New poly(ionic liquid)s based on poly(azomethine-pyridinium) salts and its use as heterogeneous catalysts for CO₂ conversion

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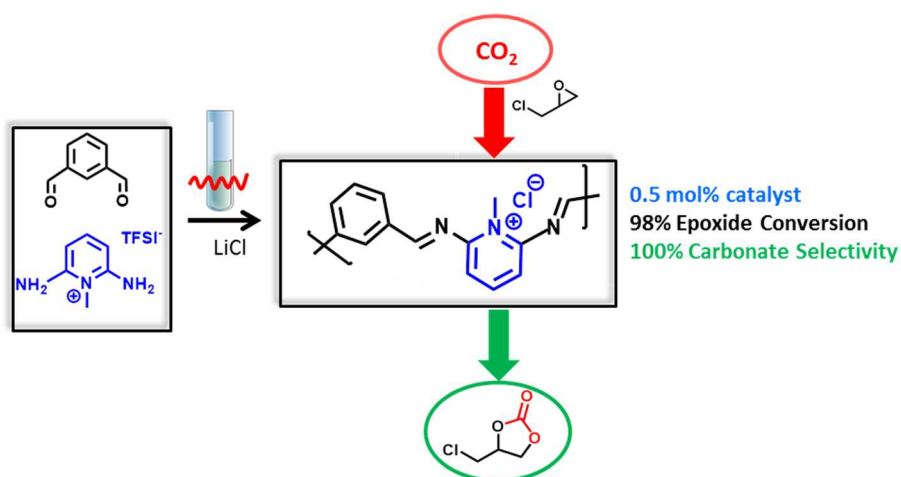
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Abstract

A fast and simple synthetic route towards a new family of poly(ionic liquids) based on aromatic crosslinked poly(azomethine-pyridinium) salts is described. These new polymers were prepared in one step from new diamine methyl pyridinium salts and isopthaldehyde, in 30 min under microwave irradiation. By this method, poly(azomethine-pyridinium) containing chloride (Cl), bis(trifluoromethylsulfonyl)imide (TFSI) and hexaflorophosphate (PF_6) as counter-anions were synthetized. This new pyridinium poly(ionic liquid)s were obtained as insoluble powders showing high thermal stability. The poly(azomethine-pyridinium)s were tested as heterogeneous catalysts in the cycloaddition of CO_2 to epichlorohydrin to obtain chloropropylene carbonate. The polymers containing chloride anion shows high content of catalytically active sites and the best performance of the series, with 100% selectivity towards the chloropropylene carbonate in a reaction without solvent at 3 bar of CO_2, 100°C and low catalyst loading (0.5 mol%).

1. Introduction

In recent years, the reaction of cycloaddition of CO_2 to epoxides is being widely investigated because it is a very attractive strategy to take advantage of undesirable CO_2 and to obtain value-added products such as cyclic carbonates [1-3]. Among the epoxides investigated, epichlorohydrin (ECH) is one of the most interesting as a source material because it can be produced from glycerin derived from vegetable oil [4]. On an industrial scale this reaction the cycloaddition of CO_2 to epoxides was made at high pressure and high temperature and typically in the presence of metal catalysts. However due to the inconvenience of using metals, enormous synthetic efforts have been made to obtain efficient metal-free catalysts to carry out this conversion. For instance by post-functionalization of different types of materials, for example microporous organic polymers with hydroxyl groups [5], mesoporous organosilica with urea groups [6], polystyrene with imidazolium hydrochloride groups [7] or porous polyphenylenes with guanidine moieties [8] have recently reported as efficient metal-free heterogeneous catalysts to perform this reaction under relatively mild conditions.

In the last years, poly(ionic liquids) have emerged as very promising heterogeneous catalysts for a number of reactions such as benzoin condensation, transesterifications, cyanosilylation or carbonatation of epoxides [9-14]. Most of the works have focused in imidazolium poly(ionic liquid)s [15-21] based in aliphatic polymer backbones such as vinylic or acrylic. However, for some reactions it is important that the catalysts show high thermal stability. For this reason, in the last years high thermally stable polymers based in polyimide backbones and aromatic porous poly(ionic liquid)s have been developed. Although imidazolium polymers have been mostly used in the reaction between epoxides and CO_2, recently it has been reported a superior catalytic performance of other cations such as quaternary ammonium based poly(ionic liquid)s

[22]. For all this reason, we thought of interest the synthesis of poly(ionic liquid)s with pyridinium cations which are well known for its catalytic uses and thermally stable polymer backbones.

Aromatic poly(imines) or poly(azomethines) (**PAMs**) [23-25] are high-performance Schiff base polymers characterized by excellent thermal stability, semiconductivity, good mechanical properties and high insolubility in most organic solvents what hinders its processing. Nevertheless, this insolubility can be exploited in the heterogeneous catalysis field. Imine or azomethine are versatile groups since can be used to prepare monodentate electron donors, in stereoselective heterocycle synthesis or for biological application since compounds containing azomethines groups possess remarkable anticancer, anibacterial or antifungal activity [26].

Thus, we have recently prepared, by microwave irradiation, a new poly(azomethine) containing pyridine groups in its structure which was used as support to obtain metal containing catalysts that were anchored through the azomethine or the pyridine groups. The novel polymers were completely insoluble and were used as heterogeneous catalysts in the above reaction working in relative soft conditions: 7 atm of CO_2, 100°C, solvent-free and using very little amount of catalysts which implies high turnover numbers [27]. The presence of ionic groups in poly(azomethine-pyridine) networks could yield interesting heterogeneous catalysts that combine the properties of both. Thus, in this work we report the preparation of new type of ionic polymers, designated as poly(azomethines-pyridinium) salts (**PAM-PyMe(X)**). The new polymers were used to investigate the catalytic activity in the cycloaddition of CO_2 to epichlorohydrin (ECH).

