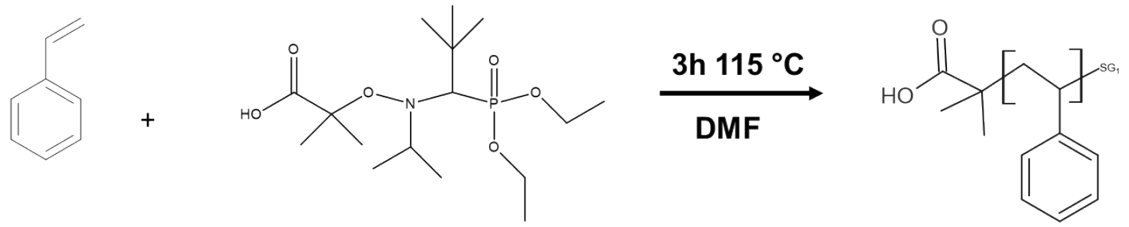
Electrode preparation and characterization

The Re@HPC/GDL[3] electrode was prepared as previously described.[3] Re@HPC (5 mg) was sonicated 1 h in absolute ethanol (200 µL) and a solution of Nafion perfluorinated resin (10 µL of a 5 wt% solution in mixture of lower aliphatic alcohols containing 5% water). The suspension was then, carefully, deposited by drop casting on a gas-diffusion Layer, GDL (AVCarb GDS 3250; 1 cm^2) in order to have a uniform deposition. The electrode was then dried in air overnight at room temperature. For all the experiments the working electrodes were prepared in the same way. For the dip-coating procedure, a dip coater was used and a solution of the polymers in MeOH was prepared with a 2 wt% concentration. The Re@HPC/GDL was immersed at different speeds of dip-coating 1000, 5000 and 10000 $\mu M.sec^{-1}$ in the BCPILs solution and left 15 sec in the solution. The thickness and the amount of BCPILs loaded on the electrode was investigated by TGA.

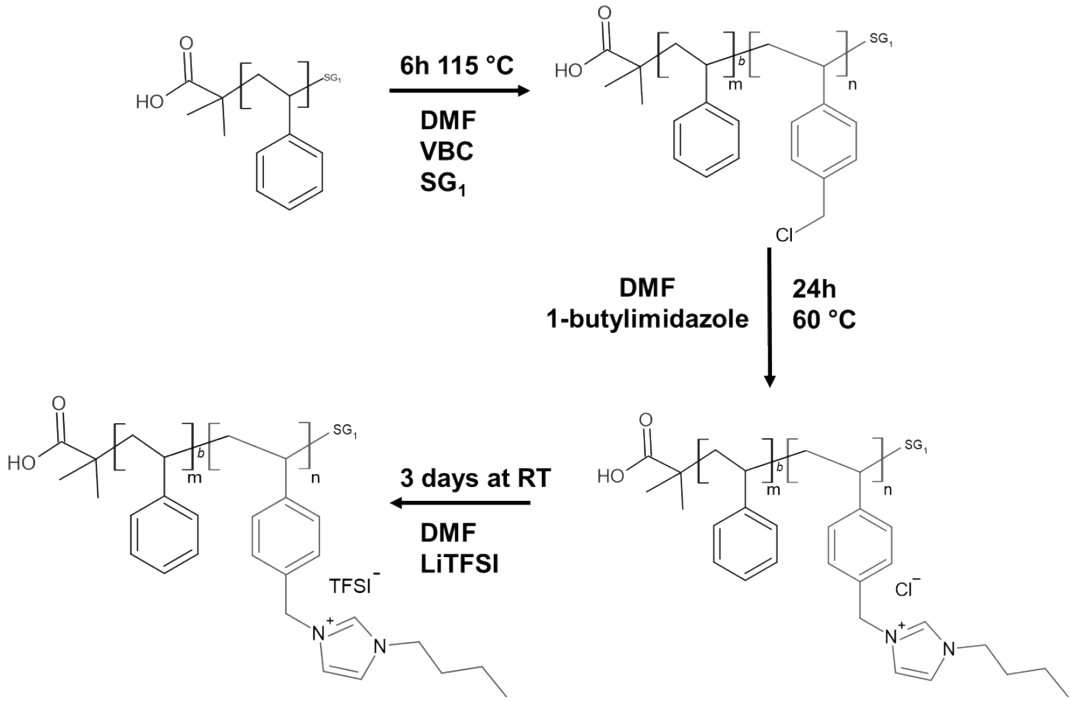
Electrochemical characterization

All electrochemical characterization and electrolysis experiments were carried out using a Metrohm PGSTAT204 potentiostat with a three-electrode cell with an Ag/AgCl/3M KCl reference electrode, a working PILs/Re@HPC/GDL electrode and platinum as counter electrode. The electrolyte was composed of a mixture of 5/95, 10/90, 25/75 and 50/50 *v/v* H_2O/EMIM (50 mL), CO_2-saturated and 0.5 M of $KHCO_3$. The electrochemical cell was first purged with CO_2 at a flow rate of 50 $mL.min^{-1}$ for 30 minutes before catalytic tests using a mass flow controller (Bronkhorst EL-FLOW

