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Recycling Borate Complex for Synthesis of Polycarbonate Polyols: Towards an Environmentally Friendly and Cost-Effective Process

Naganath Patil,^[a] Senthil Bhoopathi,^[a] Vamshi Chidara,^[a] Nikos Hadjichristidis,^[b] Yves Gnanou*,^[a] and Xiaoshuang Feng*^[a]

[a] Dr. NG Patil, Dr. S Bhoopathi, Dr. VK Chidara, Prof. Y Gnanou, Dr. X Feng.
Physical Sciences and Engineering Division,
King Abdullah University of Science and Technology (KAUST),
Thuwal 23955, Saudi Arabia
E-mail: yves.gnanou@kaust.edu.sa; fxs101@gmail.com

[b] Prof. N Hadjichristidis
KAUST Catalysis Center, Physical Sciences and Engineering Division,
King Abdullah University of Science and Technology (KAUST),
Thuwal 23955, Saudi Arabia

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Abstract: In this investigation, we unveil a metal-free process that warrants the synthesis of poly(propylene carbonate) (PPC) diols/polyols by copolymerization of carbon dioxide (CO₂) with propylene epoxide (PO) under environmentally-friendly, and cost-effective conditions; this process implies the recycling of triethylborane (TEB) and of ammonium salts that both enter in the composition of the initiators used to copolymerize CO₂ and PO. In complement to the above approach, a polymeric support poly(diallyl dimethylammonium chloride) (PDMAC), was synthesized and modified to carry ammonium carboxylate salts along its chain; the prepared polymeric initiator was utilized to copolymerize CO₂ with PO under heterogeneous conditions. Not only were the polymerization results similar to the samples obtained under homogeneous conditions, but the polymer substrate could easily be recovered by simple filtration. The integrity of the polycarbonate diols/polyols, the recycling process were followed by ¹H, ¹³B NMR, GPC, and MALDI-TOF.

Introduction

The discovery of the copolymerization of carbon dioxide (CO₂) and epoxide by Inoue et al.^[1] has created an active area of research that has led to the development of a number of catalysts, both homogeneous and heterogeneous.^[2] One promising application of such copolymerizations is the synthesis of low molar mass polycarbonate diols/polyols that can serve as precursors for the production of polyurethanes (PU) and thus replace the polyether precursors. Applications in packaging and films, coatings, adhesives, as sacrificial binders, etc. are indeed contemplated.^[2b, 3] PU prepared from PPC diols/polyols exhibit better performances at high temperatures, property retention in the presence of water, better chemical and oil resistance than those prepared from conventional polyether and polyester polyol counterparts.^[4] For such applications, the PPC diols/polyols are

required to exhibit a well-defined terminal hydroxyl functionality, low polydispersity, and tunable carbonate content.

Although considerable progress has been made in the development of homogeneous and heterogeneous catalysts for CO₂/epoxide copolymerization,^[5] the preparation of PPC diols/polyols for the production of PU is still a challenge. Polycarbonate diols/polyols produced from heterogeneous catalytic systems suffer from a carbonate content that is moderate compared to alternating PPC samples, a low linear versus cyclic selectivity and a broad polydispersity;^[6] on the other hand, PPC diols/polyols samples prepared with homogeneous catalysts are usually contaminated with mono-hydroxyl PPC chains,^[7] which can be detrimental to the subsequent step-growth reactions with diisocyanate for the synthesis of PU. In addition, the metal residues of the catalyst, if not thoroughly removed, induce color and chemical instability of the PPC samples synthesized.

In our initial report we showed that CO₂ and epoxides could be copolymerized under metal-free conditions using borate complexes associated with organic cations as initiators;^[8] we more recently described the preparation of well-defined PPC polyols exhibiting hydroxyl end-functionality ranging from 1 to 4, and tunable carbonate contents ranging from 50-95 % using borate complexes of various functionalities.^[9] The molar masses of produced polycarbonate polyols (1-10 kg/mol) were controlled by the conversion and the ratio of PO to the borate complex serving as initiator. Unlike catalytic processes which generally require only minute amounts of catalysts to drive the reaction, systems involving an initiator imply its incorporation in the created polymer chains. The smaller the chains grown, the higher the amount of initiator needed. Borate complexes that serve as initiators for the CO₂/epoxide copolymerization are made of a precursor, here succinic acid, that is first deprotonated to generate a difunctional salt which is then reacted with TEB. Compared to traditional metal catalysts, these initiators are very simple to synthesize from commercially available compounds. Given the amount of initiator required to make low molar mass polycarbonate precursors, we found it indispensable to recycle

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and reuse two components, namely TEB and tetrabutylammonium cations, out of the three that enter in the composition of borate complex initiator.