2. Experimental Part

2.1. Reagents

2,6-diaminopyridine (DA-Py) (98%) was procured from ACROS Organics and recrystallized from acetone before use. Isophthaldehyde was supplied by TCI europe and it was recrystallized from water before use. Lithium bis(trifluoromethane)sulfonamide (LiTFSI) (99%) was supplied by the courtesy of Solvionic. Methyl trifluoromethanesulfonate (MeOTf), lithium chloride (LiCl) and potassium hexafluoro phosphate (KPF_6) were supplied by Aldrich. All salts were dried under vacuum at 110 °C, 2 h before use. Solvents and other reagents were obtained from Aldrich used without further purification.

2.2. Synthesis of diamine methyl pyridinium salts

N-Methyl-2,6-diaminopyridinium trifluoromethanesulfonate (DA-PyMe(OTf): 2,6-diaminopyridine (DA-Py) (18.2 g, 167 mmol) was added into a 500 mL round bottom flask (RBF) followed by the addition of dichloroethane (250 mL). The resulting yellowish mixture was kept at 0°C for 15 min and a solution of methyl trifluoromethanesulfonate (25.1 g, 16.8 mL, 153 mmol) in 50 mL of dichloroethane was added dropwise into the RBF with continuous stirring. As the reaction proceeds, the contents of the flask became whiter and dustier. The stirring was maintained for 1.5 h at 0°C. The resulting white solid was collected by filtration, washed with dichloroethane and dried under vacuum overnight. The product was recrystallized using a hot solution of acetonitrile (15 mL) in dichloroethane (200 mL) to afford beige needle like crystals. Yield: 6g (22 mmol, 14%); m.p. 170-172°C;

FTIR (cm^{-1}): N-H stretch (3429, 3348), C-H stretch (3235), C=N stretch (1636), C=C stretch (1578, 1510), C-N stretch (1223), S=O stretch (1297, 1154), S-O stretch (1025, 783, 729, 632); ^{1}H NMR (DMSO-d_6) δ, ppm: 7.49 (m, 5H, $(-NH_2)_2+ H_4(Py)$), 6.07 (d, 2H, J 8.2Hz, H_3

and H$_5$(Py)), 3.46 (s, 3H, N-CH$_3$); ^{19}F NMR (DMSO-d$_6$) δ, ppm: -77.76 (s, OTf); Elemental analysis (CHNS) calculated (found) for C$_7$H$_{10}$F$_3$N$_3$O$_3$S: 30.77%C (31.13), 3.69%H (3.27), 15.38%N (15.28), 11.73%S (11.58).

N-Methyl-2,6-diaminopyridinium bis(trifluoromethylsulfonyl)imide (DA-PyMe(TFSI)): In a 250 mL erlenmeyer flask equipped with a magnetic stirrer, 6g (22 mmol) of (DA-PyMe(OTf)) were dissolved in 30 mL of deionized water. Bis(trifluoromethanesulfonyl)imide of lithium (12.6 g, 44 mmol) was added to this solution, with constant stirring resulting in immediate formation of white precipitates. The mixture was stirred for 3 more hours in order to ensure the complete anion exchange and then it was filtered. The white precipitates were washed thrice with 50 mL of distilled water and dried under vacuum at 60°C for 24 h. The product was recrystallized using a hot solution of acetonitrile (15 mL) in dichloroethane (200 mL) to afford colorless rectangular prism shaped crystals. Yield 8.89 g (22 mmol, *ca.* 100%); m.p. 143-145°C.

FTIR (cm^{-1}): N-H stretch (3461, 3371), C-H stretch (3250), C=N stretch (1637), C=C stretch (1582, 1512), S=O stretch (1346, 1135), C-N stretch (1298), C-F stretch (1186), S-N-S stretch (1046); ^{1}H NMR (DMSO-d$_6$) δ, ppm: 7.49 (m, 5H, (-NH$_2$)$_2$+ H$_4$ (Py), 6.07 (d, 2H, J 8.2Hz, H$_3$ and H$_5$ (Py)), 3.46 (s, 3H, N-CH$_3$); ^{19}F NMR (DMSO-d$_6$) δ, ppm: -78.72 (s, TFSI); Elemental analysis (CHNS) calculated (found) for C$_8$H$_{10}$F$_6$N$_4$O$_4$S$_2$: 23.77%C (23.9), 2.49%H (2.41), 13.86%N (13.60) 15.86%S (15.98).

N-Methyl-2,6-diaminopyridinium Hexaflorophosphate (DA-PyMe(PF$_6$)): 5 g (18.3 mmol) of (DA-PyMe(OTf)) were dissolved in 10 mL of deionized water in a 50 ml erlenmeyer flask followed by the addition of KPF$_6$ (10.1 g, 54.9 mmol). A white precipitate appeared immediately and the suspension was stirred for 4 more

hours in order to ensure the complete anion exchange and then it was filtered. The white solid was washed twice with 15mL of methanol and dried under vacuum at 50°C overnight. The product was recrystallized using a hot solution of acetonitrile (5 mL) and dichloroethane (95 mL) to afford colorless prism shaped crystals. Yield 4.63g (17.2 mmol, 94%).

^{1}H NMR (DMSO-d$_6$) δ, ppm: 7.52-7.45 (m, 5H, (-NH$_2$)$_2$+ H$_4$(Py)), 6.07 (d, J = 8.3 Hz, 2H, H$_3$ and H$_5$(Py)), 3.46 (s, 3H, N-CH$_3$). ^{19}F NMR (DMSO-d$_6$) δ, ppm: -70.09 (d, J = 711.5 Hz).