prestige FG-201CV). The experiments were carried out at a constant CO_2 flow (50 mL.min^{-1}). All potential values are given versus the potential of the Fc/Fc^+ couple added as an internal standard to the solution after measurement. In 5/95 and 10/90 *v/v* H_2O/EMIM: $E1/2(Fc/Fc^+)$ = 0.35V *vs.* Ag/AgCl, in 25/75 *v/v* H_2O/EMIM: $E1/2(Fc/Fc^+)$ = 0.30 V *vs.* Ag/AgCl and n 50/50 *v/v* H_2O/EMIM: $E1/2(Fc/Fc^+)$ = 0.28 V *vs.* Ag/AgCl (Annexe 33). H_2 and CO were identified and quantified using gas chromatography (GCMS-QP2010-plus, Shimadzu, Japan) equipped with a packed column (ShinCarbon ST, 2m; 0.53 mm, mesh80/100, Restek, USA) for permanent gases separation and a capillary column (Rtx-Wax 60m x 0.32 mm x 0.5µm, Restek, USA) for light hydrocarbons separation. Helium (6.0, AirLiquide) was used as carrier gas. A Dielectric-Barrier Discharge Ionization Detector (BID) was used to quantify all permanent gases (H_2, CO, Methane, Ethane, ethylene).



Scheme S1. Synthetic route of the PS



Scheme S2. Synthetic route of the PS-*b*-PVBIm TFSI block-copolymers starting from a small molecular weight PS (the synthesis route of the PS was omitted for as matter of clarity and shown in the Scheme S1).

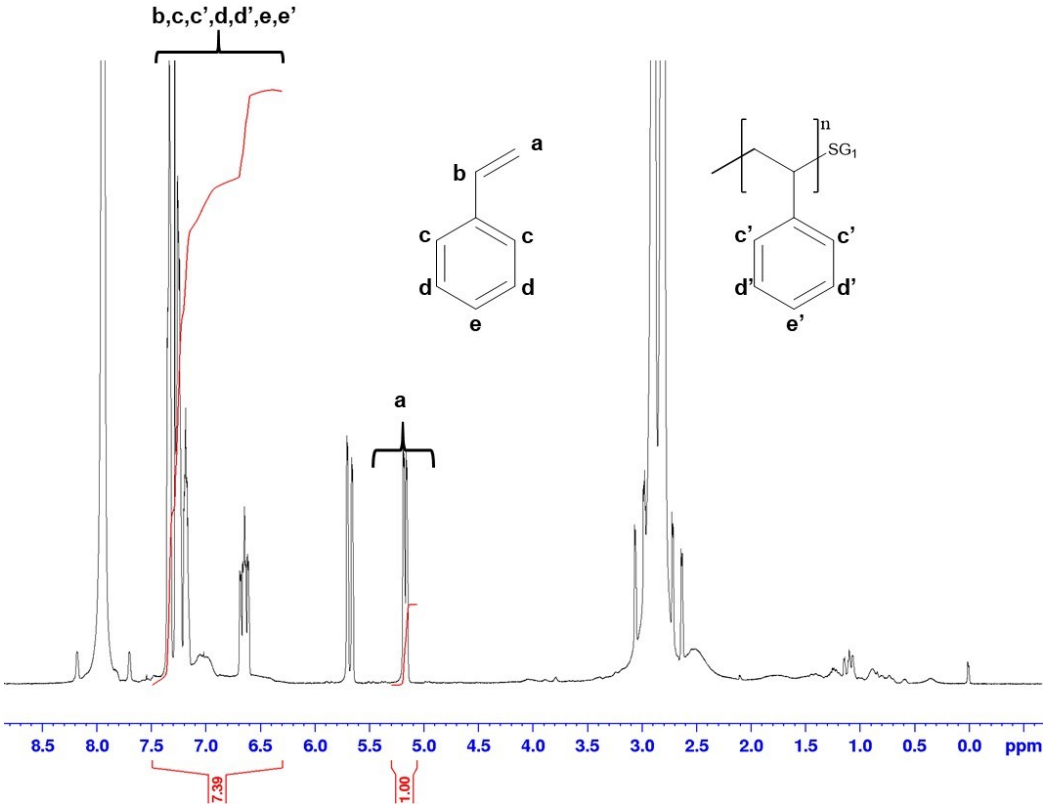


Figure S1. ^{1}H NMR in $CDCl_3$ of solution media of PS synthesis after 3 hours at 115 °C.

