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One-Pot Synthesis of Ion-Containing CO_2-Based Polycarbonates Using Protic Ionic Liquids as Chain Transfer Agents

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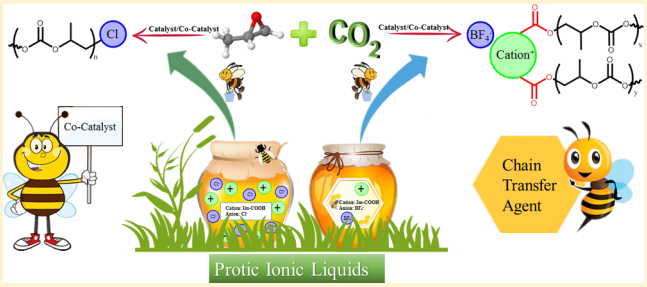
Supporting Information

ABSTRACT: An analysis of the construction of ion-containing CO_2-based polycarbonates via metal-catalyzed immortal copolymerization of propylene oxide (PO) and carbon dioxide in the presence of protic ionic liquids (ILs) as chain transfer agents is described. The reactions were catalyzed by the binary (salen)CoO_2CCF_3/onium salt system in the absence of added solvent. On the basis of the results of this study, which includes ^{1}H NMR and MALDI-TOF-MS data, it is clear that the role of the protic IL in this process is dominated by its anion. When the anion of the protic ionic liquid is nucleophilic, such as chloride, the protic ionic liquid acts as a cocatalyst in the reaction system for epoxide ring opening, and the chain transfer reaction initiated by the cation is completely suppressed. However, when the anion of the protic ionic liquid is non-nucleophilic, such as BF_4^-, the protic ionic liquid acts as an effective chain transfer agent to afford IL-based polycarbonates by rapid and reversible chain transfer processes. The resultant polymer structures were confirmed by ^{1}H NMR and MALDI-TOF-MS spectroscopies. This work provides a facile method for synthesizing ion-containing polycarbonate as well as an insight into immortal copolymerization processes utilizing protic ionic liquids as chain transfer agents.



INTRODUCTION

Carbon capture and utilization (CCU) processes represent effective options for reducing CO_2 emissions.[1] In this context, several processes are currently being employed that utilize sizable quantities of carbon dioxide, e.g., the production of urea,[2] methanol,[3,4] cyclic carbonates,[5,6] and polymers.[7] Although presently the impact of CCU with regard to climate change is of little consequence, its contribution to reducing the "greenhouse effect" would be greatly enhanced if the technology was available for efficiently converting CO_2 into energy-rich products or fuels.[8] In recent decades, the copolymerization of CO_2 and epoxides to synthesize degradable aliphatic polycarbonates has drawn considerable attention from both academia and industrial communities.[9−24] For example, aliphatic polycarbonates have been proposed as alternatives to petro-based chemicals for use in the fields of automotive, medical, and electronic industries.[25]

Today, much effort is being devoted to synthesizing CO_2-based polyols by means of immortal polymerization, since these polyols are raw materials for polyurethane production, as well as effective macroinitiators for constructing block polymers.[26] Immortal polymerization, first identified by Inoue and co-workers in 1985,[27] is an effective method for synthesizing hydroxyl end-functional polymers with narrow molecular weight distributions. In the copolymerization of epoxides and CO_2, the addition of an alcohol or carboxylic acid to the catalytic system momentarily terminates chain growth. However, a rapid and reversible chain transfer reaction occurs between the metal bound anionic growing polymer chain and the protic compound, resulting in uniform chain growth from all the added protic molecules (Scheme 1).[28,29] Notably, chain transfer reactions provide promising methods for precisely controlling topology and architecture of block or graft copolymers.

The presence of adventitious water commonly serves as a chain transfer agent in copolymerization reactions of epoxides and CO_2. This in turn accounts for the observation that in general there is not a good correlation between the copolymer's molecular weight and monomer/initiator ratio as expected for a living polymerization process.[30] In our previous studies, ABA triblock polycarbonates were synthesized by a facile and straightforward "two-step, one-pot" strategy using water as an effective chain transfer agent in a (salen)CoTFA/PPNTFA catalyst system.[31,32] The use of trifluoroacetate initiators (TFA = X in Scheme 1) is employed because they undergo hydrolysis more easily and rapidly than other end groups, thereby providing nearly 100% polyols during the polymerization process.[29,33] Wu has also explored the role of water during the copolymerization of propylene oxide and CO_2 in detail.[34] In addition to water, various chain transfer agents

