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Polymer-bound aluminium salen complex as reusable catalysts for CO₂ insertion into epoxides

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Abstract—Two polymeric aluminium salen complexes in where the backbones are either a partially crosslinked polystyrene [(Al(salen)/PS)] or poly(ethylene glycol bismethacrylate) [(Al(salen)/PEA)] have been synthesised and used for the carbon dioxide insertion into epoxides to form cyclic carbonates. The catalytic activity of these polymers is similar to that of the unsupported aluminium salen complexes, and the polymeric catalysts can be easily separated from the reaction mixture and reusable in consecutives runs. The activity and reusability of the polymeric salen complex depends on the nature of the polymer: PEA being a polymer with a high oxygen content in the backbone enhances the initial activity as compared to PS, but Al(salen)/PEA exhibits lower stability as compared to Al(salen)/PS and a Al depletion occurs upon use. The presence of nucleophiles such as *N*-methylimidazole or *N*,*N*-dimethylaminopyridine in excess increases the catalysts for this reaction.

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1. Introduction

The increase in the atmospheric concentration of carbon dioxide is playing a negative effect in the climatic change due to the green house effect and there are many international programs aimed at balancing CO₂ emission and absorption.^{1–10} The availability of CO_2 and the interest in using it as feedstock has motivated a large effort in developing industrial processes based on the use of CO₂ as C_1 raw material.^{11–20} Among the possible processes to use CO₂ as reagent, the synthesis of carbonates and polycarbonates is very appealing, due to the properties of dialkyl carbonates as solvents and also as synthetic intermediates for urethanes, ureas and isocyanates.^{20–28} On the other hand, polycarbonates have excellent properties as engineering plastics.^{29,30} For this reason the report by Nguyen that chromium salen complex is a suitable catalysts for the CO₂ insertion into epoxides to form cyclic carbonates has constituted a significant breakthrough in this area.³¹ The main reason for this is the ease of the synthesis of metal salen catalysts and that their use does not require especial

precautions to avoid the presence of moisture and oxygen. Later other reports have also described the catalytic activity of other metal salen complexes and porphyrins.^{31–39}

A general trend in catalysis is to transform a successful homogeneous catalytic process into a heterogeneous one.^{40,41} Heterogeneous catalysts can be easily separated from the reaction products and reused in successive runs, provided that they do not become deactivated in the reaction. Also, heterogeneous catalysis is more suitable for continuous flow operation that is more appropriated than batchwise processes for large scale industrial synthesis. On the other hand, from the green chemistry point of view the use of a non-recoverable catalyst, particularly considering the toxicity of some transition metals such as chromium, must be avoided. Recently, we have reported the catalytic activity of chromium salen complexes anchored on silicas as solid catalyst for the CO₂ insertion into epoxides.⁴² However, given the negative environmental impact of chromium metal, and in order to improve the 'greenness' of the metal Schiff base complex catalysts for the carbon dioxide fixation process, we wanted to replace chromium by aluminium as the Lewis metal atom of the complex. Precedents in the chemical literature have already shown that some aluminium complexes are also active for carbon dioxide insertion. $^{43-46}$ As a continuation of this research

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line, herein we describe the synthesis and catalytic activity of aluminium salen complexes covalently attached to two different polymeric backbones. We have found that these polymeric catalysts are also active to effect the CO_2 coupling to epoxides, and that the nature of polymer skeleton plays a remarkable effect in the control of the catalytic activity of the complex.

Suitable polymer-bound catalyst can be recovered and reused for several runs. In addition, to make the process completely clean, we have used recoverable polymeric nucleophile co-catalysts instead of dissolved nucleophilic molecules. Compared to other strategies in where the substrates or reagents are supported on a polymer, the approach of supporting catalyst has several advantages including: (i) the fact that no high loadings on the polymeric support are required; (ii) the amplification effect since few supported catalytic sites can effect the transformation of considerable amounts of substrate; (iii) and the higher added-value of catalysts as compared to substrates that makes advisable their recovery and reuse.