In a replica of heterogeneous catalysis, a polymeric support/precursor PDMAC^[10] was derivatized so as to carry borate initiating sites along its chains. The latter was used to initiate the CO₂/epoxide copolymerization and grow polycarbonate diols under heterogeneous conditions. Being insoluble in THF it was easy to separate the polymer-support from the polycarbonate diol formed. As in the above case, two of the three components entering the composition of this polymeric initiator, namely TEB and poly(diallyl dimethylammonium succinate) could be easily isolated and separated by simple filtration after neutralization of the reaction medium by a mixture of nBA and succinic acid. The isolated polymeric initiator could be reused in another cycle of CO₂/epoxide copolymerization. As for the polycarbonate diol, which is soluble in THF it could be isolated after several rinses with water.

Results and Discussion

Process for recycling the borate complex used as initiator for CO₂/PO copolymerization

The difunctional initiator used to trigger the CO₂/PO copolymerization is a borate complex resulting from the reaction of TEB with ditetrabutylammonium succinate (TBAS) salt. In such initiating species, only the succinate component is incorporated in the polycarbonate chain eventually formed (Scheme 1). In contrast, tetrabutylammonium (TBA) cations and TEB that are essential for the growth of the polycarbonate chains are not included in the latter and thus become useless once the polymerization is discontinued. They are thus disposed subsequently to the polymerization. For the production of 1 kg of polycarbonate of 1000 g / mol, it is thus 294 g TEB and 484 g of TBA cations that are not used and are disposed after polymerization. The purpose of this investigation is to find the way to recover most of TEB and of TBA cations and reuse in subsequent polymerizations without altering the properties and quality of the polycarbonate formed. By such recycling, our aim is to develop a cost-effective and environmentally-friendly process of CO₂/PO copolymerization. As clearly explained in a previous work, borate complexes are less nucleophilic and thus less reactive than free oxanions, which helps to suppress the formation of carbonate cyclics by backbiting. Besides the trialkyl borane required to form the borate complex by reaction with the growing anions, an excess of TEB is necessary to activate PO, which would not spontaneously react with a carbonate anion-borane complex. As a Lewis acid, TEB is a very reactive and fragile compound that is sensitive to oxygen, water and is hydrolyzed in acidic conditions.^[11] To be cost-effective, the CO₂/PO copolymerization process should meet the two following criteria: 1. maintain the structural integrity of polycarbonate formed during polymerization; 2. recover TEB and TBA to an extent as close as possible to 100% from the crude reaction mixture.

Importance of the order of addition of neutralizing agents

It is known that trialkylborane can form a stable adduct with amine, and the resulting adduct can release the initial borane upon reaction with appropriate deblockers such as trifluoroacetic acid or isocyanates which fix the amine in the form of amides and

urea, respectively.^[12] The deactivation/neutralization of the polycarbonate active species and the trapping process of both TEB and the TBA cations were carried out simultaneously upon adding an aqueous solution containing n-butylamine (nBA) to trap TEB and succinic acid to neutralize the active tetrabutylammonium ate complexes (**3**) fitting the PPC chain ends; simultaneously TEB-nBA adduct and succinic salts (**1**) were formed. Due to the presence of water, the PPC chain ends were protonated, causing the generation of end-standing hydroxyl groups. The integrity of the PPC diol formed and of the TEB-nBA adduct after this sequence of reactions was confirmed respectively by FTIR and ¹¹B NMR spectroscopy.

Scheme 1. Mechanism of CO₂/PO copolymerization using ditetrabutylammonium succinate as initiator in the presence of TEB. Application to the synthesis of PPC diol.