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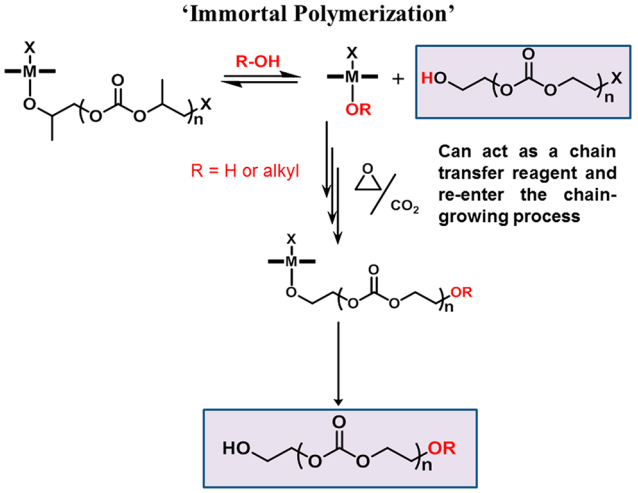
Scheme 1. Widely Accepted Proposal for Protic Molecules as Chain Transfer Agents in the Copolymerization of Epoxides and CO_2



have been investigated. For example, Lee and co-workers explored compounds containing −OH or −COOH groups acting as chain transfer agents in the copolymerization of PO/CO_2 and obtained CO_2-based polyols with controllable molecular weight.[35] Moreover, these same researchers employed CO_2-based polyols bearing the organophosphorus group to prepare flame-retarding polyurethane.[36] Recently, Liu's research group has investigated various polybasic organic acids as chain transfer agents to obtain CO_2-based polyols,[37] oligo(carbonate−ether) triol,[38] and oligo(carbonate−ether) tetraol.[39]

As previously mentioned, a significant driving force for synthesizing CO_2-based polyols is for their use in condensation reactions with diisocyanates to produce polyurethanes, polymers which occupy an important position in modern society. Currently, growing attention is being paid to preparing various types of ion-containing polyurethanes or polyurethane ionomers because of their unique morphologies and properties. These latter characteristics are attributed to the combined effects of Coulombic, hydrogen bonding, and hydrophobic interactions.[40,41] For the production of ion-containing polyurethanes, the key material is the ion-containing polyols. Ionic liquids (ILs) as emerging green solvents have been widely studied and applied in many areas such as catalysts,[6,42] CO_2 absorption,[43] solvents,[44] and so forth. Thereinto, protic ionic liquids when functionalized with −OH or −COOH groups as one of the task specific ionic liquids might have great potential as chain transfer agents by means of immortal copolymerization processes with epoxides and CO_2 to provide ion-containing polyols. At this time, we report studies of protic ionic liquids serving as chain transfer agents in CO_2/epoxide copolymerization processes.

In this article, a series of protic ionic liquids (Figure 1) were synthesized and utilized as chain transfer agents in the copolymerization of PO/CO_2 using binary (salen)CoTFA/onium salt catalysts (Figure 2) to prepare CO_2-based polycarbonates. For the copolymerization reactions, the cation of the ionic liquid with −OH or −COOH groups may participate in the chain transfer reaction, while the anion may act as the initiator in the early stages of the process. Thus, the roles of the cation and anion of the protic ILs were systematically examined. To improve the selectivity for the ion-containing CO_2-based polycarbonates among the polycarbonate product, the acidity and the anion of the IL were altered. Based on the results of these experimental observations, along with ^{1}H NMR and MALDI-TOF-MS spectra, a mechanism for the copolymerization of CO_2 and PO in the presence of protic ILs using a (*R*,*R*)SalenCoTFA binary catalyst system is proposed.

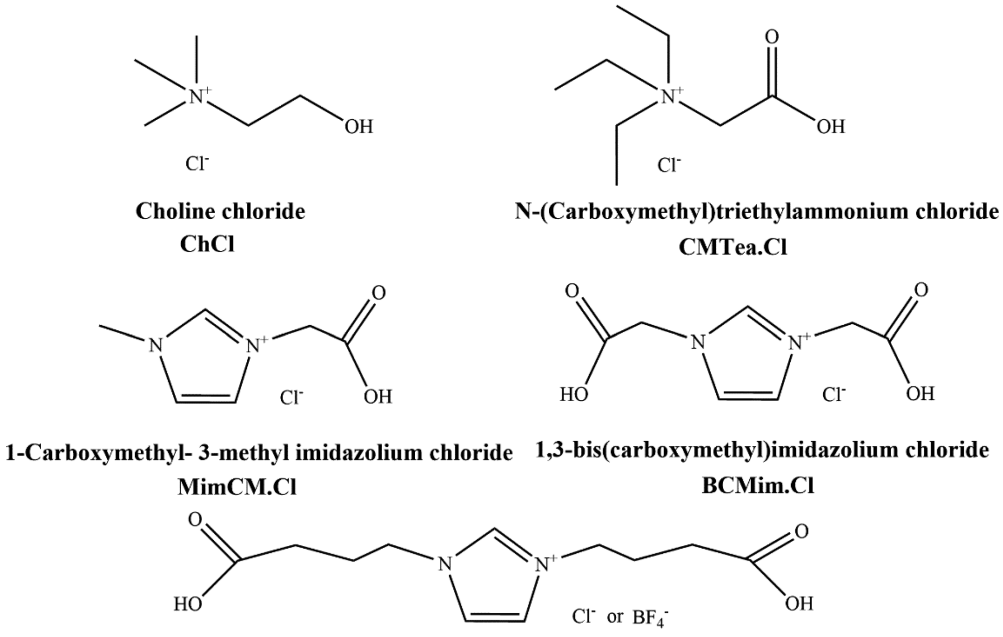


Figure 1. Structures and abbreviations of the protic ionic liquids utilized in these studies.