2. Results and discussion

2.1. Polymeric catalyst preparation

For the present work we have prepared two different polymers containing covalently anchored Al(salen) complex. One of them in where the polymer backbone was a partially crosslinked poly(styrene-*co-p*-divinylbenzene) having some pendant amino methyl groups. These lateral groups were used to construct a salen ligand covalently attached to the polystyrene polymer. The polymer-bound ligand was obtained in three steps from 2,6-diformil-4-*tert*-butylphenol. The last step was metal complexation by reacting diethylaluminium chloride with the polymer-bound ligand under inert atmosphere in the absence of humidity. In this way, Al(salen) complex was attached to the polymer backbone through imino groups. Scheme 1 shows the route followed to prepare the 6-methimine substituted Al(salen) complex bonded to polystyrene.

Working with CO₂ one important parameter to favour its reactivity is to use a medium that is able to dissolve a sufficiently high concentration of CO₂. Thus, we anticipated based on previous literature reports that the affinity for CO₂ of polystyrene-derived polymers may be hot as high as desirable, and therefore, the CO₂ insertion reaction should occur mostly on the interface between the solid polymeric catalyst and the fluid phase.^{47–50} In this context we wanted to compare the activity of polystyrene anchored Al(salen) complexes with that of an analogous Al(salen) complex anchored on a different backbone that could show different affinity for CO₂. In this regard it is known that polymers containing ethylene dioxy groups can be suitable to dissolve significantly high CO₂ concentrations due to a high oxygen density in the polymer backbone.^{51–56}

Aimed at the purpose of having an Al(salen) complex anchored on a polymer with ethylenedioxy units, we designed a synthetic strategy completely different to that shown in Scheme 1. For having a polymer containing ethylendioxy units our approach was not to use a preformed



Scheme 1. Synthetic route for the preparation of Al(salen)/PS.



Al(salen)/PEA

Scheme 2. Synthetic route for the preparation of Al(salen)/PEA.

polymer, but to perform a copolymerization with a salen ligand containing reactive styryl units. Thus, in this case, the key salen derivative is one containing *p*-styryl units in peripheral positions of the salen ligand. The corresponding compound was obtained from 4-styryl-6-tert-butylsalicylaldehyde synthesised through a Pd catalyzed Suzuki cross coupling between p-styrylboronic acid and the para brominated salen ligand, as it has been reported previously.⁵⁷ With the *p*-styryl substituted salen ligand we proceeded to perform a copolymerisation with ethylene bismethacrylate using AIBN as radical initiator and an inert atmosphere. The actual synthetic route is illustrated in Scheme 2. The last step in the synthesis was again the formation of the aluminium complex by reacting in dichloromethane an organometallic diethylaluminium chloride as metal source compound. All the synthetic intermediates required in the synthesis indicated in Scheme 2 were characterized by analytical and spectroscopic methods.

Polymers Al(salen)/PS and Al(salen)/PEA were characterizated by analytical and spectroscopic techniques. The aluminium content of Al(salen)/PS and Al(salen)/PEA were 1.26 and 0.42 mmol \times g⁻¹, respectively. IR spectra of the polymers were in agreement with the simultaneous presence of Al(salen) complex and the organic polymer. Figure 1 shows the IR spectra of Al(salen)/PS and Al(salen)/PEA polymers.



Figure 1. IR spectra of Al(salen) (a); Al(salen)/PS (b); Al(salen)/PEA (c) recorded at room temperature in KBr disks.



Scheme 3. Procedure for the preparation of a PEG solid phase containing Al(salen) and cesium carbonate.