2.3. Synthesis of poly(azomethine-pyridinium) salts PAM-PyMe(X) by microwave irradiation

PAM-PyMe(Cl) and PAM-PyMe(PF$_6$)(Cl): In a microwave vial of 30 mL provided with magnetic stirring, 0.001 mol of diamines (DA-PyMe(TFSI) or DA-PyMe(PF$_6$)) and 0.001 mmol of isophthaldehyde and a mixture of 1.5 mL of N-methylpyrrolidone (NMP) and 1.5 mL of N,N-dimethylpropylene urea (DMPU) was stirred under nitrogen atmosphere for 20 min and then 0.127 g (0.003 mmol) of LiCl were added. Then the vial was introduced in a microwave oven and was heated using the next protocol: increase the temperature from 25 to 180 °C in 1 min, maintenance at this temperature for 10 min and cooling to 55 °C. This sequence was performed three times. The precipitate formed was filtered on a Büchner funnel and was then washed under stirring over 1h with N,N-dimethylformamide, tetrahydrofuran, dichloromethane and finally with methanol for 4 hours. PAM-PyMe(Cl) and PAM-PyMe(PF$_6$)(Cl) were filtered and dried at 120 °C under vacuum overnight to obtain 0.380 g (71% yield in weight) and 0.326 g (81% yield in weight) respectively.

PAM-PyMe(TFSI): In a microwave vial of 30 mL provided with magnetic stirring, 0.001 mol of DA-PyMe(TFSI) and 0.001 mmol of isophthaldehyde and a mixture of 1.5 mL of N-methylpyrrolidone (NMP) and 1.5 mL of N,N-dimethylpropylene urea (DMPU) was stirred under nitrogen atmosphere for 20 min and then 0.861 g (0.003 mmol) of LiTFSI were added. Then the vial was introduced in a microwave oven and was heated using the above MW protocol. The garnet viscous solution obtained was poured over a glass which was gradually heated from 70 to 120 degrees overnight. Then, the polymer was taken from the glass as solid and washed with water, THF and MeOH under vigorous stirring. The garnet polymer was filtered and dried at 120 °C under vacuum overnight to obtain 0.415 g of final product (78% yield in weight).

2.4. Measurements and equipment

Polymers were synthesized in a Microwave Synthesis Reactor Anton Paar Monowave 300 using operating at a constant power of 75W.

Elemental analyses were made with a Carlo Erba EA1108 elemental analyzer (C, H, N and S). Phosphorous content were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Perkin Elmer OPTIMA 2100 DV. Fourier Transform Infrared Spectra (FTIR) were recorded on a Perkin-Elmer RX-1 instrument. NMR measurements of the diamino monomers (dissolved in DMSO-d_6) were carried out on a Bruker AVANCE 400 spectrometer. Solid state ^{13}C NMR spectroscopic analysis of polymers were performed on a Bruker 400 AVANCE III WB spectrometer 9.40T. Cross-polarization magic-angle spinning (CP/MAS) 13C NMR spectra of PAM-PyMe(X) polymers were recorded using a 4mm MASDVT probe at a spinning of 12 KHz, using the cross polarization pulse sequence, at 100.63 MHz, a time domain of 2K, a spectral width of 29 KHz, a contact time of 1.5ms and an interpulse delay of 5s.

The thermal stability of polymers was measured using a TA instruments Q500 device. The samples were heated from 25 to 800°C with a heating rate of 10°C/min under air atmosphere with a gas flow rate of 60 mL/min.

Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface.

2.5. Catalytic activity

General procedure of cycloaddition of CO_2 to epichlorohydrin (ECH): In a Picoclave Büchi glass reactor of 10 mL, were placed 0.25 mL (0.00315 mol) of ECH and PAM-PyMe(X) catalysts (1-0.35 mol%). Then, the reactor was charged with CO_2 (Pressures of 1, 3 and 7 bar). The reaction mixture was stirred at 100 °C during the times collected in Table 2). All reactions were monitored by gas chromatography on a Konik HRGC 4000B GC-MS chromatograph with a cross-linked (95%)-dimethyl-(5%)-diphenylpolysiloxane (Teknokroma TRB-5MS) column of 30 meters of length; helium as carrier gas, 20 psi; injector temperature: 230 °C; detector temperature: 250 °C. The oven program was 70 °C (1 min), 9 °C min^{-1} to 220 °C (5 min), retention times: ECH: 3.5 min, Cyclic carbonate (ECHC): 18.5 min.

Recycling experiments

In a Picoclave Büchi glass reactor of 10 mL, were placed 2 mL (0.0252 mol) of ECH and 0.5 mol% of **PAM-PyMe(Cl)**. Then, the reactor was charged with CO_2 (3 bar) and the reaction mixture was stirred at 100 °C during 6h. Then the catalyst was filtered and washed with ethanol and acetone and dried overnight at 80 °C. Then, the catalysts was

weighted and added to the amount of epichlorohydrin needed to maintain the substrate- catalyst ratio established (0.5 mol%). This protocol was done 3 more times.

3. Results and Discussion

3.1. Synthesis and characterization of diamine methyl pyridinium salts

The synthetic route of the ionic diamino monomers, DA-PyMe(TFSI) and DA-PyMe(PF$_6$) (Scheme 1), involves the reaction of 2,6-diaminopyridine (DA-Py) with methyl trifluoromethane-sulfonate (MeOTf) in dichloroethane [28] yielding the methyl-diaminopyridinium trifluoromethanesulfonate (DA-PyMe(OTf)). Subsequently, undergoes anion exchange, using lithium bis(trifluoromethane)sulfonamide (LiTFSI) or potassium hexaflorophosphate (KPF$_6$) as salts, gives the corresponding quaternary diamines, methyl-diaminopyridinium bis(trifluoromethanesulfonyl)imide (DA-PyMe(TFSI)) and methyl-diaminopyridinium hexaflorophosphate (DA-PyMe(PF$_6$)).