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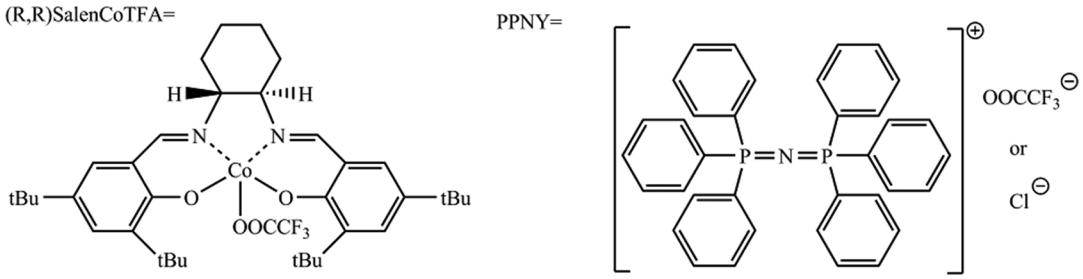

Figure 2. Structure of (*R*,*R*)SalenCoTFA/PPNY (Y = TFA, Cl).

Table 1. CO_2/PO Copolymerization in the Presence of Protic Ionic Liquids Containing Chloride Anion[a]

entry	co-cat.	IL	[IL]/[cat.]	time (h)	conv (%)	selectivity[b] (%)	M_n[c] (g/mol)	PDI[c]
1	PPNTFA	ChCl	5	20	96	93:7	11300	1.20
2	PPNTFA	CMTea.Cl	2.5	20	96	99:1	12700	1.21
3	PPNTFA	CMTea.Cl	5	20	>99	93:7	7300	1.08
4	PPNTFA	CMTea.Cl	10	20	>99	70:30	3854	1.11
5	PPNCl	CMTea.Cl	2.5	20	98	98:2	15397	1.14
6	PPNCl	CMTea.Cl	5	20	>99	73:27	10800	1.22
7	PPNTFA	MimCM.Cl	2.5	20	91.8	99:1	14600	1.23
8	PPNTFA	MimCM.Cl	5	20	72.4	99:1	6900	1.10
9	PPNCl	MimCM.Cl	2.5	20	93.5	96:4	16550	1.18
10	PPNCl	MimCM.Cl	5	20	75.8	99:1	6950	1.07
11	PPNCl	MimCM.Cl	10	20	48.5	96:4	3000	1.03
12	PPNTFA	BCMim.Cl	1.25	20				
13	PPNTFA	BCPim.Cl	1.25	20	94	99:1	25000	1.15
14	PPNTFA	BCPim.Cl	2.5	20	96	99:1	15600	1.12
15	PPNTFA	BCPim.Cl	3.75	20	92	97:3	9450	1.09
16	PPNTFA	BCPim.Cl	5	20	83	92:8	–[d]	–[d]

[a]Reaction conditions: (salen)CoTFA/PPNY/PO (Y = TFA, Cl) = 1/1/1000 (molar ratio); a certain amount of protic ionic liquid was added into a 15 mL predried autoclave which was pressurized to 2.5 MPa by CO_2 at 25 °C. [b]Selectivity for copolymers vs cyclic carbonates determined by ^{1}H NMR spectroscopy. [c]Measured by GPC. [d]Owing to the interaction of the charged polymers with the GPC column, the M_n and PDI measured by GPC are unreliable.

RESULTS AND DISCUSSION

Initially, we examined the copolymerization of propylene oxide (PO) and CO_2 in the presence of various amounts of different protic ionic liquid chain transfer agents containing the nucleophilic chloride anion. It should be noted that unlike conventional CTAs, e.g., adipic acid, both the anion and cation of these protic ILs could have an effect on the copolymerization reaction. That is, the chloride anion is one of the most commonly used initiators for epoxide/CO_2 coupling processes.[15,45] Thus, clarification of the role of the anion in these polymerization processes is of utmost importance in understanding the use of these protic ILs as CTAs. Four types of protic ILs containing nucleophilic chloride anions were employed as additives. The results of this study are summarized in Table 1.