Finally, we included in our study a different recoverable catalytic system consisting in a CO₂-phylic PEG polymer containing dissolved the Al(salen) complex and Cs₂CO₃ as base (Scheme 3). Since PEG (average MW 6000 Da) is a solid at room temperature, but melted at 40 °C, we have taken advantage of it and dissolved the Al(salen) and Cs₂CO₃ on melt PEG. After dissolving in PEG Al(salen) and Cs₂CO₃ remain on the PEG phase during the recovery of the reaction products.

2.2. Catalytic activity

As a model reaction to test the catalytic activity of the two polymeric Al(salen) complexes, we selected the CO_2 insertion into styrene oxide (Scheme 4). The series of reactions were carried out in a mechanically stirred autoclave working in supercritical CO2 at 80 °C and 100 bar (CO₂ critical point: $T_c = 31$ °C; $P_c = 74$ bar). Through the series of reactions we varied the amount of nucleophile co-catalyst to determine the optimum Al(salen)/ nucleophile molar ratio. It has been demonstrated that the presence of N-methylimidazole and other bases in adequate metal-to-base molar ratios can enhance considerably the catalytic activity, the presence of base playing a detrimental effect if a large excess is used.^{35,37} For the sake of comparison we have included also in our study a nonpolymeric Al(salen) complex. The list of reactions performed and the results obtained are summarized in Table 1.

Some preliminary experiments were carried out using lesser amounts of styrene oxide (400 mg) but these experiments were flawed by the poor recovery of the reaction mixture upon reactor discharge. Working under supercritical conditions in a 125 mL autoclave with 4 g of styrene oxide the mass balances of the reaction were almost complete (see Table 1). In addition, we purposely stopped the reactions at low conversion in order to obtain a valid information of the relative catalytic activity of the different polymer-supported aluminium complexes catalysts. It is obvious that at sufficiently long times for which complete conversions are achieved, the information about the distinctive performance and activity of the catalyst will be lost.

The reaction mixtures were analysed by GC and IR, and the amount of cyclic carbonate quantified by GC using the external standard method. In most of the experiments, the only product observed was the corresponding five member ring cyclic carbonate, but in some cases the corresponding glycol and polycarbonate were also observed (Scheme 4). Phenyl ethylene glycol comes from the hydrolytic epoxide aperture catalyzed by acids.

In the literature it has been shown that epoxides of cycloalkenes give exclusively or predominantly polycarbonates while epoxides of acyclic alkenes lead predominantly cyclic carbonates.³⁸ Therefore, in our case we expected to obtain mostly the cyclic carbonate. Nevertheless, we assessed in each reaction mixture the presence or absence of polycarbonate by IR spectroscopy. While pentacyclic carbonate exhibits a carbonyl stretching vibration band 1820 cm^{-1} , the corresponding carbonyl in the polymeric carbonate band appears at 1750 cm^{-1} . Figure 2 shows two



Scheme 4. Reaction products observed for the catalytic CO₂ coupling with styrene oxide.

Run	Catalyst [catalyst-to-substrate mol %]	Mass balance (%)	Conversion ^a (%)	Yield (%)	TON
1	Al(salen) [0.1]	91	19	17	59
2	$Al(salen)^{b}[0.1]$	100	20	17	59
3	$Al(salen)^{c}[0.1]$	98	4	3	10
4	$Al(salen)^d$ [0.1]	97	4	3	10
5	Al(salen)/PEA (use 1) [0.14]	87	22	19	47
6	Al(salen)/PEA (use 2) [0.14]	95	9	6	15
7	Al(salen)/PEA (use 3) [0.14]	92	9	6	15
8	Al(salen)/PEA ^e [0.14]	98	8	8	20
9	Al(salen)/PEA ^f [2]	95	89	78	39
10	Al(salen)/PS (use 1) [0.44]	100	9	9	7
11	Al(salen)/PS (use 3) [0.44]	97	9	9	7
12	[PEG-Al-CsCO ₃] ^g [0.1]	$86^{\rm f}$	15	11	38

Table 1. Results obtained at 6 h reaction time for the CO₂ insertion into styrene oxide (4 mL) catalyzed by Al(salen) complexes and nucleophile (3.6% mol) at 80 °C and 100 bar in a mechanically stirred (300 rpm) autoclave (125 mL)

^a Based on the disappearance of styrene.