DA-PyMe(OTf) is an interesting intermediate because is extremely soluble in water and allows a quickly anion exchange affording new quaternary pyridinium salts which precipitates in water.
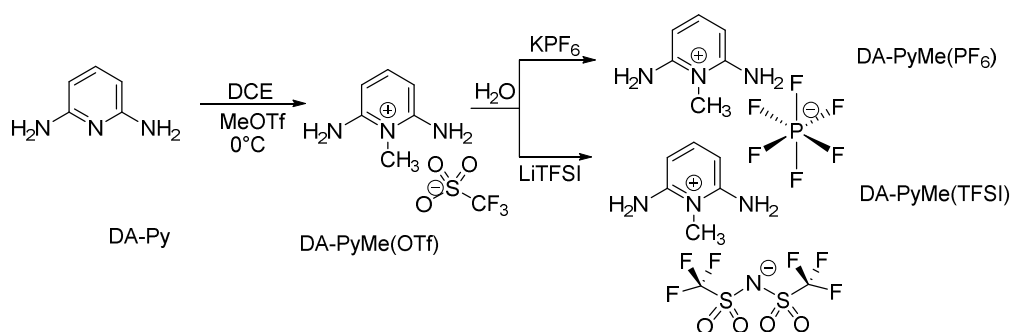
Scheme 1: Synthetic protocol of the ionic diamino monomers, DA-PyMe(TFSI) and DA-PyMe(PF$_6$).

The chemical structures of these new ionic diamine monomers were confirmed by ^{1}H NMR, FTIR and elemental analysis (see experimental part). Single crystals of DA-PyMe(TFSI) and DA-PyMe(PF$_6$) were obtained from the corresponding water solutions. Figure 1 shows the molecular structures for both salts. DA-PyMe(TFSI) crystallizes in the orthorhombic (P2$_1$2$_1$2$_1$) and DA-PyMe(PF$_6$) in the monoclinic system (C2/c). (For details see ESI).
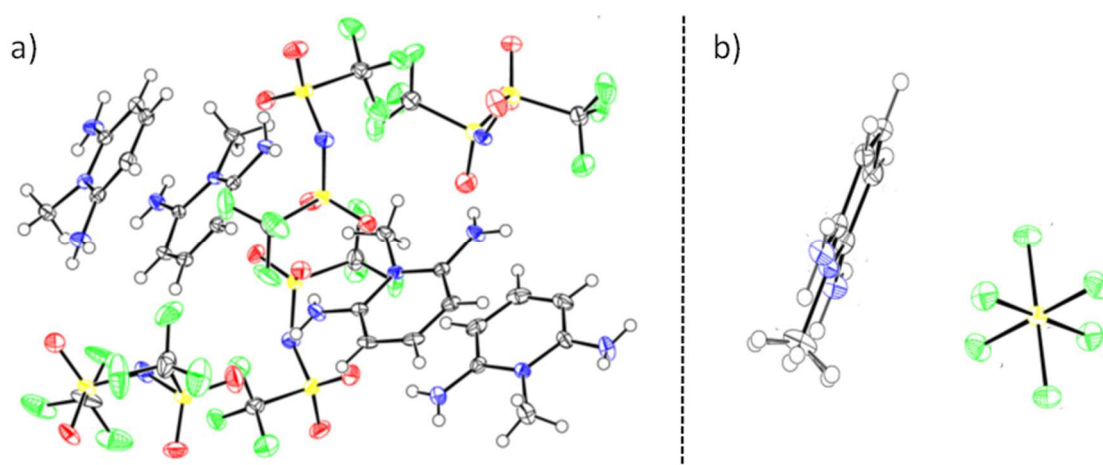

Figure 1. ORTEP structure view of DA-PyMe(TFSI) (a) and DA-PyMe(PF$_6$) (b)

3.2. Synthesis and characterization of poly(azomethines-pyridinium)salts (PAM-PyMe(X)

Poly(azomethines-pyridinium) poly(ionic liquids) were prepared under microwave irradiation using isophtaldehyde and one of the two diamino-methylpyridinium salts (DA-PyMe (TFSI) or DA-PyMe(PF6), Scheme 2). Thus, isophtaldehyde and DA-PyMe (TFSI) were dissolved in a mixture of N-methylpyrrolidone (NMP) and N,N-dimethylpropylene urea (DMPU) and the mixture was stirred under nitrogen atmosphere for 20 min. A mixture of NMP and DMPU was chosen to carry out the reaction because in a previous work reported by us 2,6-diaminopyridine and isophthaldehyde was heated in this mixture of solvents under

microwave irradiation yielding an insoluble and cross-linked polyazomethine network

[27]. Then LiCl was added and the mixture was heated during 30 min under microwave

at 180 °C. The polymer precipitates during the heating giving an initial evidence for the

formation of an insoluble cross-linked polymeric structure. First characterization by

elemental analysis (Table 1) and infrared spectroscopy (Figure 2) revealed the absence

of sulfur in this polymer, which indicated that there was a complete exchange between

the anions, TFSI⁻ and Cl⁻. Thus, in this conditions **PAM-PyMe(Cl)** was obtained.