As shown in Table 1, the obtained polycarbonates all exhibit narrow molecular weight distributions (PDI < 1.23) no matter which protic IL was used in the copolymerization process. Moreover, the molecular weights decreased with the molar ratio of IL/cat. increase, thereby indicating that the molecular weight of the polycarbonate can be controlled by the concentration of the IL. At the same ratio of IL/cat. of 5.0 (entries 1, 3, and 8), the M_n values of the polycarbonates of 11300, 7300, and 6900 g/mol decreased in the order ChCl > CMTea.Cl > MimCM.Cl. Furthermore, the PDIs of these three polycarbonates were 1.20, 1.08, and 1.10, respectively, suggesting ILs containing carboxyl groups are better chain transfer agents. These results are in accordance with previous findings by Wang and co-workers.[39] A series of copolymerization reactions employing CMTea.Cl as chain transfer agents are listed in Table 1, entries 2–6. These results clearly illustrate that the conversion of PO increases with the molar ratio of IL/cat., reaching nearly 100% when the molar ratio of CMTea.Cl/cat. was above 5. However, the selectivity of polycarbonate over cyclic carbonate sharply decreased as the molar ratio of CMTea.Cl/cat. increased from 5 to 10. Because the chloride ion is the better initiator (*vide infra*), as expected upon changing the cocatalyst from PPNTFA to PPNCl (entries 3 and 6), while maintaining the IL/cat. ratio at 5, the selectivity of copolymer was also decreased.

To investigate the effect of the acidity of the protic IL on the copolymerization reaction, MimCm.Cl was synthesized which has a stronger acidity than CMTea.Cl because of its electron-withdrawing imidazole ring. The results using MimCM.Cl are summarized in Table 1, entries 7–11, which indicated the selectivity for copolymer to be unchanged with an increase in MimCM.Cl/cat. with a decrease in PDI. However, there is a sharp decrease in the conversion of PO monomer with increasing quantities of MimCM.Cl, indicative of a decrease in catalytic activity with IL's acid strength. To further confirm this finding, BCMim.Cl and BCPim.Cl were examined for their effect on the copolymerization process. The pK_a values of these acidic ILs are 1.9 (MimCM.Cl) , 1.33 (BCMim.Cl), and 3.46 (BCPim.Cl).[46] When the IL with the strongest acidity,

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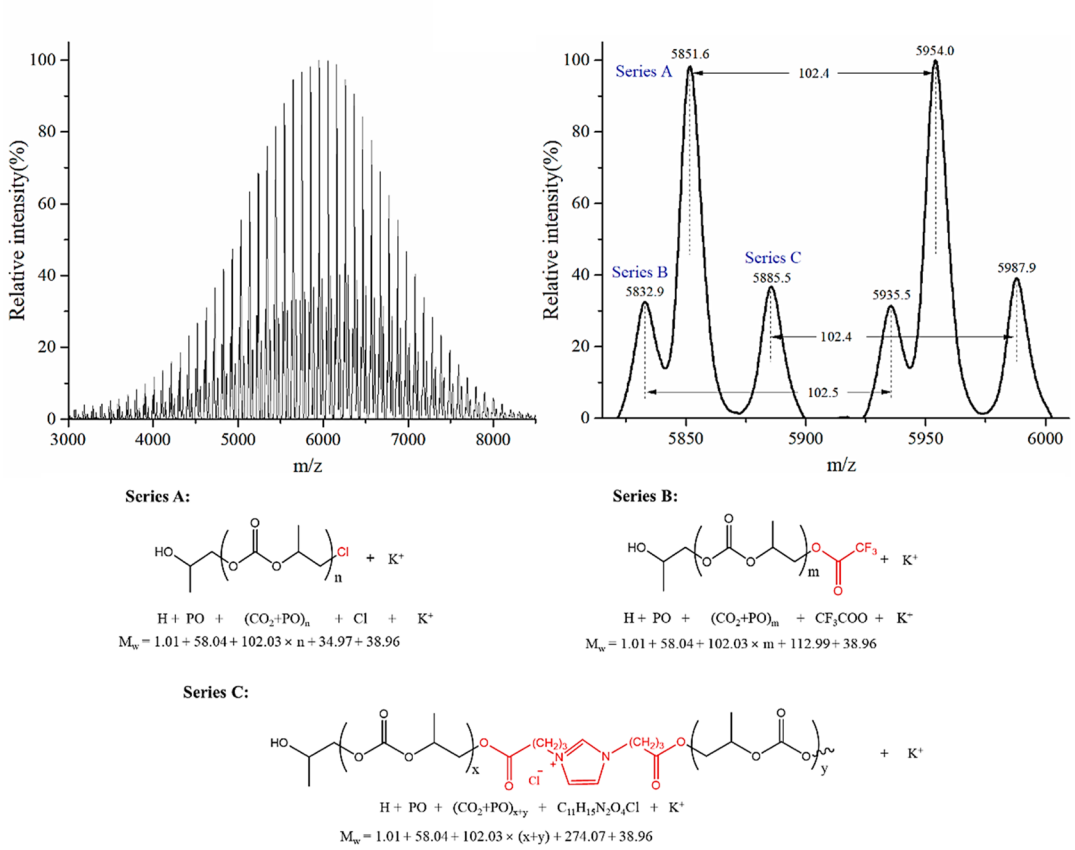

Figure 3. MALDI-TOF-MS spectrum of the product prepared by adding BCPim.Cl as chain transfer agent (entry15, Table 1).

BCMim.Cl, was employed as CTA, production of polycarbonate was quenched (entry 12). By way of contrast, the use of BCPim.Cl (entry 14) compared favorably with MimCm.Cl (entry 7) in copolymer production. This is an interesting observation, for our goal is to synthesize ion-containing polycarbonate diols.