^b Dimethylaminopyridine was used instead of *N*-methylimidazole.

 $^{\rm c}P = 20$ bar.

^d 2 equiv of *N*-methylimidazole

^e Dimethylaminopyridine polymer-bound was used as co-catalyst.

^f Reaction time 15 h.

^g 1% of polymer it was observed as by-product.

representative IR spectra of the reaction mixture to illustrate how the presence or absence of polycarbonate can be determined by this technique.

Before performing experiments with polymeric salen catalyst, we carried out a preliminary study on the activity of Al(salen) complex not covalently bonded to any support (0.1% mol) varying the excess of *N*-methylimidazole as cocatalyst. The results are contained in Table 1 and it can be seen that the presence of bases in a large excess plays a large beneficial influence on the conversion. When no supercritical conditions were used (Table 1, entry 3) the conversion reached was considerably lower. The positive influence of the supercritical conditions can be interpreted considering that when no supercritical conditions are used, there should be two phases, one of them being liquid styrene oxide saturated in CO₂, but most of the CO₂ being in a separate gas phase. In contrast under supercritical conditions a single phase should be ideally present inside the reactor in where supercritical CO_2 dissolves styrene oxide. The ability of supercritical CO_2 to mix with hydrocarbons is well known



Figure 2. IR spectra of two reaction mixtures obtained after the treatment of styrene epoxide (35 mmol) with CO_2 in autoclave (125 mL) at 80 °C and 100 bar using Al(salen)/PEA (a) or Al(salen)/PS (b) as catalysts. The peaks at 1750 cm⁻¹ indicates the presence of polycarbonate, while the peak at 1815 cm⁻¹ corresponds to cyclic carbonate.

and used as a tool to control some properties of supercritical CO_2 phase. $^{58-60}$

With the aim of having a reusable and recoverable polymeric catalyst we proceeded to perform the same reaction under supercritical CO_2 conditions using Al(salen)/PEA solids. The results are also contained in Table 1.

Noteworthy was that the initial activity of fresh Al(salen)/ PEA was significantly higher than that of the analogous Al(salen)/PS, although the turnover number for unsupported Al(salen) was still higher than those obtained using polymeric Al(salen)/PEA. These results can be easily interpreted considering that the PEA backbone exhibits a high oxygen density, in contrast to the PS skeleton that is only a hydrocarbon. Also noteworthy was that the higher activity of Al(salen)/PEA results in a somewhat lower selectivity towards the cyclic carbonate since some polycarbonate is formed in this case. The polymeric carbonate becomes deposited on the catalyst. The presence of polycarbonate on Al(salen)/PEA results in a change of the texture of the initially soft and sticky Al(salen)/PEA powder that becomes much harder. The presence of polycarbonate can be spectroscopically determined by observing in the IR spectrum of the used Al(salen)/PEA catalyst the presence of a band 1750 cm^{-1} corresponding to the stretching vibration to the carbonate group to the polymer (see Fig. 2). Also, optical microscopy (Fig. 3) reveals a variation on the Al(salen)/PEA particle morphology with different size and optical properties that those the fresh Al(salen)/PEA catalyst. In contrast to the behaviour of Al(salen)/PEA, Al(salen)/PS does no form detectable amounts of polycarbonate as evidenced by IR spectroscopy (absence of 1750 cm^{-1} peak, see Fig. 2). However, optical microscopy reveals that the initial spherical shape of the PS beads also disappears upon catalyst use (Fig. 4). Although polymer attrition can not be disregarded, the mild mechanical stirring used to perform the reactions makes more probable that changes in the polymer morphology are due to the influence of the reaction and interaction with CO_2 .