It is essential that both nBA and succinic acid be added simultaneously (Table 1). If nBA is added first into the "living" polymer mixture to trap TEB, and SA is introduced in the reaction medium in a second step to neutralize ammonium alkoxide, the "living" polycarbonate undergoes a fast degradation as indicated by FTIR spectroscopy. As shown in Figure 1a, 44 % of cyclic PC is formed in 10 minutes compared to the 3% of cyclic PC present in the reaction medium after polymerization (Figure 1d). This result suggests that upon uncapping TEB from the growing ate complex and generating very reactive bare anions at chain-ends, backbiting reactions occur at a fast step. Even if water is present as a protic source and is added concomitantly to nBA the chain ends get only slowly protonate, letting the remaining bare anions to degrade PPC into cyclic propylene carbonate (Figure 1b). In order to perfectly maintain the structural integrity of the synthesized PPC, both nBA and succinic acid in an aqueous solution must be added together to ensure a) the neutralization of chain ends, b) the trapping of TEB by nBA and c) the migration of TBA cations from PPC chain-ends to more acidic succinic acid. Under these conditions, no degradation of PPC was observed, as shown in Figure 1c, the relative intensity of absorption peak corresponding to cyclic PC remained unchanged; notably, TEB was intact and trapped by nBA. As shown by ¹¹B NMR spectroscopy in Figure 2, before neutralization/termination, two types of borane could be detected: the main peak in Figure 2a corresponds to the borate complex (**3**) appearing at 54 ppm and the small peak at 86 ppm is due to free TEB (**2**). After addition of nBA and succinic acid, most of TEB was trapped by nBA in the form of TEB-nBA that was detected at -3.0 ppm (Figure 2b); the peak at 52.7 ppm indicates that not all borate complex (54 ppm) can be transferred into TEB-nBA adduct; the slight deviation from 54 ppm may well be the result of dynamic equilibrium between the types of species. The absence of any other peaks corresponding to oxygenated boranes (56 ppm for B(OEt)(Et)₂ and 32 ppm for B(OEt)₂Et)^[13] indicates that the released TEB was not hydrolyzed by the presence of SA during the neutralization. Upon increasing the quantity of nBA to 1.2 eq. with respect to TEB, only the TEB-

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nBA adduct is detected at -3.0 ppm (Figure 2c), and PPC remains unaffected (Figure 1c). We also tried to add subsequently succinic acid first and nBA in a second step. In that case, the TBA cations do migrate from the chain ends to succinic acid to form TBAS salts, but unfortunately, TEB gets hydrolyzed in the presence of acid, and not all TEB could be recovered in the form of TEB-nBA adduct (peaks at 56 ppm for B(OEt)(Et)₂ and at 6.2 ppm for its nBA adduct in ¹¹B NMR, Figure S1). This last experiment confirms that both nBA and TEB must be added simultaneously to avoid the degradation of TEB and to preserve the integrity of the PPC chains.

Table 1. Process optimization for the recycling of TEB^[a]

#	Termination condition	Stability of PPC diol (% Cyclic PC formed)	TEB-nBA conversion %
1	nBA (1 eq.) followed by SA	44	>95
2	nBA (1 eq. in water); followed by SA	20	>95
3	nBA (1 eq.) + SA + water together	<1	>93
4	nBA (1.2 eq.) + SA + water together	<1	>99

[a] Cyclic PC was estimated based on FTIR absorption spectroscopy with reference to peaks corresponding to linear polypropylene carbonate, the equivalent of nBA is calculated based on TEB.

Figure 1. FTIR spectra of the polymer reaction mixture after addition of a) n-butyl amine; b) n-butyl amine with deionized water; c) a mixture of the n-butyl amine with succinic acid in water; d) crude reaction mixture before termination.

After succeeding to neutralize the polymer polycarbonate chain ends and completing the conversion of TEB into TEB-nBA adduct, we then focused on the deblocking reaction of this adduct and the recovery of the released TEB. Magenau et al. mentioned in a recent publication that 32 eq. of propionic acid or isophorone

diisocyanate is necessary to free TEB from its adduct with amines,^[12a] which led us to disregard this solution for the recycling of TEB given its cost. As a more efficient deblocker we resorted to tosylisocyanate (TI), a more nucleophilic species than isophorone diisocyanate and a cheap commercial compound. Pure TEB-nBA adduct (Figure S2) prepared by mixing TEB with nBA was thus reacted with one equivalent of TI in THF for 15 min., the reaction mixture was characterized by ¹¹B NMR spectroscopy. As shown in Figure 2c, the peak at -3 ppm corresponding to TEB-nBA adduct totally vanished, and instead, only one peak at 86 ppm corresponding to free TEB (Figure 2d) was detected, indicating a quantitative deblocking.

