Cationic Polymers Bearing Quaternary Ammonium Groups-Catalyzed CO₂ Fixation with Epoxides

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Abstract

A series of cationic polymers containing quaternary ammonium groups turned out to be powerful catalysts for the CO₂-fixation of epoxides under an atmospheric pressure of CO₂ at elevated temperature. A variety of differently substituted aromatic and aliphatic epoxides were well tolerated and the polymeric catalysts could easily be recovered by a simple filtration and reused without any loss in catalytic activity.

Keywords Polycations · Quaternary ammonium groups · Catalysis · CO₂ fixation

1 Introduction

Polyelectrolytes are of fundamental and practical importance since many of them play critical biological functions in nature [1–3]. An important subgroup, also known as ionenes, refers to polycations carrying quaternary ammonium groups in the backbone [1, 4–10]. These polymers are typically synthesized by (1) chain or step polymerization of suitable monomers (e.g. Menshutkin reaction between bis-tertiary amines and activated dihalides, self-polyaddition of aminoalkylhalides) or (2) cationic functionalization of reactive precursor polymers [11, 12]. The practical importance of these macromolecules lies on the large number of applications in daily life, biosciences and industrial processes (e.g. as antibacterial agents or building blocks for the preparation

of chromatography stationary phases, simplexes or gels, among other uses) [4, 13, 14].

Recently, we have reported a series of ionene polymers based on *N,N'*-(*p*-phenylene)dibenzamide and α,ω -tertiary diamines, where the substitution pattern on the central benzene ring (i.e. *ortho*-, *meta*-, *para*-) in some of these polymers was found to play a key role on the hydrogelation [15], dye uptake [16] and antimicrobial properties [17]. In addition, our groups and others have shown that these versatile polymers can also serve as easily recoverable and reusable phase-transfer catalysts for a variety of different transformations [18–20].

Intrigued by the catalytic potential of these highly-functionalized polymers and in continuation of our research focus on multifunctional (chiral) ammonium salt catalysis (for two recent contributions please see Ref. [21, 22]), we became interested in elucidating the catalytic potential of ionenes for more challenging reactions. One transformation that has attracted considerable attention over the last years is the incorporation of CO₂ into epoxides to access cyclic carbonates (for selected rather recent reports with different catalyst systems please see Ref. [23–40]). This transformation is not only interesting because of the importance of the hereby obtained dioxolanes [41, 42], but it also provides a powerful approach for the utilization of CO₂ as a simple one carbon-source for organic transformations [43, 44]. Accordingly, there is a strong interest in the development of new and alternative catalyst systems to carry out such reactions under operationally simple and mild conditions. Some rather recent reports describing the use of functionalized polymers

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to catalyze the CO₂ fixation with epoxides caught our interest [45–47]. Considering the previously described potential of ionenes as catalysts [18], we thus now started a program with the focusing on investigating a variety of structurally different polycations bearing ammonium groups **A–F** for their potential to catalyze the CO₂ incorporation into epoxides **1** under an atmospheric pressure of CO₂ (Scheme 1).

2 Results and Discussion

It has been well documented that the nature of the halide counter anion can play a crucial role in such ammonium salt catalyzed CO₂-incorporation reactions [48, 49] and we thus tested Cl and I-containing polymers **A–F** for this study. Our investigations started by using simple styrene oxide **1a** (R = Ph, Scheme 1) as the epoxide component and carrying out the CO₂ fixation under solvent free conditions with an atmospheric pressure of CO₂ (by using a simple balloon) (Table 1).