^{1}H NMR and MALDI-TOF-MS spectroscopies were used to assess the effectiveness of ILs as chain transfer agents in the copolymerization reactions of propylene oxide and CO_2. For example, when employing BCPim.Cl as chain transfer agent (entry 15, Table 1), the copolymer produced contained weak resonances in the proton NMR spectrum at 2.54, 2.33, and 3.65 ppm assigned to the $-CH_2-$ groups of the IL (Figure S1). However, these proton signals are so weak such that the M_n value measured by GPC would be greatly inconsistent with that determined by NMR. Indeed, the MALDI-TOF-MS spectrum depicted in Figure 3 displays a trimodal distribution, with the major species being the chloride-initiated polycarbonate.

It is of interest to note that the catalyst and cocatalyst do not contain a chloride ion; hence, the chloride ion from the IL participates in the early stages of the copolymerization process. This was further supported by changing the cocatalyst from PPNTFA to PPNCl (entries 3 and 6); the selectivity for copolymer significantly decreased. Consistent with literature predence, the backbiting pathway for cyclic carbonate production is enhanced with increasing concentrations of chloride anion.[47] The other two minor carbonate chains were initiated by trifluoroacetate and chain transferred by BCPim cation, respectively. Although the cation of BCPimCl serves as a CTA, the major role of BCPimCl is to provide the chloride anion as an initiator of the copolymerization process. Similar results were found from the MALDI-TOF-MS spectra of polymers derived from CMTea.Cl and MimCM.Cl employed as chain transfer agents (Figures S2 and S3). Furthermore, the molecular weights of the copolymers were found to be significantly lower than the theoretical values in the presence of ILs and can thereby precisely be controlled by the amount of added IL.

These results are in accordance with the work reported by Lee and co-workers where polymer chain growth resulted not only from the anions in the catalyst system but also from adipic acid which served as a chain transfer agent.[35] In general, the chain transfer process is shown to be much faster than chain propagation as well as being reversible.[48] In this instance, where large concentrations of chloride ions presence in the reaction system derived from the protic IL, the chain transfer reaction by the cation of the IL is suppressed. This is the result of a fast chloride ligand exchange reaction with the growing anionic polymer chain or, in other words, a faster chain transfer reaction involving chloride anions. *Hence, the solution for utilizing protic ILs as CTAs for providing ion-containing polycarbonates is to eliminate the nucleophilic nature of the anion associated with the ionic liquid.*

To achieve our goal of developing an efficient synthesis of ion-containing polycarbonates via an immortal copolymerization of propylene oxide and CO_2, we simply replaced the chloride anion in BCPim.Cl with BF_4^-, which was easily implemented by an ion exchange method.[49] The use of BF_4^- as a non-nucleophilic anion in the copolymerization of epoxides and CO_2 has been discussed elsewhere.[15,50] The results of our studies of the copolymerization reactions of PO and CO_2 in

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Table 2. Effects of $BCPim.BF_4$ on the Copolymerization of CO_2/PO[a]

entry	co-cat.	CTA	[CTA]/[cat.]	time (h)	conv[b] (%)	selectivity[b] (%)	M_n[b] (g/mol) (^{1}H NMR)	M_n[c] (g/mol) (theor)
1	PPNTFA	$BCPim.BF_4$	5	20	48	92:8	16500	9300
2	PPNTFA	$BCPim.BF_4$	2.5	60	96	94:6	73400	37200
3	PPNTFA	$BCPim.BF_4$	5	60	92	92:8	36200	19100
4	PPNTFA	$BCPim.BF_4$	7.5	60	90	94:6	13400	12600
5	PPNTFA	$BCPim.BF_4$	10	60	87	92:8	9050	9200
6[d]	PPNTFA	$BCPim.BF_4$	10	60	94	98:2	4650	6050
7	PPNTFA	$BCPim.BF_4$	12.5	60	80	98:2	6200	6900
8[d]	PPNTFA	$BCPim.BF_4$	12.5	64	93	98:2	3900	4900
9	PPNTFA	$BCPim.BF_4$	15	60	10			

[a]Reaction conditions: (salen)CoTFA/PPNTFA/PO = 1/1/1000, molar ratio, a certain amount of protic ionic liquid was added into a 15 mL predried autoclave which was pressurized to 2.5 MPa by CO_2 at 25 °C. [b]Determined by ^{1}H NMR spectroscopy, based on comparing the relative integrals of polycarbonate and $BCPim.BF_4$. [c]Calculated according to $M_n = n_{PO} \times C_{PO} \times S_{polymer}/n_{BCPim.BF4} + (M_{BCPim.BF4})$, where n_{PO} is the amount of PO added into the reaction system, C_{PO} is the conversion of PO after reaction, $S_{polymer}$ is the selectivity of polycarbonate over cyclic carbonate, $n_{BCPim.BF4}$ is the amount of $BCPim.BF_4$ fed into the reaction system, and $M_{BCPim.BF4}$ is the molecular weight of $BCPim.BF_4$. [d]Same reaction conditions except that (salen)CoTFA/PPNTFA/PO = 1/1/600.