Figure 2. ¹¹B NMR evolution of the TEB state during its recycling process. a) at the end of polymerization; b) trap TEB with equivalent of n-butyl amine; c) trap TEB with excess (1.2 eq.) of n-butyl amine; d) recovered TEB after deblocking TEB-nBA adduct by p-toluenesulfonyl isocyanate; e) commercial TEB.

Having addressed the two critical issues of polymer neutralization/termination and deblocking for recycling, the complete recycling process was designed based on the solubility difference between PPC diol, the TEB-nBA adduct and TBAS: the corresponding diagram is shown in Scheme 2.

Efficiency of recovery/recycling

In summary, after the step 1, which corresponds to the copolymerization of PO with CO₂, a mixture (4) of 1 eq. of succinic acid and 1.8 eq. of n-butyl amine with respect to TBA cations in 20 eq. of deionized and degassed water was added to the reaction mixture to neutralize the polycarbonate active chain-ends (step 2). The solution was stirred for 10 minutes to ensure the complete formation of the TEB-nBA adduct (6) and the TBAS salt (1) without affecting the structural integrity of the dihydroxy-ended polymer chains (5). The reaction medium was then rinsed with hexane to extract the TEB-nBA adduct (step 3). Both the polycarbonate (5) and the TBAS salt (1), being insoluble in hexane, were isolated by centrifugation; upon washing the solid phase with deionized water, the TBAS (1) could be separated from the polycarbonate diol (5) (step 4). Step 6 consisted in the concentration of the hexane solution containing TEB-nBA adduct; upon adding TSI (1.5 eq. with respect to TBA cations) in step 7 and stirring the medium for 15 minutes TEB was freed and isolated by distillation, the remained sulfonylurea tolbutamide by-product can lower the glucose concentration in blood and be utilized in non-insulin-dependent diabetes treatment,^[14] or be used as hydrogen-bonding organocatalysts for ring-opening polymerization.^[15]

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Scheme 2. Diagram of the simultaneous recycling process of TEB and tetrabutylammonium cations in the preparation of PPC diol.

Figure 3. ^1H NMR quantification of recovered TEB with commercial TEB as reference and naphthalene as internal standard. a) commercial grade TEB (1M in THF); b) recovered TEB after polymerization.

Each of the above steps was monitored by FTIR and NMR, more than 95% of the initial TEB could be recovered after distillation and thus reused to launch another cycle of CO_2/PO

copolymerization reaction. The same results were obtained as in optimization experiments (Figure S3-S5), confirming the integrity of the PPC diol sample isolated. In step 5, the TBAS salt (**1**) was dried by lyophilization; 99% of the initial salt could be recovered as measured by gravimetry and further used for the next cycle of copolymerization.^[9] The characterization by ^{11}B NMR of the recovered TEB showed only one peak at 86 ppm (Figure 2d), and thus the same chemical shift as that of the commercial TEB (Figure 2e). The recycling yield was estimated by ^1H NMR using commercial TEB in THF (1M) as reference and naphthalene as an internal standard (Figure 3). After recovery of TEB and tetrabutylammonium cations through its trap by succinic acid, another cycle of CO_2/PO copolymerization was carried out following the process shown in Scheme 2. The same results, as described above, were obtained after each cycle of copolymerization.