b)
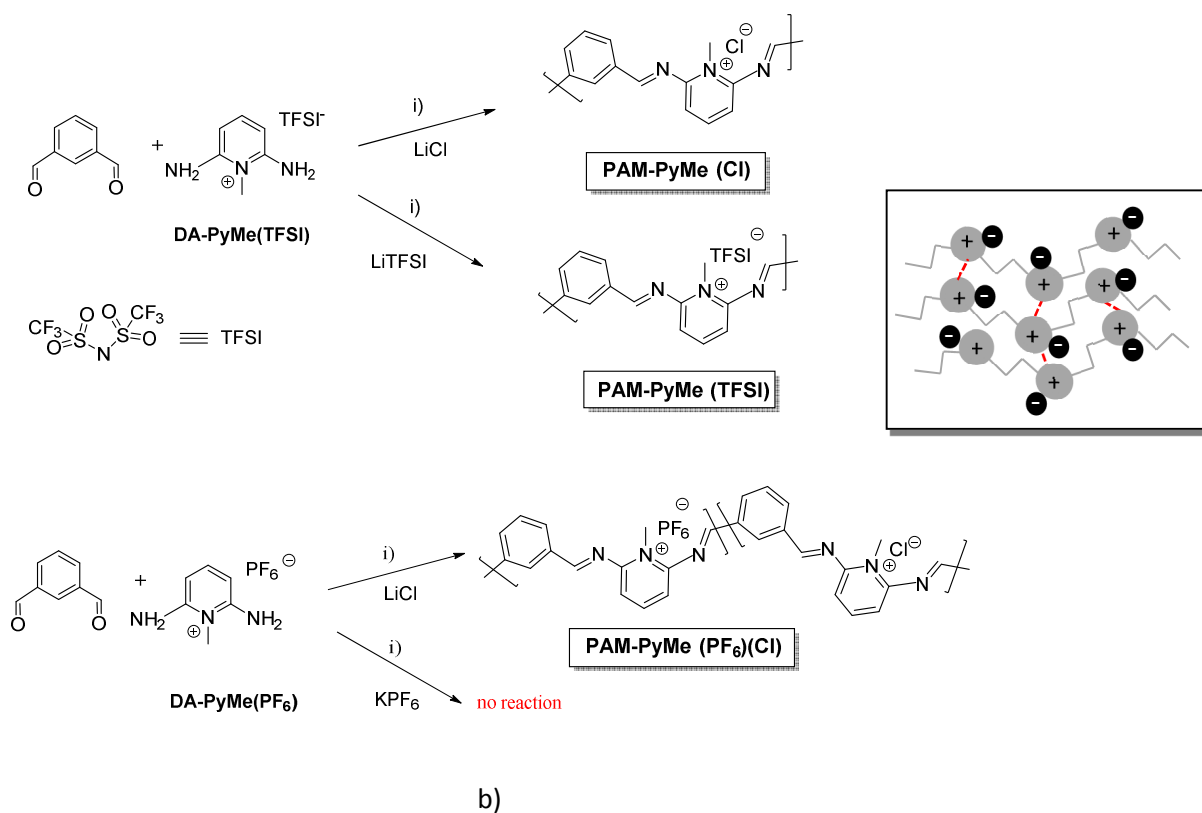
Scheme 2. Synthesis of poly(azomethines-pyridinium) salts under microwave irradiation: i) NMP/DMPU, MW, 30 min, 180°C and representation of the cross-linked poly(azomethines-pyridinium) salts

However, when the reaction was carried out in absence of LiCl no polymer was obtained.

Just replacing LiCl by LiTFSI, the formation of the desired polymer (**PAM-PyMe(TFSI)**)

was achieved. When DA-PyMe(PF₆) was reacted with isophtaldehyde in the presence of

LiCl, only a partial exchange between anions occurs and the resulting polymer contains 50% of PF_6 anions and 50% of chlorides. All attempts to obtain a polymer containing exclusively hexafluorophosphate anions (using KPF_6 instead of LiCl) were unsuccessful. In the absence of salt, no polymer was formed. The intermediate diamine DA-PyMe(OTf) was also polymerized with isophtaldehyde in the presence of LiOTf using the same procedure. However, a partially soluble polymer was obtained being discarded to be used as a heterogeneous catalyst. The pyridinium salt content was calculated by means of elemental analysis. **PAM-PyMe(Cl)** showed the highest content of catalytically active sites of the series, being also higher than the reported values for other poly(ionic liquids) [16,18].

Table 1. Elemental analysis of poly(azomethines-pyridinium) salts

Polymer		C(%)	H(%)	N(%)	S(%)	P(%)[a]	Pyridinium salt (mmol/g)[b]
PAM-PyMe(Cl)	Calculated	65.24	4.66	16.34	-	-	-
	Found	67.39	5.41	17.33	-	-	4.12
PAM-PyMe(TFSI)	Calculated	38.24	2.49	11.1	12.7	-	-
	Found	38.86	3.03	10.78	9.58	-	1.92
PAM-PyMe(PF₆)(Cl)	Calculated	53.80	3.84	13.46	-	4.92	-
	Found	49.68	4.59	12.16	-	4.21	2.89

(a) determined by ICP (b) [(%N/nN)/14]*10

The FTIR spectra of poly(azomethines-pyridium) salts (Figure 2) showed the characteristics bands of quaternary pyridinium salts [29]: two strong bands around 2800-3000 cm^{-1} corresponding to the C-H aromatic bonds and strong bands between