Figure 3. Optical microscopy of Al(salen)/PEA powder before (left) and after(right) being used as catalyst for the CO_2 insertion into styrene oxide. Particle size and texture of Al(salen)/PEA changes upon its use as catalyst.



Figure 4. Optical microscopy of Al(salen)/PS powder before (left) and after (right) being used as catalyst for the CO_2 insertion into styrene oxide. The typical spherical shape of the Al(salen)/PS beads disappears upon catalyst use.

Concerning the reaction conversion, when higher amounts of Al(salen)/PEA catalyst is present and the reaction time is longer (Table 1, entry 9), then, obviously the yield of the cyclic carbonate increases, although the turnover number decreases somewhat with respect to those experiments using higher substrate-to catalyst molar ratio.

According to the proposed reaction mechanism for the *N*-methylimidazole enhancement of the catalytic activity of Cr(salen) complexes for the CO₂ insertion into epoxides,^{35–37,61} the key intermediate consists in a distorted octahedrally coordinated chromium ion interacting at the apical positions with the nucleophile and the epoxide. In other words, the role of *N*-methylimidazole has been proposed to be the softening of the chromium-epoxide interaction by *N*-methylimidazole coordination to the



Scheme 5. Proposed structure of activated epoxide in where the nucleophile co-catalyst is simultaneously bonded to the epoxide-chromium(salen) intermediate.

chromium (Scheme 5). If this were so, in our case using polymer-bound Al(salen) complexes, addition of the supported base co-catalyst should inhibit dramatically its co-catalyst role by impeding the interaction between the polymer bound nucleophile and the polymer bound metal salen complex that will be in different solid phases. According to this, the expected yield of the CO_2 coupling using a mixture of polymeric Al(salen) and polymeric nucleophile should be much lower, since the promoting effect the nucleophile will be lost.

However, as it can be seen in Table 1, this was not exactly the case and a mixture of polymeric dimethylaminopyridine and polymeric aluminium salen complex gives also rise to the formation of cyclic carbonate with only half the turnover activity than those obtained using molecular nucleophiles (compare entries 5 and 8). Polymeric dialkylaminopyridine (see structure and preparation procedure in Scheme 6) was prepared as previously reported in the literature.⁶² A blank control in where the same experiment using Al(salen)/PEA as catalyst was used in the absence of any nucleophile (either molecular or polymeric) under the same conditions gave essentially no epoxide conversion.

This result using polymeric dialkylaminopyridine seems to indicate that the reaction mechanism should be probably revisited to take in consideration that the formation of a single species between the nucleophile and the metal complex as shown in Scheme 5 may not be absolutely necessary. From the practical point of view, the use of both



Scheme 6. Route for the preparation of the polystyrene containing pendant dialkylaminopyridine units.

polymeric nucleophile and polymeric metal complex has even more advantages in terms complete reusability of the catalytic system and avoidance of waste.

A different reusable system that was also tested for this reaction was a mixture of Al(salen) and Cs₂CO₃ dissolved in polyethyleneglycol (PEG) (Table 1, entry 12). PEG (av. MW 600 Da) becomes liquid at about 40 °C and is a suitable solvent for CO_2 reactions due to the high CO_2 solubility in PEG. After the reaction and upon cooling, the mixture becomes solid and the catalyst and base remains in the solid PEG phase, while the cyclic carbonate can be extracted with diethyl ether or methanol. Cs_2CO_3 is a suitable base in PEG media since large alkali metal ions become solvated through interaction with ethylendioxy oxygens, increasing the solubility and boosting the nucleophilic strength of the base. As it can be seen in the Table 1, also this system based with PEG in where there is no covalent linkage between the polymer acting as solvent and the complex could be of interest for performing the CO₂ insertion into epoxides, while still permitting reusability of the metal complex and nucleophile.