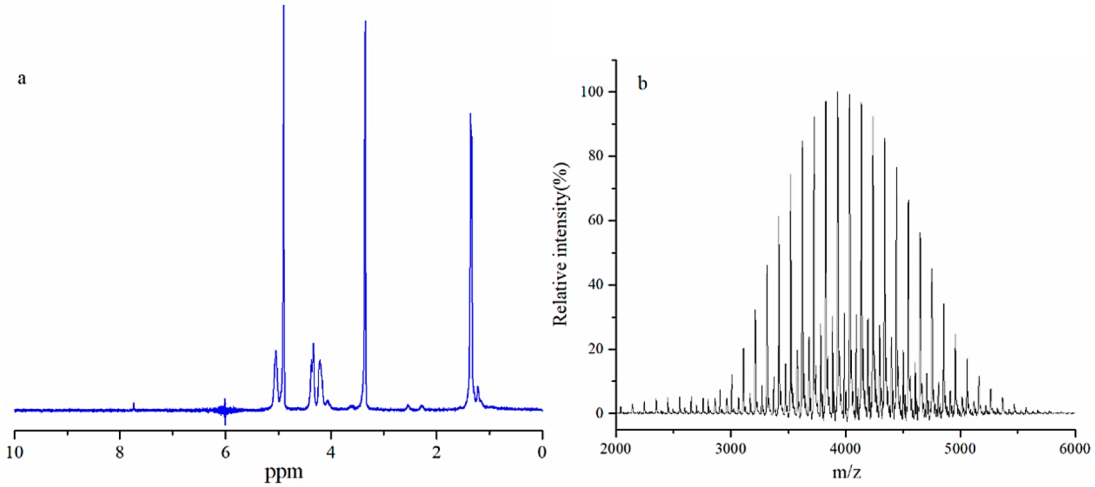

Figure 4. (a) ^{1}H NMR spectrum using CD_3OD as solvent. (b) MALDI-TOF-MS spectrum of the product prepared using $BCPim.BF_4$ (entry 7, Table 2).

the presence of the protic IL $BCPim.BF_4$ as a chain transfer agent are summarized in Table 2.

As can be seen in Table 1 (entry 16) and Table 2 (entry 1) for reactions otherwise run under identical conditions, the catalytic activity decreases in the presence of $BCPim.BF_4$ relative to BCPim.Cl. However, the selectivity for copolymer remains high at 92% in both cases. To address the role of $BCPim.BF_4$ in the copolymerization process, ^{1}H NMR spectroscopy was employed. In Figure S4, the proton signals in the region 2.20−2.60 ppm are ascribed to the $-CH_2-$ groups in $BCPim.BF_4$, which are consistent with those seen in Figure S1 for the BCPim.Cl derived copolymer. Moreover, the ^{1}H NMR spectrum of the copolymer obtained from $BCPim.BF_4$ displays a resonance at 7.40 ppm due to the hydrogen atom on the imidazole ring which is too weak to be observed in the polymer from the chloride analogue. Although the ^{1}H NMR signals of the IL are relatively stronger in the copolymer of the BF_4^- derivative, the M_n values calculated from ^{1}H NMR spectroscopy were abnormally higher than their expected values for [IL]/cat. ratios ≤5, suggesting only partial BCPim incorporation in these instances. The MALDI-TOF-MS spectrum of the polycarbonate obtained in entry 3 of Table 2 is shown in Figure S5. Three species were observed: $[BCPim.BF_4(PO-CO_2)_m(PO)_2]K^+$, $[BCPim.BF_4(PO-CO_2)_m(PO)_3]K^+$, and $[TFA(PO-CO_2)_m(PO)]K^+$, with the $BCPim.BF_4$-based polycarbonate being the dominant product. Hence, as anticipated, the chain transfer reaction is accelerated upon changing the anion from Cl^- to BF_4^-, which demonstrates the dramatic role of the anion in the IL on the copolymerization process. Moreover, it should be noted that small quantities of ether linkages are seen in the $BCPim.BF_4$ derived polycarbonate. Because the charged copolymers' molecular weights could not be reliably determined by GPC, the M_n values were calculated by ^{1}H NMR measurements. When the [IL]/cat. exceeded 7.5, there was good agreement between calculated and theoretical M_n values. At high [IL]/cat. (entry 9, Table 2), PO conversion was very low, suggestive of (salen)CoTFA deactivation with the addition of excessive amounts of IL.