As the developed ionene synthesis provides the chloride salts directly we tested these compounds as catalysts in the beginning (entries 1–15). The first results obtained when using the 1,4-diazabicyclo[2.2.2]octane (DABCO)-based ionenes **A** were rather disappointing as no dioxolane **2a** was formed at 60 °C (entries 1 and 2) and only small

amounts were formed after 4 h at 120 °C (entries 3–5). The same rather low reactivity was then observed by using the **B**-chloride series with a C2 ammonium group linker, (entries 6–8). By using the other polymers **C–F** under these conditions however, some very interesting observations were made (entries 9–15). With increasing linker length the catalytic performance of the ionene chlorides improved significantly, especially for the 1,4-regioisomers like compound **C**^{1,4} (entry 11) and compound **D**^{1,4} (entry 13). In both cases catalyst quantities of 0.5–1 mol% allowed us to reach conversions of more than 50% after 4 h reaction time (120 °C), and almost complete conversion when doubling the reaction time in the presence of 0.5 mol% **D**^{1,4} (entry 14). In addition, also the cyclohexyl-based polymer **E** and the pyridinium-based **F** showed some promising initial catalytic potential (entries 15, 16).

To investigate the influence of the counter anion we next tested the corresponding iodide-based polymers (entries 17–24). These salts were prepared by carrying out a chloride to iodide exchange of the initially used salts (see the supporting information for details). Very interestingly, this lead to a significant improvement in case of the **A** and **B** series (entries 17–20), which performed rather slow with chlorides only. On the other hand, those polymers that performed well for the chloride salts already (i.e. **C**^{1,4} and **D**^{1,4}) performed less satisfactory when using the iodides instead

Scheme 1 Cationic polymers **A–F** used as catalysts for the CO₂ fixation of epoxides **1**

Table 1 Catalyst screening for the CO₂-fixation with styrene oxide **1a**

Entry ^a	Catalyst	Catalyst load- ing (mol%) ^b	T (°C)	t (h)	Conv. (%) ^c
1	A ^{1,4} (X=Cl)	0.5	60	4	0
2	A ^{1,4} (X=Cl)	0.5	60	18	0
3	A ^{1,4} (X=Cl)	0.5/1	120	4	7/11
4	A ^{1,2} (X=Cl)	0.5	120	4	5
5	A ^{1,3} (X=Cl)	0.5	120	4	Traces
6	B ^{1,2} (X=Cl)	0.5	120	4	Traces
7	B ^{1,3} (X=Cl)	0.5	120	4	Traces
8	B ^{1,4} (X=Cl)	0.5/1	120	4	3/7
9	C ^{1,2} (X=Cl)	0.5	120	4	7
10	C ^{1,3} (X=Cl)	0.5	120	4	3
11	C ^{1,4} (X=Cl)	0.5/1	120	4	44/59
12	D ^{1,3} (X=Cl)	0.5	120	4	Traces
13	D ^{1,4} (X=Cl)	0.1/0.5/1	120	4	11/58/62
14	D ^{1,4} (X=Cl)	0.5	120	8	>90%
15	E (X=Cl)	1	120	4	22
16	F (X=Cl)	0.1 / 1	120	4	Traces/58
17	A ^{1,2} (X=I)	0.5	120	4	59
18	A ^{1,3} (X=I)	0.5	120	4	26
19	A ^{1,4} (X=I)	0.5	120	4	32
20	B ^{1,4} (X=I)	0.5	120	4	50
21	C ^{1,4} (X=I)	0.5	120	4	52
22	D ^{1,4} (X=I)	0.5	120	4	25
23	E (X=I)	0.5	120	4	Traces
24	F (X=I)	0.5	120	4	66
25 ^d	A ^{1,2} (X=Cl)	0.5	120	4	45
26 ^d	A ^{1,3} (X=Cl)	0.5	120	4	22
27 ^d	A ^{1,4} (X=Cl)	0.5	120	4	40
28 ^d	B ^{1,4} (X=Cl)	0.5	120	4	60
29 ^d	C ^{1,4} (X=Cl)	0.5	120	4	63
30 ^d	D ^{1,4} (X=Cl)	0.5	120	4	68
31 ^e	D ^{1,4} (X=Cl)	0.5	120	4	61