Polymeric initiator for copolymerization of CO_2 and epoxide

As indicated in the above section, the synthesis of polycarbonate diols was carried out under homogeneous conditions with the advantage of resorting to commercially available reactants. The recycling of TEB, the TBA cations, and also the isolation of the polycarbonate diol formed required two specific steps of washing/extraction with hexane and water, respectively. We reasoned that the recycling process could be simpler and easier to handle if the initiating species, responsible for the CO_2/PO

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Table 2. TEB assisted copolymerization of propylene oxide and carbon dioxide. [a]

Entry	Initiator	[M]:[I]:[A]	Selectivity (%) ^[b]	PC (%) ^[b]	Yield (%) ^[c]	$M_n(\text{NMR})$ ^[d] (10 ³)	$M_n(\text{GPC})$ ^[e] (10 ³)/Đ
1	PDMA-S	20:1:3	>99	95	76	1.5	1.4/1.3
2	PDMA-S	40:1:3	>99	91	83	3.5	4.1/1.2
3 ^[f]	Recycle 1	40:1:3	96	88	83	3.6	4.0/1.2
4	Recycle 2	40:1:3	92	90	82	3.4	3.9/1.2
5	Recycle 3	40:1:3	92	90	76	3.2	3.5/1.2
6	PDMA-S	40:1:3	>99	88	80	3.4	3.7/1.1
7 ^[g]	PDMA-Triol	40:1:3	>99	96	85	3.7	3.9/1.2

[a] Polymerizations were carried out in 50 mL Parr reactor under 10 bar CO₂ with stirring at 50 °C. [b] Determined from ¹H NMR of crude product. [c] Calculated by gravimetric method. [d] M_n (NMR) was calculated based NMR data. [e] Determined by GPC with THF as eluent and calibrated by polystyrene standard. [f] Initiator recycled from entry 2. [g] Initiator recycled from entry 6 neutralized by tricarballic acid.

copolymerization, could be supported on a purposely prepared polyelectrolyte-type polymer that would be easy to separate by simple filtration of the reaction medium. Instead of soluble organic ammonium salts, we thus turned to a polyelectrolyte carrying ammonium cations associated with hydroxide anions. Upon substituting the latter anions for carboxylate groups, we could thus fix on this polymer the initiating sites for the copolymerization of CO₂ and PO. As mentioned before, because of the insolubility of these polymeric salts in the organic phase, the separation can be easier, and achieved through filtration after neutralization of the copolymerization reaction. The synthesis of this polymeric initiator is shown in Scheme 3. Starting from commercially available PDMAC ($M_n < 100000$ g/mol) or obtained through Butler's cyclocopolymerization of diallyldimethylammonium chloride (DMAC),^[10d] chloride anions were completely exchanged for OH⁻ anions using an exchange resin to get PDMA-OH, which could directly serve as an initiator for the preparation of PPC diol, after substituting OH⁻ anions for succinate anions using succinic acid (PDMA-S, Figure S6); for the preparation PPC polytriols a triacid was used.^[9]

Scheme 3. Synthesis of polymeric initiator PDMA-S.

Our previous work demonstrated that the size of the cations matters and that smaller cations salts than TBA like lithium, sodium, tetramethyl, and tetraethylammonium yield polycarbonates with low carbonate content and low linear vs. cyclic selectivity.^[8] The polymerization behavior of PDMA-S with tetrahydropyrrole ring carrying two methyl groups was first tested under the copolymerization conditions established for TBAS (molar ratio of I/TEB = 1/3).^[9] The polymerization results are summarized in Table 2.

Entry 1 and 2 correspond to PPC diols initiated by PDMA-S where molar masses equal to 2000 and 4000 g/mol were targeted. The PPC diols obtained exhibited a carbonate content above 90% and a high linear vs. cyclic selectivity. The peak at 2.68 ppm in ¹H NMR (Figure 4a) corresponds to the succinate moiety and

MALDI-TOF (Figure S7-8) characterization results confirmed the incorporation of succinate moieties into the polycarbonate; the GPC analysis gave the expected molar masses with monomodal and narrow distributions (Figure 5).