1400 and 1630 cm^{-1} attributed to the vibrations of conjugated C=C and C=N bonds. The IR spectrum of **PAM-PyMe(TFSI)** shows also the characteristics bands of the TFSI anion [30]. Two bands at 1186 and 1350 cm^{-1} and one at 1050 cm^{-1} attributed to the antisymmetric and symmetric stretching vibrations of the SO$_2$ group, respectively. Moreover, the spectrum exhibits also the deformation stretching vibrations of SO$_2$ and CF$_3$ groups at 614 and 567 cm^{-1} respectively. The IR spectrum of **PAM-PyMe(PF$_6$)(Cl)** shows also the characteristics bands of the antisymmetric and symmetric stretching vibrations of PF$_6$ [31] anion at 835 and 865 cm^{-1}, respectively.
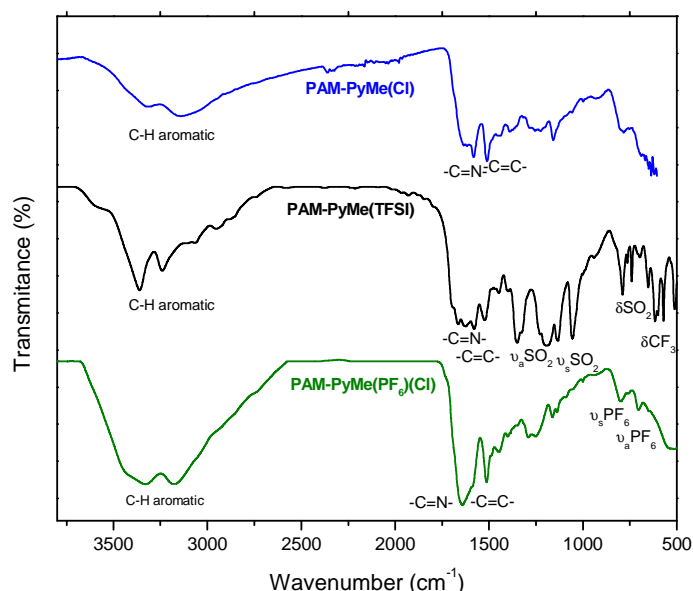

Figure 2. IR spectra (vertically shifted) of poly(azomethines-pyridium) salts

The thermal stability of the three polymers was studied by TGA (Figure 3). All of them showed a high thermal stability due to the extended aromatic conjugation and the high cross-linking degree. **PAM-PyMe(Cl)** and **PAM-PyMe(PF$_6$)(Cl)** shows a first weight loss around 250 °C probably attributed to the loss of chloride anions and a second degradation step at high temperature (500 °C) due to the degradation of the polymer backbone. **PAM-PyMe(TFSI)** showed the highest thermal stability as in the case of other poly(ionic liquid)s with a degradation patterns also in two stages. The first step occurs

at 450 °C and could be attributed to the TFSI loss while the generalized polymer backbone degradation takes places at 600 °C.
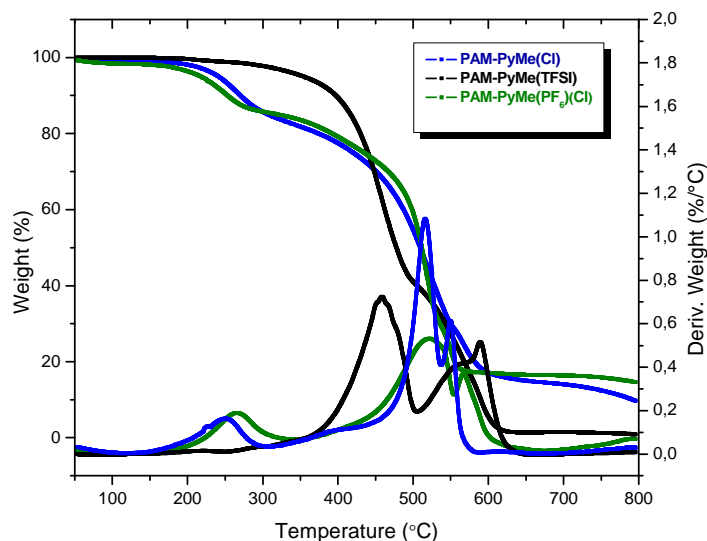

Figure 3. Thermogravimetrical analysis of poly(azomethines-pyridium) salts

The molecular structure of the three polymers was analyzed also by solid-state ^{13}C-NMR (Figure 4). All spectra show a signal around 155 ppm attributed to the imine carbons and quaternary carbons of the pyridine units. The intense signal centered at 130 ppm was ascribed to the tertiary carbons of the phenyl groups and the signals at 110 and 140 ppm to the remaining tertiary and quaternary aromatic carbons. Finally the signals centered between 45 and 32 ppm were attributed to the methyl groups of the pyridine unit which could be varying their displacement slightly, depending on the cation or cations of the structure.

All in all, the poly(azomethines-pyridium) presented the typical features of poly(azomethines) such as thermally stable backbones and unsolubility together with the ones of poly(ionic liquid)s such as presence of pyridinium cations and possibility of exchanging the anions showing improved thermal stability in the case of TFSI$^-$ as compared to PF$_6^-$ or Cl$^-$.
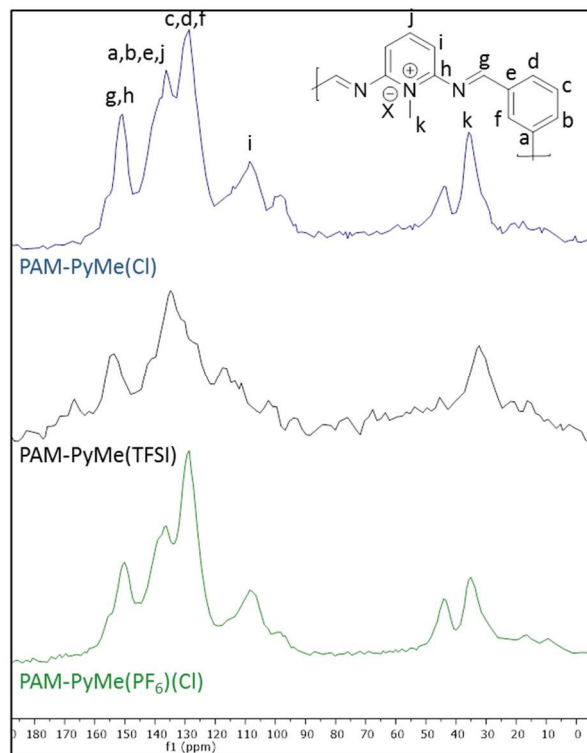
Figure 4: Solid state ^{13}C-NMR spectra of **PAM-PyMe(X)**.