$$6Hm + 5Hp = 7.39$$

$$1Hm = 1$$

$$\%\ Conversion = \frac{Hp}{Hm + Hp} * 100$$

Equation S1. Equations for the conversion calculation. Hm is protons monomer and Hp protons polymer. The area of the peaks highlighted in blue (7.39) was obtained by calibrating the area of the peak highlighted in green at 1.

$$2Hm + 2Hp = 2.63$$

$$1Hm = 1$$

$$\%\ Conversion = \frac{Hp}{Hm + Hp} * 100$$

Equation S2. Equations for the conversion calculation. Hm is protons monomer and Hp protons polymer. The total area of the peaks highlighted in blue and green at 4.5 ppm (2.63) was obtained by calibrating the area of the peak highlighted in blue at 6.25 ppm at 1.

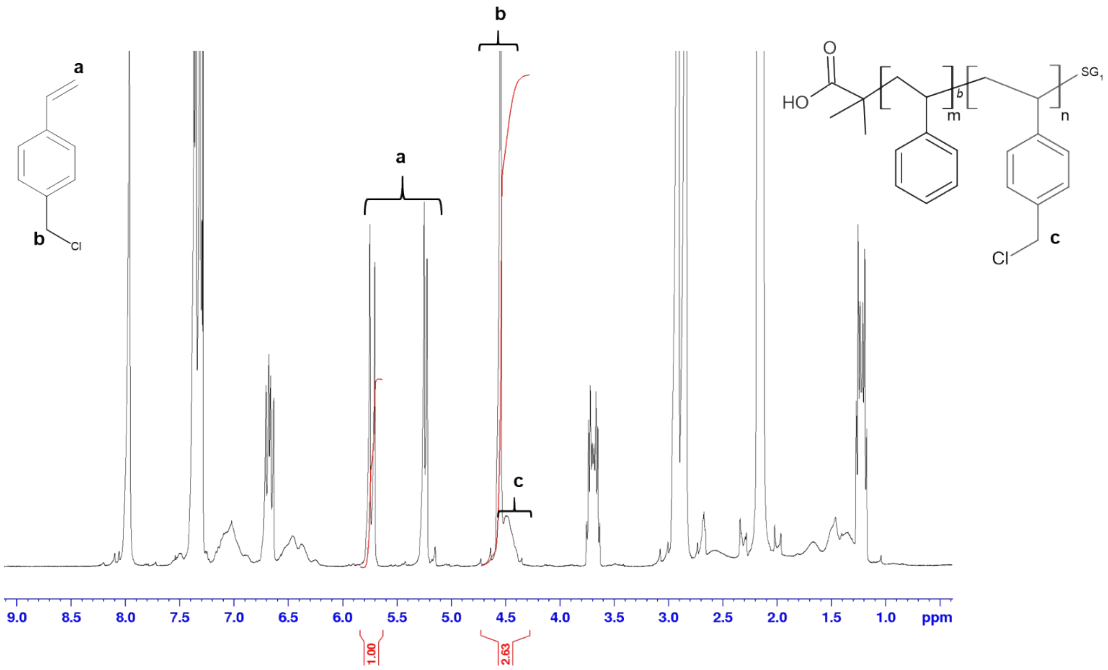


Figure S2. ^{1}H NMR in $CDCl_3$ of solution media of PS-*b*-PVBC synthesis after 6 hours at 115 °C.

$$DPn = ([M]_0 / [I]_0) * (conversion)$$

Equation S3. Degree of polymerization.

$$h0 = c\left(\frac{\eta U0}{\rho g}\right)^{1/2}$$

Equation S4. Theoretical equation for the thickenss pof the polymer layer deposted where: h_0= thickness, C= solution concentration, η= viscosity, ρ= solution density, U_0= withdraw speed