Figure 4. a) ¹H NMR and b) ¹¹B NMR characterization result for crude PPC-diol (entry 2) in CDCl₃

These copolymerization results initiated by PDMA-S show that ammonium cations and their methyl and methylene groups that are part of the pyrrolidine rings behave similarly to the TBA cations during the copolymerization despite the low initial solubility of the polymeric initiator; we could observe that PDMA-S was very pure as all chloride anions could be exchanged in favor of hydroxyl and the succinate anions. Based on these results, the recycling of this support was tried. After neutralization/termination of the growing polycarbonate chains as described in the previous section, the PDMA-S spontaneously precipitated from the THF-rich reaction medium and could be collected just by centrifugation. As for TEB it could be isolated in the form of the TEB-nBA adduct as shows the peak at -3 ppm of ¹¹B NMR spectrum of the crude polymerization mixture (Figure 4b). The dried polymeric initiator was charged for the next run of copolymerization, the molar masses of the PPC diols isolated matched well with the expected values after several cycles (entry 3-5, Table 2), indicating the robustness of the process that could be repeated several times with a quantitative recovery and recycling of TEB and the polymeric support (Figure S9-11).

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Instead of neutralizing the reaction medium with succinic acid to regenerate the initiating sites supported by PDMA, we added one equivalent of tricarballic acid, to generate on the polymeric support trifunctional initiators which eventually afforded, after CO₂/PO copolymerization, a PPC-triol sample (entry 7, Table 2, Figure S12-14). We demonstrate here that the functionality of prepared PPC polyols can be easily switched upon selecting carboxylic acids of various functionality as neutralization agents for the same polymeric ammonium backbone/support.

Figure 5. GPC traces of Polycarbonate polyol samples initiated by PDMA-S from Table 2; PPC-diol-1 (entry 1), PPC-diol-2 (entry 2), PPC-diol-3 (entry 3), PPC-diol-4 (entry 4), PPC-diol-5 (entry 5), PPC-diol-6 (entry 6) and PPC-triol-1 (entry 7)

Conclusion

Polycarbonate diols/polyols appear as attractive and promising substitutes for conventional polyether polyols that are used in the polyurethane industry. They are degradable, provide better mechanical properties to the resulting polyurethanes, and can be manufactured in an economically efficient and environmentally friendly way, as evidenced in this study. Metal-free anionic approach for copolymerization of CO₂ with PO can indeed afford well-defined PPC diols and polyols with tunable carbonate content and functionality. We demonstrated that TEB and ammonium cations entering in the composition of the borate initiator could be simultaneously recycled with a quantitative recovery for the ammonium cations and >95% for TEB in a cost-effective way. On the other hand, a polymeric support carrying the same initiating sites as those utilized in homogeneous CO₂/PO copolymerizations was found to exhibit the same polymerization performance as soluble salts, the advantage over the latter lies in the very easy recycling of polymeric support. These two environment-friendly and clean processes that were described could be used for large scale PPC polyol production in industrial applications.

Experimental Section

All chemicals were purchased from Aldrich Chemicals and used as received unless otherwise mentioned. Propylene oxide was dried over CaH₂ and distilled under reduced pressure. Tetrahydrofuran (THF) was dried over sodium metal and distilled under reduced pressure. CO₂ (99.995%), purchased from Abdullah Hashim Industrial & Gas Co., was further purified by passing through a CO₂ purifier (VICI Co., US). All ¹H and ¹³C NMR and ¹¹B NMR spectra were recorded on a Bruker AVANCE III-400 Hz instrument. GPC traces were recorded against polystyrene standard by VISCOTEK VE2001 equipped with Styragel HR2 THF and Styragel HR4 columns using THF (1 mL/min) as eluent. MALDI-TOF MS experiments were carried out by using trans-2-[3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix in THF at a loading of 1:5 with sodium trifluoroacetate as an ionizing agent.

1. Preparation of PPC diol with simultaneous recycling of tetrabutylammonium initiator and TEB

1.1 Preparation of PPC diol

The polymerization experiments were carried out according to the reported procedure.^[9] After completion of the reaction, the work-up process was the one as shown in Scheme 2. The reactor was cooled, then the unreacted CO₂ was slowly released and the polymer solution was diluted with THF and stirred for 10 min. A mixture of succinic acid (39.4 mg, 0.33 mmol), *n*-butyl amine (0.12 mL, 1.2 mmol), and deionized water (0.120 mL, 6.66 mmol) was added to the reaction mixture and stirred for 10 min. The whole solution was precipitated using hexane and stirred vigorously. The organic layer was separated for the recycling of TEB. The polymer was precipitated using deionized water, and the crude product at the bottom was further washed with deionized water. After decanting, the polymer (PPC diol) was collected and dried in vacuum at 40 °C. The aqueous layers were merged to recycle soluble ditetrabutylammonium succinate in the next step.