In fact, reusability of polymeric catalyst was performed by simple filtration of the solid from the reaction mixture and washing it with dimethylcarbonate and ethanol. After drying, the solids were used as catalysts for a new batch under the same conditions. The results obtained are also shown in Table 1 (entries 6, 7 and 11). It can be seen there that while the activity of fresh Al(salen)/PS is lower than that of Al(salen)/PEA, upon reuse the activity of Al(salen)/ PS remains as in the first use. In contrast, the activity of Al(salen)/PEA undergoes a significant decrease between the first and second runs, although then the activity is maintained going from the second to the third use and is still higher than that of Al(salen)/PS. These results can be interpreted considering that miscibility CO₂ in the polymeric PEA skeleton is high, this leading to partial depletion of the Al(salen) complex, most probably by extracting the aluminium cation producing the leaching of Al from the polymer to the liquid phase. In support of this, IR spectroscopy reveals that the characteristic Al(salen)

complex IR bands at 1640 cm^{-1} is significantly disminished after the first use of the polymeric Al(salen)/PEA catalyst.

3. Conclusions

Aluminium salen complex anchored to polymeric backbones is an active catalyst for the CO₂ insertion into epoxide. However, as anticipated, polymeric catalysts exhibit somewhat lower turnover numbers than that of the non-polymeric complex. The activity of fresh polymeric catalyst depends on the composition of the backbone and its affinity for CO_2 . PEA is more suitable in this regard than partially crosslinked PS. However, stability and reusability on the catalyst also depends on the nature of the polymer and from this point of view Al(salen) bonded to PS appears as a more stable catalyst than when bonded to PEA, in where a susptancial diminution in the number of Al(salen) complexes is observed after the first use. The use of PEG as co-solvent and cesium carbonate as a base is also an interesting medium that permits the reusability of the system. Finally also the base can be anchored in a polymeric skeleton without producing a detrimental effect of the catalytic activity of the system. This is in contrast of could have been expected in view of the accepted reaction mechanism and the role of nucleophiles as catalyst promoter. Given the interest of this reaction and the possibility to perform enantioselective CO₂ insertions, current work is aimed at expanding the process using other epoxides as starting materials and to determine the enantiomeric excess achieved for asymmetric epoxides.

4. Experimental

4.1. General

IR spectra of polymer bound Al(salen) were recorded on a Nicolet 710 FT-IR spectophotometer using KBr disks. The polymer (10 mg) was mixed in a mortar with dry KBr (20 mg) and the mixture pressed at 1 ton \times cm⁻² for 2 min.

Optical microscopy of the polymeric catalysts were obtained with a Leica DFC 300FX microscope placing the powder between slides. Images were saved and manipulated using IMSO program package.

4.2. Preparation of Al(salen)/PS catalyst

2,6-Diformyl-4-*tert*-butylphenol was prepared from 4-*tert*butylphenol as reported in the literature.⁶³ Al(salen)/PS was prepared using as support (0.6 g) of commercial aminomethylated poly(styrene-*co*-divinylbenzene) (2% wt of divinylbenzene) that was added to a solution of 2,6diformyl-4-*tert*-butylphenol (216 mg, 1.05 mmol) in ethanol (10 mL). Polystyrene *co*-DVD (2%) aminomethylated (1.6 mmol N/g) was purchased from Aldrich.

The mixture of polystyrene and dialdehyde was magnetically stirred for 2 h at reflux temperature. The solid was removed by filtration, Soxhlet extracted with dichloromethane for 24 h and dried under vacuum. In the second step, the previous functionalised solid and (R,R)-1,2diaminocyclohexane (120 mg, 1.05 mmol) were added to ethanol (10 mL), stirred magnetically while refluxing for 2 h. The solid was filtered, Soxhlet extracted with dichloromethane for 24 h, and dried under vacuum. The solid obtained in the previous step having cyclohexadiamine units was added to a solution of 3,5-tert-butylsalicylaldehyde (246 mg, 1.05 mmol) in ethanol (10 mL), and the mixture stirred at reflux temperature. After 2 h, the solid was removed by filtration, Soxhlet extracted with dichloromethane for 24 h and dried under vacuum. The synthesis of Al(salen)/PS was accomplished at room temperature under nitrogen atmosphere, charging in a flamed flask Al(salen)/ PS and dry dichloromethane (10 mL). Diethyl aluminium chloride (1 mL, 1.8 mmol, 1.8 M solution in toluene) was added slowly to the stirred solution. After 4 h, the solid was removed by filtration, Soxhlet extracted with dichloromethane for 24 h and dried under vacuum. The content of aluminium was 1.26 mmol Al/g as determined by absorption spectroscopy corresponding to 77% of the maximum polymer loading according to the density of aminomethyl groups in PS.