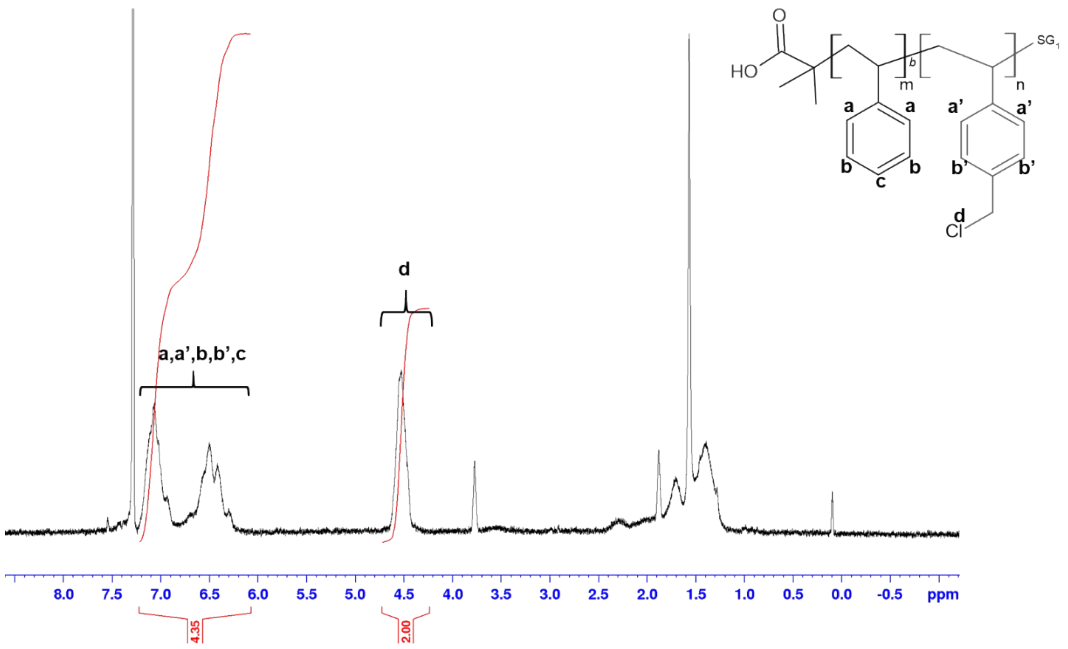


Figure S3. ^{1}H NMR in $CDCl_3$ of purified PS-*b*-PVBC.

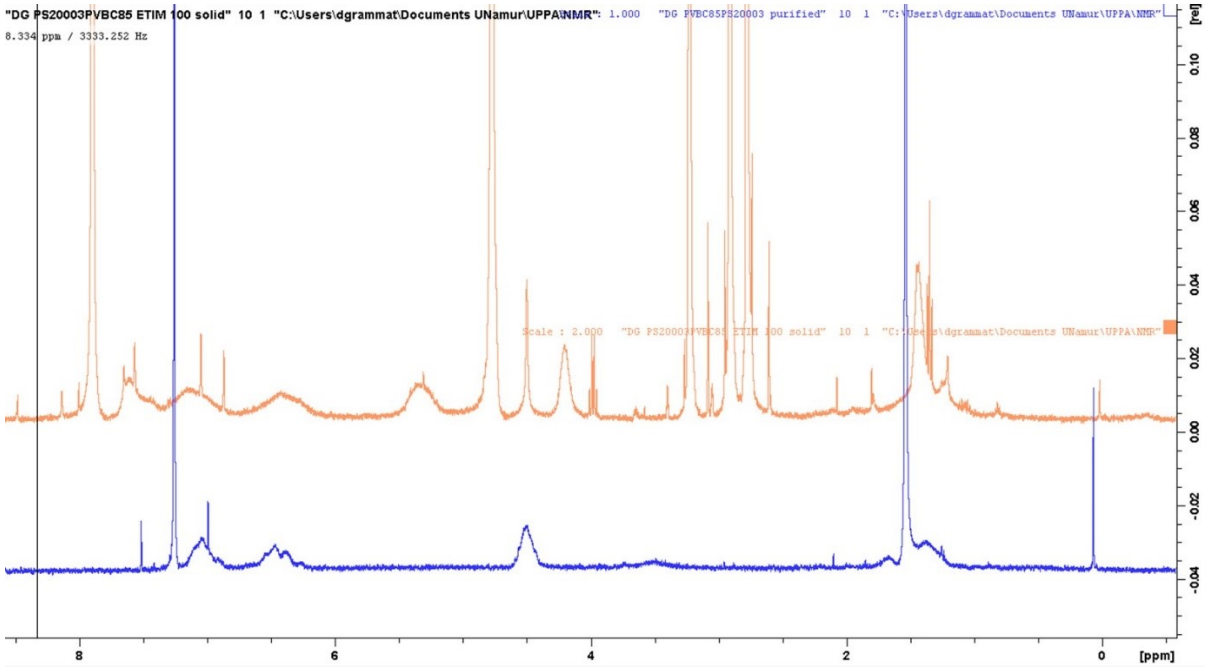


Figure S4. Stack ^{1}H NMR of PS-*b*-PVBC (in $CDCl_3$) in blue and PS-*b*-PVBEI Cl (in MeOD) in orange.