The three poly(azomethines-pyridium) salts showed a very different morphology as it was observed by electronic scanning spectroscopy (Figure 5). **PAM-PyMe (TFSI)** showed a very rude structure formed by laminated blocks of very different sizes. However **PAM-PyMe(Cl)** and **PAM-PyMe(PF6)(Cl)** showed very nice morphologies formed only by sphere-shaped in the first case and by spherical and cubic structures of sizes ranging between 0,5 and 2,5 μm in the second. These SEM pictures showed the great influence of the anions in the morphology of the unsoluble poly(azomethine-pyridinium) polymers.
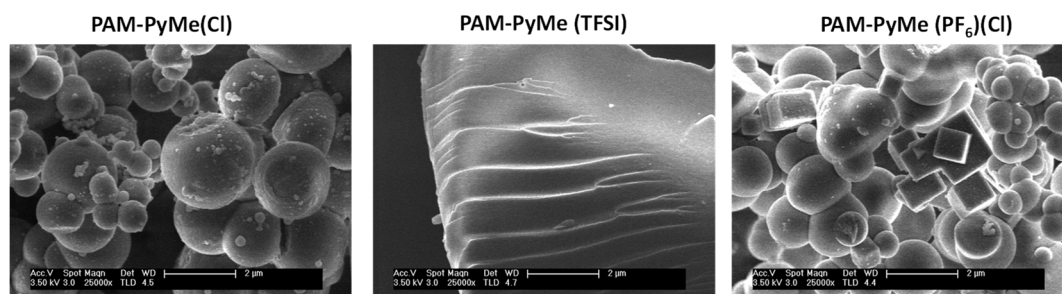

Figure 5. SEM images of poly(azomethine-pyridinium) salts PAM-PyMe(X).

3.3. Catalytic Activity

The catalytic activity of poly(azomethines-pyridium) salts was evaluated in the cycloaddition of CO_2 to epoxides. We have chosen **PAM-PyMe(Cl)** as catalyst and epichlorohydrin (ECH) as model substrate and the reaction was performed without solvent under the conditions previously reported by us, 7 atm of CO_2, 100°C [21]. Table 2 shows the results obtained with different catalyst amounts (1.5 and 0.35 mol%); as can be observed, complete conversion of epoxide was achieved up to 0.5 mol% catalyst (entries 1-3) obtaining selectively chloropropylene carbonate (CPC). However, the use a less amount of catalysts (0.35 mol%) and even increasing the reaction time (entries 4 and 5) was not enough to achieve high conversion rates and product yields. Thus, establishing the amount of catalysts in 0.5 mol%, the reaction was tested using **PAM-PyMe(TFSI)** and **PAM-PyMe(Cl)(PF$_6$)** as catalysts (entries 6-9).

The results obtained suggest that the anion is important in the cycloaddition reaction. Thus, the chloride anion, which is the more nucleophilic and smaller, was more reactive for CO_2 cycloaddition than the other anions. This fact was previously observed for other quaternary ammonium based mesoporous poly(ionic liquid)s or ionic liquids containing Cl, PF_6 or BF_4 anions [22, 32].

Taking into account the above results, **PAM-PyMe(Cl)** was selected to carry out the reaction at lower pressures. Thus, the reaction was done at 3 bar of CO_2 and, after 4 h of reaction (entry 10), a 73.5% of cyclic carbonate was achieved and after 6 hours the reaction was almost completed (entry 11). Diminishing the CO_2 pressures to 1 bar (entry 12) only 77% of cyclic carbonate was obtained after 20 h of reaction. Taking into account the above results we establish 3 bar of CO_2 pressure, 6 hours of reaction and 0.5 mol% of **PAM-PyMe(Cl)** as catalysts to perform the cycloaddition of CO_2 to ECH in a competitive way.

Catalytic activity of **PAM-PyMe(Cl)** in the cycloaddition of CO_2 to epichlorhydrin was compared those reported for with some poly(ionic liquid)s containing imidazolium salts (entries 13-15) or quaternary ammonium salts (entries 16,17). Excepting the quaternary ammonium based mesoporous poly(ionic liquid) (entry 17), all heterogeneous catalysts reported, performs the conversion at a higher pressures and temperatures than **PAM-PyMe(Cl)**. Besides, our catalyst shows the highest TON value due to the really small amount of catalyst that we used in our experiments (0.5 mol%), compared to the reported (1.3-2.6 mol%). Taking into account the above results we can stablish that **PAM-PyMe(Cl)** is a very effective and competitive catalyst to convert CO_2 into chloropropylene carbonate.