4.3. Preparation of Al(salen)/PEA catalyst

Divinyl salen ligand was prepared as reported by Seebach and co-workers.⁵⁷ A mixture of divinyl salen ligand (0.70 g, 1.10 mmol) and ethylene glycol bis(methacrylate) (2.07 mL, 10.96 mmol) was dissolved in toluene (7 mL) and ethanol (3 mL). The polymerisation mixture was bubbled with nitrogen for 30 min. 2,2'-Azobisisobutyronitrile (25 mg) was added, and the mixture was heated at 80 °C for 24 h in nitrogen atmosphere. The polymer (Alsalen/PEA) was removed by filtration, Soxhlet extracted with dichloromethane for 24 h and dried under vacuum.

A flamed flask was charged with salen/PEA (1.2 g) and dry dichloromethane (12 mL) and the solution purged with nitrogen atmosphere at room temperature for 1 h. Then, 300μ L of diethyl aluminium chloride (1.8 M solution in toluene, 0.52 mmol) was added slowly to the stirred solution. After 4 h, the solid was removed by filtration, Soxhlet extracted with dichloromethane for 24 h and dried

under vacuum. The content of aluminium was determined by absorption spectroscopy (0.42 mmol Al/g) corresponding to about 95% of the maximum loading capacity according to the ligand and the N content (0.88 mmol/g).

4.4. Preparation of [PEG-Al-CsO₃]

PEG (250 mg) and Cs_2CO_3 (41 mg) were dissolved in water (2 mL) and stirred for 15 min. After this time, the water is removed under vacuum. Independently, PEG (250 mg) and Al(salen) complex (2.6 mg) were dissolved in dichloromethane (2 mL), and the dichloromethane is removed under vacuum. The two PEG solids, one containing the base and the other Al(salen) complex, were mixed mechanically and melted at 40 °C. The resulting solid was dried under vacuum for 6 h.

4.5. Preparation of DMAP-polymer

4-[*N*-methyl-*N*-(*p*-vinylbenzyl)amino]pyridine was prepared starting from 4-(methylamino)pyridine sodium salt and *p*-(chloromethyl)styrene. This *N*,*N*-dialkylaminopyridine derivative was copolymerised with styrene (1 equiv) and divinylbenzene (0.02 equiv) to give the polymer-bound 4-(*N*-benzyl-*N*-methylamino)pyridine. A more detailed experimental procedure can be found elsewhere.⁶²

4.6. Reaction procedure

Styrene oxide (4 mL) and the appropriate amount of Al(salen) catalyst and co-catalyst is placed in a 125 mL stainless steel autoclave that is subsequently charged with liquid CO₂ until an approximate pressure of 75 bars is reached. Then, the temperature is increased at 80 °C while the mixture is mechanically stirred. The approximate pressure is 100 bar. The reaction mixture was maintained under these conditions for 6 h. After this time the system was allowed to cool at ambient temperature and, then, the reactor valve is opened and the reactor pressure smoothly decreased over a period of 12 h. The reaction mixture was extracted with diethyl ether, the polymer washed with ethanol and the product analysed by IR of the mixture (to assess the absence of polycarbonate) and GC or GC/MS. The products were identified by comparison with authentic samples.

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