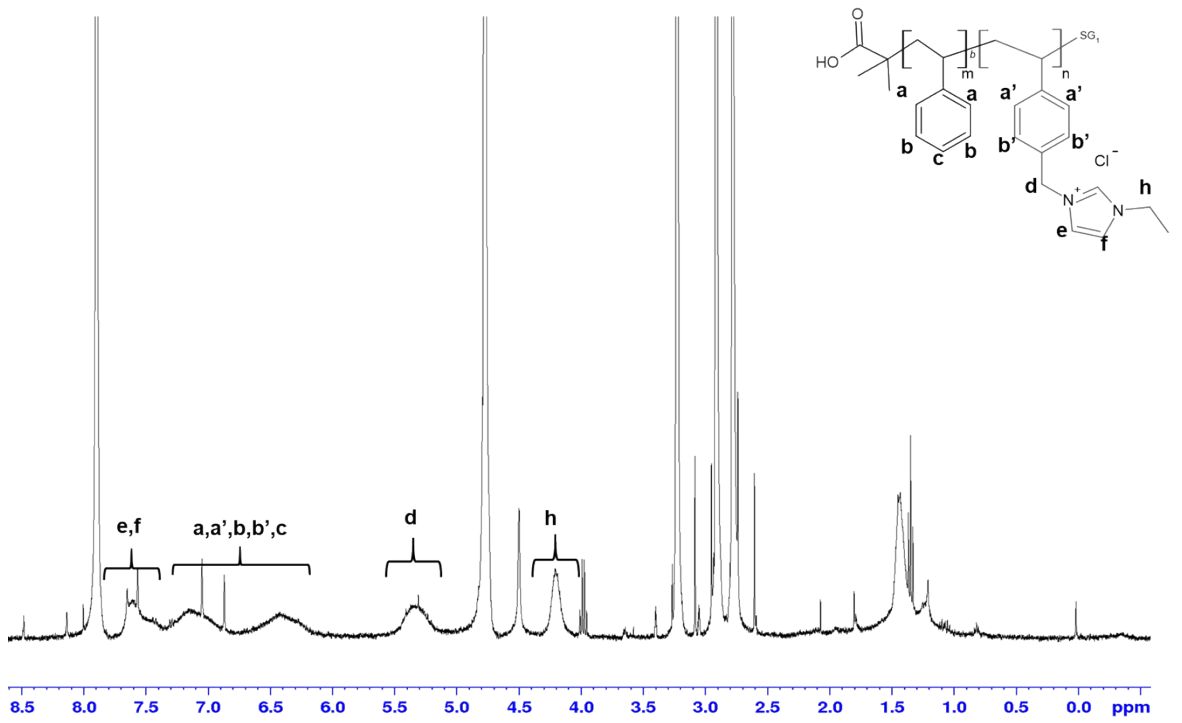


Figure S5. [1]H NMR in MeOD of the crude PS-*b*-PVBEI Cl.

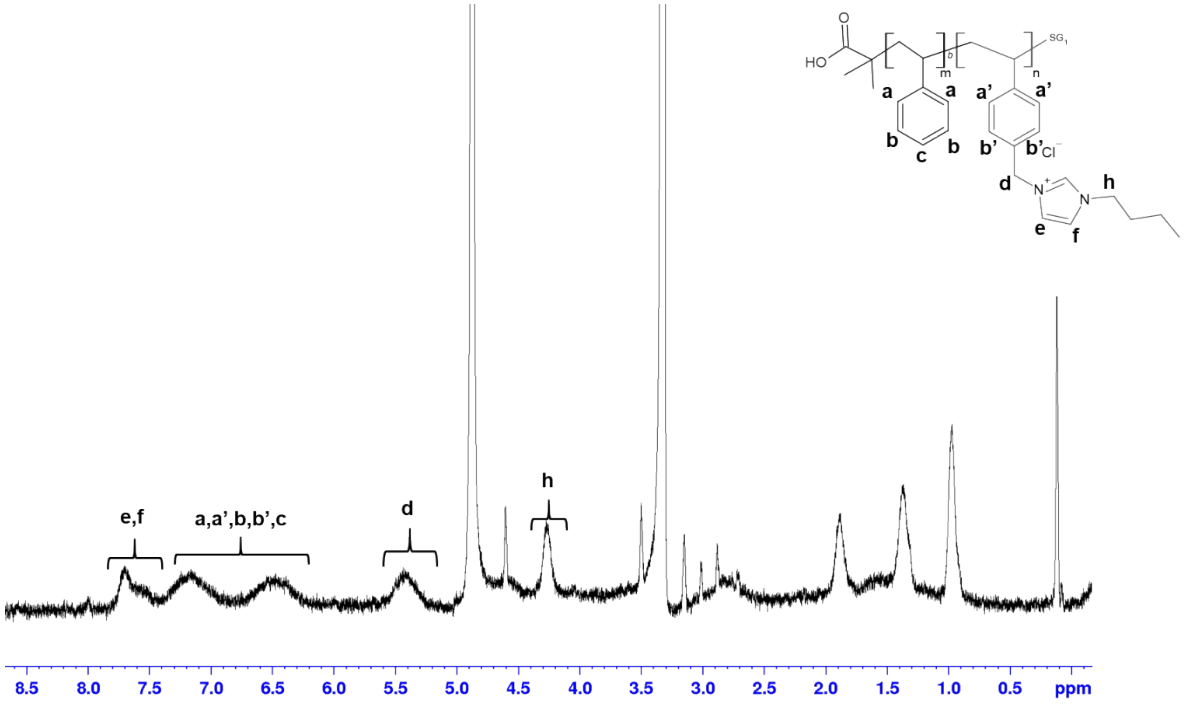


Figure S6. [1]H NMR in MeOD of the purified PS-*b*-PVBBI Cl.