Table 2. PAM-PyMe(X) catalyzed the cycloaddition of CO_2 to epichlorohydrin (ECH)[a]

ECH → CPC
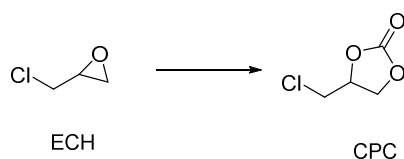
Entry	Catalyst	Cat. (mol%)	PCO₂ (bar)(°C)	t (h)	ECH (%)[b]	CPC(%)[b]	TON[c]
1	**PAM-PyMe(Cl)**	1	7 (100)	4	0	100	69
2	**PAM-PyMe(Cl)**	1.5	7 (100)	4	0	100	134
3	**PAM-PyMe(Cl)**	0.5	7 (100)	4	0	100	208
4	**PAM-PyMe(Cl)**	0.35	7 (100)	4	76	24	67
5	**PAM-PyMe(Cl)**	0.35	7 (100)	8	23	77	215
6	**PAM-PyMe(TFSI)**	0.5	7 (100)	4	100	0	-
7	**PAM-PyMe(TFSI)**	0.5	7 (100)	24	100	0	-

8	PAM-PyMe(PF6)(Cl)	0.5	7 (100)	4	20	80	
9	PAM-PyMe(PF6)(Cl)	0.5	7 (100)	24	3	97	
10	PAM-PyMe(Cl)	0.5	3 (100)	4	26.5	73.5	153
11	PAM-PyMe(Cl)	0.5	3 (100)	6	2	98	203
12	PAM-PyMe(Cl)	0.5	1 (100)	20	23	77	160
13	PDMBr[d]	1.3	10 (110)	2	0.6	98.8	76.5
14	SI-Imid[e]	10[f]	6 (130)	4	2	88	-
15	PS-HEIMBr[g]	1.6	25 (115)	3	-	92	-
16	PS-DHEEAB [h]	2	20 (110C)	3	1	99	49.5
17	PBDA-Cl-SCD[i]	2.4	1 (90)	6	0.6	99.4	41.4

[a] All reactions were done without solvent using 0.25 mL of ECH (0.00315 mol),[b] determined by CG after reaction [c] Turnover number : mmol substrate converted/mmol catalyst (refers to cation content); [d] PDMBr: mesoporous poly(ionic liquid)s containing imidazolium salt. Data taken from reference [15]; SI-Imid: imidazole anchored onto SiO_2. Data taken from reference [19]; [f] weight%; [g] PS-HEIMBr : Polyestryrene containing 1-(2-Hydroxyl-ethyl)-imidazolium salts. Data taken from reference [21]; [h] PS-DHEEAB: Polystyrene-bound diethanolamine based ionic liquids. Data taken from reference [20]; [i] PBDA-Cl-SCD: Quaternary ammonium based mesoporous poly(ionic liquid) containing chloride anions and prepared by SCD (supercritical CO_2 drying). Data taken from reference [22].

We also studied the cycloaddition of CO_2 to other epoxides such propylene oxide styrene oxide and cyclopentene oxide, using the same reaction conditions and 0.5 mol% of catalysts. 75% of propylene oxide was converted into the corresponding carbonate after 6 h. However the conversions with larger epoxides such as styrene oxide or with cyclohexene oxide which is an internal epoxide were less than 2%.

To study the recyclability of **PAM-PyMe(Cl)**, consecutive runs were done (Figure 6), using 0.5 mol% of catalyst, 3 bar of CO_2, 100°C and 6h of reaction. After each run, the catalyst was removed by filtration, washed with ethanol and acetone and dried

overnight at 80 °C to be used again in a fresh reaction. The epichlorohydrin conversion was maintained for four cycles (96.4-98%) obtaining chloropropylene carbonate as unique product in all cases (selectivity 100%).
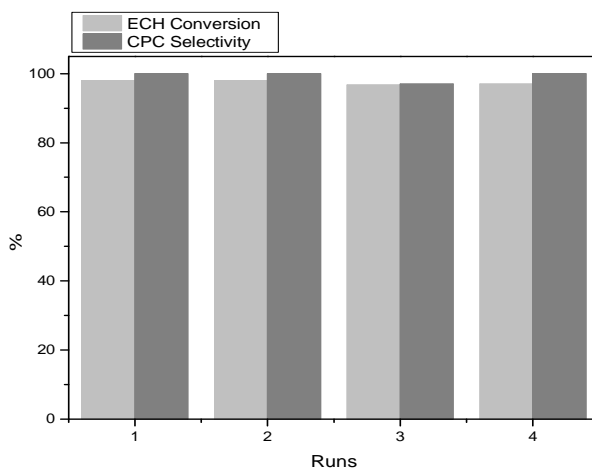

Figure 6. Recycling experiments of **PAM-PyMe(Cl)**

Finally, to confirm the catalysts is working in a heterogeneous way, a control experiment was done using 0.5 mol% of **PAM-PyMe(Cl)** and stopping the reaction after 2 hours. Then the catalyst was removed by filtration and the reaction was stirred 4 h more. After this time the yield of chloropropylene carbonate did not increase which confirms there is not lixiviation of the catalysts.

Taking into account the above results, **PAM-PyMe(Cl)** is a very promising heterogeneous catalysts which will be further explored in another catalytic reactions and will be published further.

Conclusions

A new family of poly(ionic liquid)s having pyridinium cations and a poly(azomethine) backbone is reported here. Microwave irradiation has been successfully employed to

prepare in 30 mins a series of crosslinked poly(azomethine-pyridinium) salts containing Cl^-, $TFSI^-$ and PF_6^- anions, by reacting isophthaldehyde and two new diamine methyl pyridinium salts. Depending on the salt used in the synthesis, an anion exchange occurs, which opens the possibility of obtaining different polymers from the same monomer. The catalytic activity of these polymers in the CO_2 cycloaddition reaction depends of the nucleophilic character and size of the anion. Thus, the poly(azomethine-pyridinium) that contain chloride anions is the most promising catalysts of this series. It converts CO_2 into chloropropylene carbonate in a very sustainable reaction, at 100 °C, using only 3 bar of CO_2 and what is more interesting with only 0.5 mol% of catalyst, in a reaction without solvent or any additive. As a consequence, of the high substrate conversion (up 98%) and the small amount of catalysts used, the turnover number of this catalyst is higher than reported for other heterogeneous catalysts in the same reaction.

Acknowledgements

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