The ^{1}H NMR and MALDI-TOF-MS spectra of the $BCPim.BF_4$-based polycarbonates (entry 7, Table 2) are depicted in Figure 4. Of importance, this ion-containing polycarbonates dissolves in CD_3OD as indicated in Figure 4, indicative of the $BCPim.BF_4$-based polycarbonates being amphiphilic. The trifluoroacetate-initiated copolymer is not present in significant quantity as confirmed by the MALDI-TOF-MS spectrum in Figure 4, where only $BCPim.BF_4$-based polycarbonates were observed: $[BCPim.BF_4(PO-CO_2)_m-$

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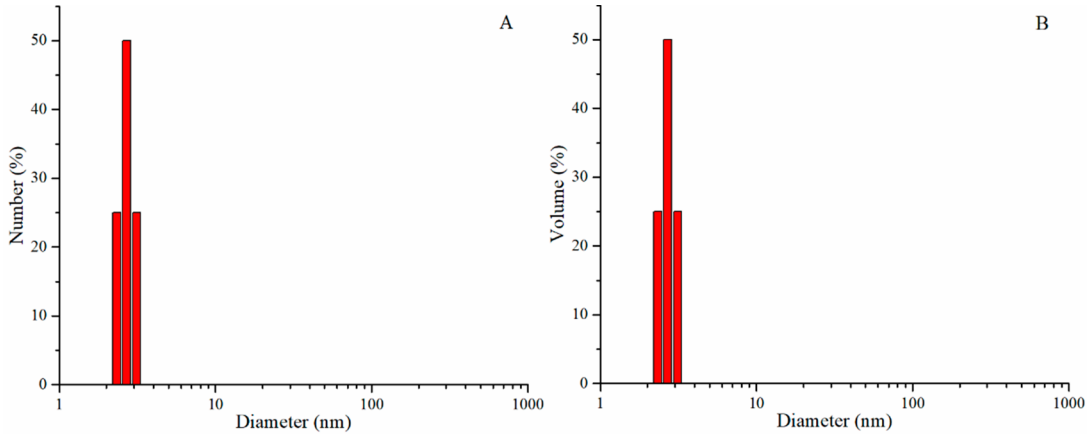


Figure 5. Dynamics light scattering results of nanoparticles of polymer (entry 8, Table 2).

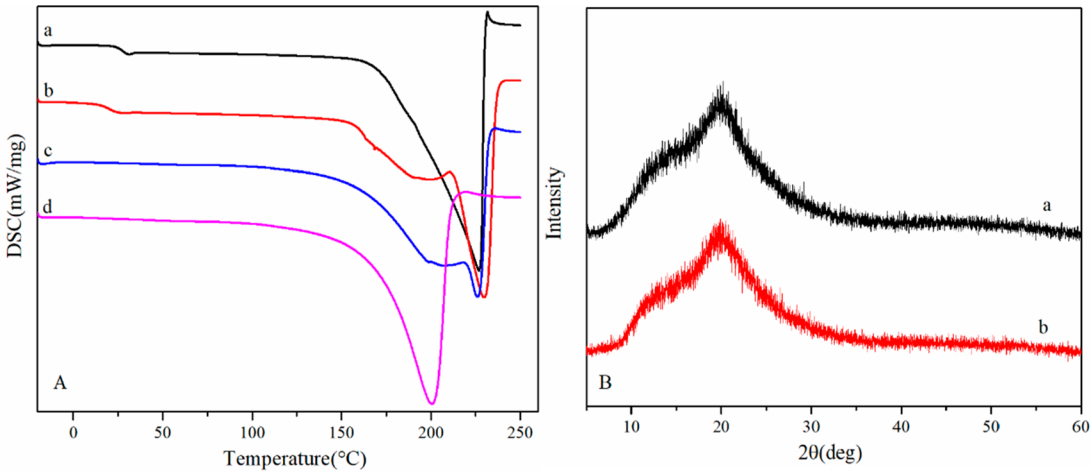
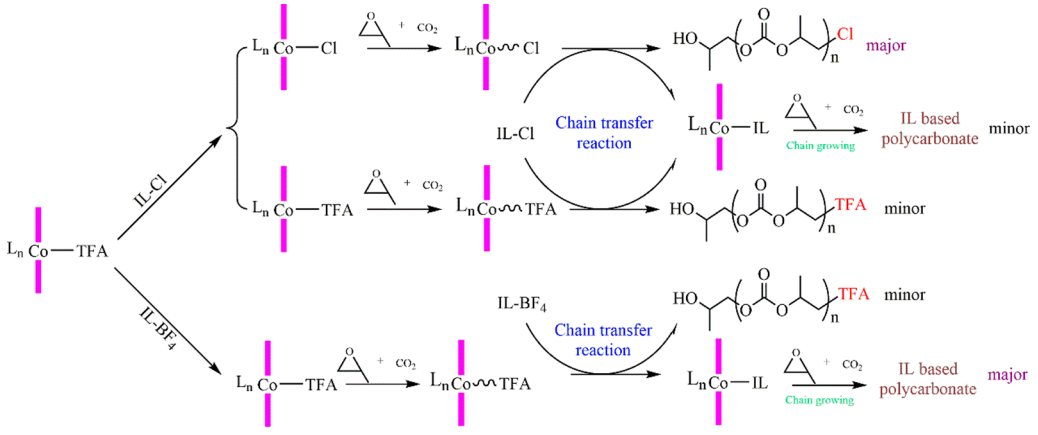


Figure 6. (A) DSC thermograms of various ion-containing polycarbonate: (a) entry 2, (b) entry 4, (c) entry 5, and (d) entry 7. (B) powder XRD profiles of selected ion-containing polycarbonates: (a) entry 2 and (b) entry 7. All entries are from Table 2.