Table S1. Macromolecular features of the block copolymer ionic liquid BCPILs synthesized

Polymer	Imidazole group	Counter-ion	Molecular weight* kDa	Solubility
PS-*b*-PVBEI Cl	1-Ethylimidazole	Cl	50	MeOH/H_2O
PS-*b*-PVBEI TFSI	1-Ethylimidazole	TFSI	n/a**	n/a**
PS-*b*-PVBBI Cl	1-Butylimidazole	Cl	55	MeOH/EtOH
PS-*b*-PVBBI TFSI	1-Butylimidazole	TFSI	102	MeOH/EtOH

**Calculated from the ^{1}H NMR spectra considering a full substitution of the chloride*

***Not applicable due to the non-solubility in usual solvents*

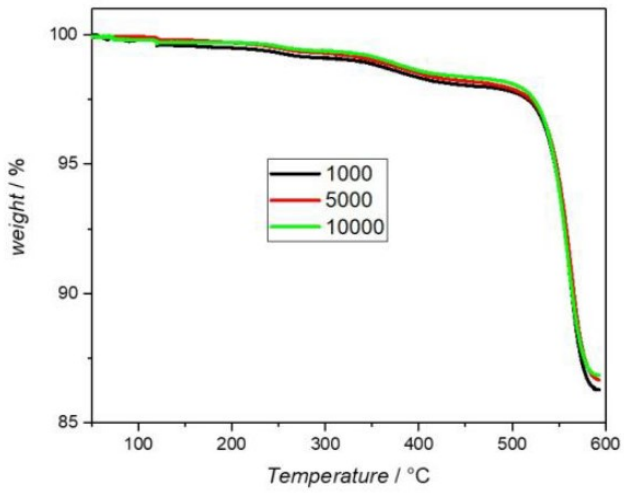


Figure S7. TGA analysis of 2wt% in MeOH PS-*b*-PVBBI TFSI//Re@HPC/GDL electrodes dip-coated at 1000, 5000 and 10000 µm.sec^{-1}.

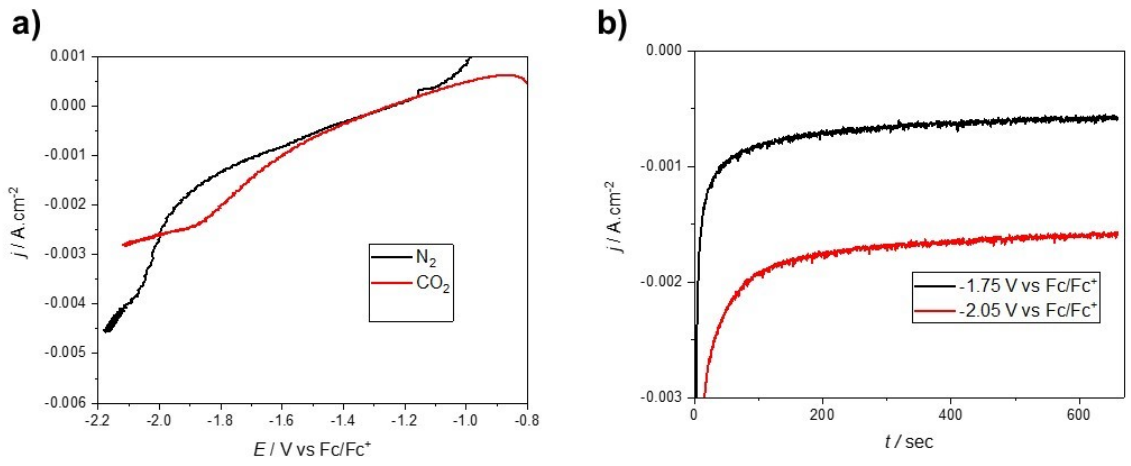


Figure S8. Controlled potential electrolysis of CO_2 using the PS-*b*-PVBBI TFSI/Re@HPC/GDL electrode: a) LSV in 5% *v/v* H_2O/EMIM saturated with CO_2 (red) or with N_2 (black), scan rate 20 $mV.s^{-1}$ and b) total current density at various applied potentials as a function of time.