^a4 mmol scale (neat)^bMol% catalyst were calculated based on the repeating monomeric catalytically active units of the ionenes (please see the SI for further details concerning the ionenes used in this study)^cJudged by ¹H NMR of the crude reaction mixture (isolated yields are usually in the same range as conversion)^dAddition of 1 mol% NaI (the use of 1 mol% NaI in the absence of any catalyst leads to only 10% conversion after 4 h under these conditions)^eAddition of 1 mol% NaBr

(entries 21,22). According to mechanistic studies by others [48, 49], the nucleophilic counter anion plays a crucial role in the initial epoxide opening. The results obtained in our experiments may thus be rationalized by different halide-binding affinities of the different polymers. While for the shorter ionenes it seems reasonable (based on the observed trends in reactivity) that chlorides are more closely bound to

the polymer backbone and thus less readily available for the nucleophilic attack of the epoxide (compared to the bigger and more easily polarizable iodide), it seems that iodides are on the other hand more tightly attached to the polymers in those cases where longer linkers between the ammonium groups are present (thus explaining the different trend in reactivity in these cases). Finally, we tested the use of chloride-based ionenes and adding additional NaI to the reaction mixture (entries 25–30). Interestingly, in these experiments again the **A** and **B** series performed clearly superior compared to the sole use of the Cl-ionenes (compare entries 25 vs. 4, 26 vs. 5, 27 vs. 3, and 28 vs. 8). It should be noted that NaI alone allows for approximately 10% conversion under these conditions in the absence of any catalyst, thus a synergistic effect of the use of NaI together with the cationic polymers was clearly proven herein. The results are again not that much better for the **C** and **D** series (entries 29,30) which is in accordance to the observations made when using the isolated salts alone (the slightly higher yields may be rationalized by some minor catalytic contribution of the excess NaI). Finally, it was also shown that addition of NaBr has more or less no positive effect (entry 31).

Altogether this screening of different cationic polymers revealed a rather complex structure-catalytic activity relationship and with respect to ease of operation we thus decided to carry out further studies (i.e. investigation of the application scope) with the chloride-containing ionene **D**^{1,4} under the conditions shown in entry 14. It was also clearly shown that the catalyst can easily be recycled by a simple filtration from the crude reaction mixture and reused for at least four further reactions without any significant loss in activity. As shown in Table 2, the application scope of this reaction is relatively broad and a variety of differently substituted aliphatic and aromatic epoxides performed very well under the catalysis of ionene **D**^{1,4}. For comparison, the reactions were all run at 120 °C with 0.5 mol% of the catalyst for either 1, 4, or 10 h. The only real limitation was observed when using nitro-styrene oxide (entry 14), which gave almost no cyclic carbonate but instead decomposed totally under the reaction conditions.

Mechanistically, the CO₂ fixation with epoxides in the presence of nucleophilic catalysts has been discussed and investigated in much detail [23, 40, 48–50]. It is commonly believed that the epoxide is activated towards nucleophilic attack by the Lewis- or Bronsted-acidic catalyst and that the nucleophilic source opens the epoxide by addition to the less substituted carbon (for two recent mechanistic investigations see Ref. [40, 49]). As a simple test to investigate whether epoxide opening really occurs preferably via nucleophilic addition to the less-substituted carbon or if maybe a more S_N1-type mechanism proceeding via attack to the benzylic position is likely we tested the CO₂-fixation with the deuterium-labelled styrene oxides **1a-D2** and **1a-D1** (Scheme 2). It was clearly shown