Scheme 2. Plausible Mechanism of Protic Ionic Liquid as Chain Transfer Agent in the Copolymerization of PO and CO_2 Catalyzed by SalenCoTFA/PPNTFA



$(PO)_2]Na^+$, $[BCPim.BF_4(PO{-}CO_2)_m(PO)_2]K^+$, $[BCPim.BF_4$-$(PO{-}CO_2)_m(PO)_3]Na^+$, and $[BCPim.BF_4(PO{-}CO_2)_m$-$(PO)_3]K^+$. In summary, the BCPim.BF_4-based polycarbonates were successfully synthesized by means of immortal copolymerization of CO_2/PO in the presence of BCPim.BF_4 as chain transfer agent using the (salen)CoTFA/PPNTFA catalyst.

As discussed above, the BCPim.BF_4-derived polycarbonate dissolves in methanol at ambient temperature. In previous studies, we have reported that anionic and cationic block polymer dissolve in deionized water and self-assemble to form nanoparticles with high uniformity.[32] Thus, as the affinity between polycarbonates and methanol is weak, it is possible that ion-containing polycarbonates self-assemble to provide nanoparticles in methanol. In this regard, the polymer from entry 8, Table 2, was investigated using dynamic light scattering (DLS). Indeed, the ion-containing polycarbonate

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does form nanoparticles in methanol with a narrow particle size distribution, providing a relatively low hydrodynamic diameter of 2.71 ± 0.79 nm, indicating that the introduction of ions into the polycarbonate increases its affinity for methanol (Figure 5). Hence, the ion-containing polymers reported upon herein are amphiphilic.

The thermal properties of the ion-containing polycarbonates were determined by differential scanning calorimetry (DSC) which reveal a gradual decrease in the T_g (glass transition temperature) with increasing CTA content. As seen in Figure 6a, entry 2, a T_g of about 40 °C is observed, which decreases to about 35 °C for entry 4. Furthermore, a quite sharp and high crystallization endothermic peak and the T_m (melting temperature) values decrease with increasing CTA content, with a value of 200 °C for the copolymer derived from entry 7 of Table 2. These results indicate that these polycarbonates exhibit some degree of crystallinity.[51,52] To investigate this further by XRD methods, as shown in Figure 6B, broad diffraction peaks were observed at 2θ = 19.8 °C with a shoulder at 13°, regardless of the CTA's composition, which corresponds to the crystalline segments in the polycarbonates. Nevertheless, the degree of crystallinity in these ion-containing polycarbonates is low.

A plausible mechanism for the role of protic ILs in the immortal copolymerization reaction of PO and CO_2 in the presence of (salen)CoTFA/onium salt catalysts is provided in Scheme 2. The ILs examined in this report can be classified into two groups: ILs with nucleophilic chloride anions and ILs with non-nucleophilic BF_4^- anions. For ILs with chloride anions as shown in Scheme 2, Cl^- initiates PO ring opening followed by carbonate chain growth as verified by MALDI-TOF-MS. Under these conditions, only a small portion of the protic IL participates in a chain transfer process to produce IL-based polycarbonates. Hence, the chloride ion plays a pivotal role in the copolymerization process, and the chain transfer reaction by protic IL is suppressed. By way of contrast, for ILs with BF_4^- anions, the cationic portion of the IL deprotonates the growing anionic copolymer chain end of PPC and becomes a new initiator for the growing polymer chain. After alternating PO and CO_2 enchainment, as well as rapid interchange between the neutral and growing polymer chains, the protic IL-based polycarbonate is obtained as indicated in Scheme 2.

CONCLUDING REMARKS

In this report, several protic ionic liquids were chosen as chain transfer agents and introduced into the copolymerization of PO/CO_2. By adjusting the acidity and the anion of the protic IL, protic IL-based polycarbonates were obtained by means of immortal copolymerization. The structures of protic IL-based polycarbonates were confirmed by ^{1}H NMR and MALDI-TOF-MS spectra. It was interesting to note that the anion type of protic ionic liquid had a significant impact on the role of ionic liquids in the reaction process. When the anions were nucleophilic, they dominated the reaction process and suppressed the cations participation in the chain transfer reaction. Conversely, when the anions were non-nucleophilic, the cations dominated the reaction and underwent chain transfer reactions to form protic IL-based polycarbonates. In this manner, the ion-containing polycarbonates were easily prepared by immortal copolymerization using protic ILs as chain transfer agents. This work not only extends the applications of protic ionic liquids but also provides a novel method to synthesize ion-containing polycarbonates, materials which may have significance in the polyurethane industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01834.

Full experimental details on the preparation of protic ionic liquid, general experimental procedures, and characterizations of resulting copolymers (DOCX)

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Notes

The authors declare no competing financial interest.

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