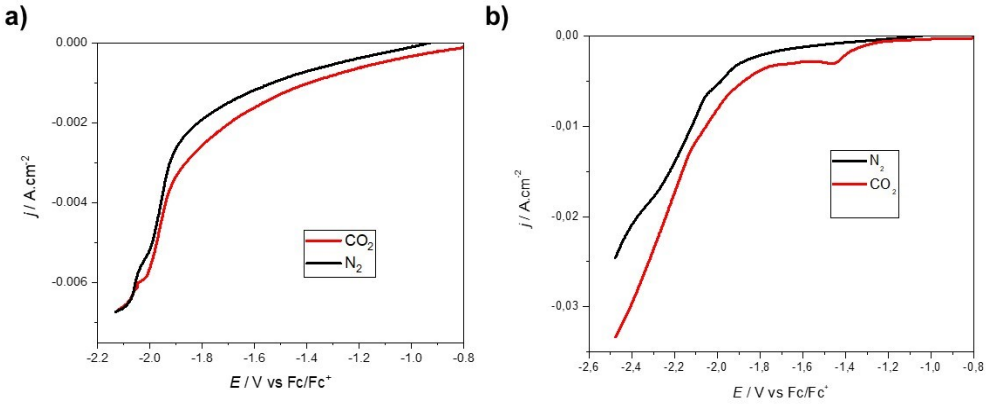


Figure S9. Controlled potential electrolysis of CO_2 using the PS-*b*-PVBBI TFSI/Re@HPC/GDL electrode; LSV in 25% a) and 50% b) *v/v* H_2O/EMIM saturated with CO_2 (red) or with N_2 (black), scan rate 20 $mV.s^{-1}$.

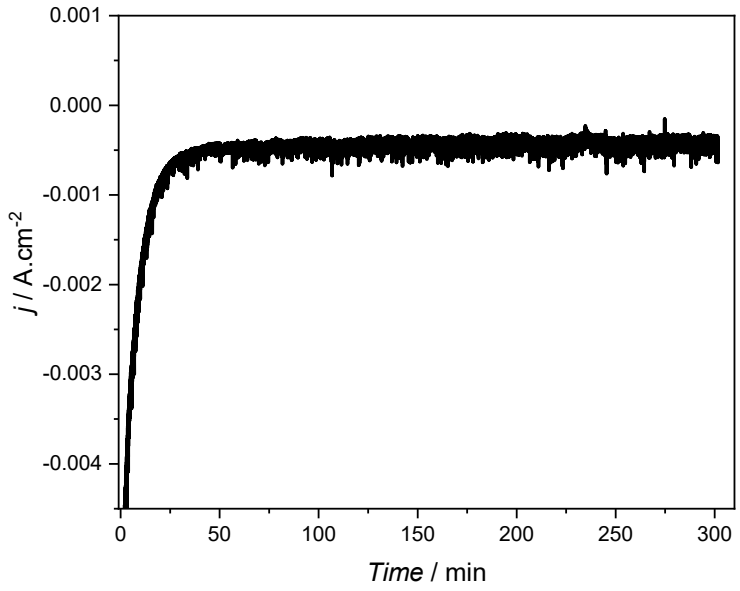


Figure S10. 5h Long-term electrolysis. Current density as a function of time during CPE at -1.85 V *vs* Fc/Fc^+ under CO_2 in 10% *v/v* H_2O/EMIM using the PS-*b*-PVBBI TFSI/Re@HPC/GDL electrode.