Table 2 Application scope

Entry ^a	R	t (h)	Conv. (%) ^b	Yield (%) ^c
1	Ph	1	25	nd
2	Ph	4	57	nd
3	Ph	8	> 90	90
4	Ph	10	> 95	94
5	4-Cl-C ₆ H ₄ -	1	96	96
6	4-Cl-C ₆ H ₄ -	4	65	nd
7	4-Cl-C ₆ H ₄ -	10	> 95	95
8	4-F-C ₆ H ₄ -	1	31	nd
9	4-F-C ₆ H ₄ -	4	71	nd
10	4-F-C ₆ H ₄ -	10	> 95	96
11	Bn	1	33	nd
12	Bn	4	75	nd
13	Bn	10	> 95	95
14	4-NO ₂ -C ₆ H ₄ -	10	2	nd
15	ClCH ₂ -	1	50	nd
16	ClCH ₂ -	4	> 95	nd
17	ClCH ₂ -	10	> 95	95
18	PhOCH ₂ -	1	80	nd
19	PhOCH ₂ -	4	> 95	nd
20	PhOCH ₂ -	10	> 95	96
21	BnOCH ₂ -	1	51	nd
22	BnOCH ₂ -	4	> 95	nd
23	BnOCH ₂ -	10	> 95	95
24	But-3-enyl-	10	48	nd

^a4 mmol scale (neat) using 0.5 mol% catalyst (based on the repeating monomeric catalytically active units of the ionenes) and 1 atm CO₂

^bJudged by ¹H NMR of the crude reaction mixture (isolated yields are usually in the same range as conversion)

^cIsolated yields

nd not determined

that the di-deuterated **1a-D2** reacts measurably slower than the parent non-deuterated **1a** and the epoxide deuterated in the benzylic position (**1a-D1**). This kinetic isotope effect is therefore a clear hint that nucleophilic attack indeed occurs at the less-substituted carbon, as proposed by others for different catalyst systems [40, 49].

3 Conclusion

A detailed screening of different ionene polymers showed that these cationic polymers are powerful catalysts for the CO₂-fixation of epoxides under an atmospheric pressure

Scheme 2 Use of deuterium-labeled epoxides reveals a pronounced kinetic isotope effect for the less-substituted carbon as shown in the CO_2 fixation with **1a–D2**

of CO_2 . Depending on the polymer backbone, either the corresponding iodides or chlorides turned out to be best-suited for this transformation, illustrating that both, the nature of the multifunctional polymer backbone, and the nucleophilic counter anion play an important role in this transformation. A variety of different epoxides were well tolerated and the polymeric catalysts could easily be recycled by a simple filtration. Some mechanistic insights in this reaction were obtained by using deuterated starting materials, as the observed kinetic isotope effect provides evidence for a mechanism in which the nucleophile preferentially adds to the less hindered epoxide carbon.

4 Experimental

4.1 General Information

1H -, ^{13}C -, and ^{19}F -NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer, a Bruker Avance 500 MHz spectrometer, and on a Bruker Avance III 700 MHz spectrometer with TCI cryoprobe. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. MALDI-TOF measurements were collected with a Bruker Autoflex III Smartbeam spectrometer and on an Agilent atmospheric pressure photoionization (APPI) source on an Agilent 6520 quadrupole time-of-flight (QTOF) in the positive mode. The

ionenes were synthesized as described recently [15, 17]. The used epoxides were purchased from commercial suppliers and used without further purification. The deuterated epoxides were synthesized as described in the online supporting information.

4.2 General CO_2 -Fixation Procedure

The reactions were carried out using a Radleys Carousel 12 Plus Reaction Station™. A mixture of 0.2 mmol of the corresponding ionene (based on the repeating monomeric catalytically active units of the ionene) was weighed in a reaction tube ($\varnothing$ 16 mm). After the addition of 4 mmol epoxide and heating the mixture to $120^\circ C$ a CO_2 atmosphere was provided by using a simple balloon and stirring was started (1000 rpm). After the given reaction time, the mixture was cooled down to room temperature and either filtered using a fritted glass funnel (P 4) to recover the ionenes, or directly flushed through a short column of silica gel (heptanes/EtOAc = 10:1–3:1 as eluent) to afford the literature known cyclic carbonates **2** (further details and analytical data can be found in the SI).

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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