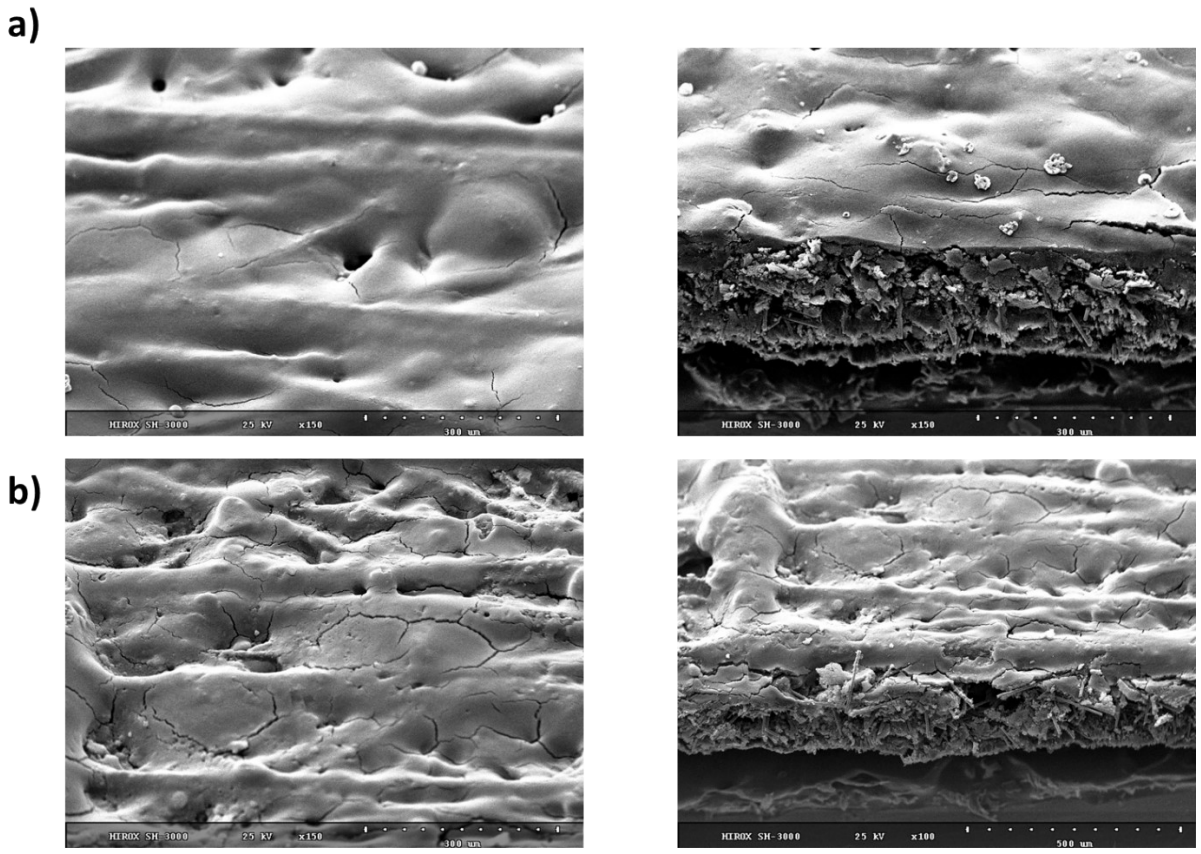


Figure S11. Surface and cross-section SEM images of PS-*b*-PVBBI TFSI/Re@HPC/GDL, tilted at 45°, before (a) and after (b) 5 h electrolysis at -1.85 *vs* Fc/Fc^+ under CO_2 in 10% *v/v* H_2O/EMIM.

Table S2. Summary table of dip-coating and TGA experiments. Electrode left 15 sec in solution of 2 wt % of PS-*b*-PVBBI TFSI in MeOH for dip-coating.

Speed dip-coating µm.sec^{-1}	**Weight loss %**
1000	1.8
5000	1.9
10000	1.6

Table S3. Summary of the FEs and ratio CO/(CO+H_2) obtained with Re@HPC/GDL and PS-*b*-PVBBI TFSI/Re@HPC/GDL in electrolytes with different percentages of water and at different potentials applied. * *FEs for the long term electrolysis in Figure S11, respectively after 60, 120, 180, 240 and 300 minutes.*

Electrode	**Electrolyte H_2O/EMIM-BF_4**	**Potential V *vs.* Fc/Fc^+**	**FE H_2**	**FE CO**	**FE HCOOH**	$\frac{CO}{(CO+H2)}$
Re@HPC/GDL[3]	1 % *v/v*	-1,75	2	77	-	97
	5 % *v/v*	-1,75	9	79	-	90
		-1,85	5	70	20	93
		-1,95	18	22	50	55
		-2,05	20	3	76	13
	10 % *v/v*	-1,75	33	47	-	61
PS-*b*-PVBBI TFSI/Re@HPC/GDL	5 % *v/v*	-1,85	1	9	-	90
	10 % *v/v*	-1,65	-	9	-	100
		-1,85	-	23	-	100
		*-1,85	10	11	-	52
			8,2	11	-	57
			6,5	11	-	63
			6,8	11	-	62
			6,6	11	-	63
	25 % *v/v*	-1,9	22	12	-	35
	50 % *v/v*	-1,48	58	11	-	16
		-1,88	72	2	-	2

Table S4. TON and TOF values for CO prodcution calculated for the most relevant electrodes tested.

Electrode	Electrolyte H_2O/EMIM-BF_4	Potential V *vs.* Fc/Fc^+	TON_{CO}	TOF_{CO} (s^{-1})
Re@HPC/GDL[3]	5 % *v/v*	-1,75	260*	0,3*
PS-*b*-PVBBI TFSI/Re@HPC/GDL	10 % *v/v*	-1,85	2,1**	0,003**
	10 % *v/v*	-1,85	64,65***	0,004***

** Calculated after 15 min of CPE*

*** Calculated after 10 min of CPE*

**** Calculated after 5 hours CPE*

References

1 R. B. Grubbs, *Polym. Rev.*, 2011, **51**, 104–137.

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