1.2 Recycling of ditetrabutylammonium succinate

The collected aqueous layer was concentrated to be dryness and then further purified by lyophilization. The recovered tetrabutylammonium salts could be used into the next cycle of polymerization.

1.3 Recycling of TEB

The hexane layer obtained above was concentrated to remove hexane, THF, and excess *n*-butylamine. The residue containing TEB-butylamine adduct was dissolved in 0.5 mL of dry THF. To that formed solution was added tosyl isocyanate (0.150 mL, 1.0 mmol). Then this solution was subjected to distillation (40–80 °C) under static reduced pressure; to recover TEB completely from urea containing solution. Triethylborane, together with THF was collected, and the recycling yield found was 95% (using naphthalene as internal standard).

TEB-nBA: ¹H NMR (500MHz, CDCl₃): 2.55 (t, 2H), 1.45 (m, 2H), 1.32 (m, 2H), 0.89 (t, 3H), 0.64 (t, 9H), 0.08 (q, 6H). ¹¹B NMR (500MHz, CDCl₃): -2.81.

Recovered TEB: ¹H NMR (500MHz, CDCl₃): 1.21 (q, 6H), 0.97 (t, 9H). ¹¹B NMR (500MHz, CDCl₃): 86.

2. Synthesis of polymeric initiator PDMA-Succinate (PDMA-S)

2.1 Synthesis of PDMAC

A polymeric support was prepared according to the reported procedure with modification.^[10d] Into a 50 mL schlenk flask, a 65% aqueous solution of diallyldimethylammonium chloride (DMAC) (7.78 mL, 31.1 mmol) was transferred and diluted with 5 mL methanol. This solution was purged with argon by bubbling for 1h. Into another vial, AIBN (0.254 g, 1.5 mmol) was dissolved into 1 mL of methanol, purged by argon bubbling for 10 min, and then transferred to the above reaction mixture. The reaction was carried out for 5h by immersing Schlenk flask into a preheated oil bath at 80 °C. After completion of the reaction the viscous reaction mixture was diluted with methanol and precipitated using acetone. The precipitated polymer was collected, and dried under vacuum at 40 °C.

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2.2 Preparation of PDMA-OH

In a 250 mL round bottom flask containing an aqueous solution of 40 % wt. PDMAC equipped with a stir bar, an anion exchange resin, was added and stirred for 48h at 40 °C, allowing to exchange chloride ions of PDMAC for hydroxide anions PDMA-OH. The ion exchange resin was removed by filtration; water was removed by lyophilization to obtain dry PDMA-OH.

2.3 Preparation of PDMA-S

In a 100 ml round-bottomed flask, PDMA-OH (3g, 21.1 mmol) was dissolved in 20 mL of deionized water. Succinic acid (1.25 g, 10.5 mmol) was added to the above solution. The completion of the neutralization reaction was followed by the phenolphthalein indicator. Then the water was removed from the reaction mixture by lyophilization to obtain PDMA-S as a white powder, which was stored under argon.

3. Polymerization with simultaneous recycling of polymeric initiator and TEB

A reported polymerization procedure was followed with modification.^[9] For entry 6, a pre-dried 50 mL Parr reactor with a magnetic stirrer in an oven at 120 °C overnight, was placed into the glove box chamber. The reactor was cooled into the freezer, then PDMA-S (0.2g, 0.59 mmol succinate) was placed into the bottom of the reactor. Over this 1M solution of TEB in THF (1.76 mL, 1.76 mmol) was added and then stirred for 5 min; then propylene oxide (1.65 mL, 23.5 mmol) was quickly added, the reactor was sealed immediately, taken out from the glove box and charged with CO₂ to a pressure of 10 bar. The copolymerization was carried out at 50 °C for 14 hr., the reactor after completion of CO₂/PO copolymerization was cooled to room temperature, and CO₂ was released up to 1 bar. The reactor was transferred to the glove box and opened after the release of all CO₂. A small amount of THF was added to reduce the viscosity of the reaction mixture. A mixture of succinic acid (69.4 mg, 0.59 mmol), n-Butyl amine (0.218 mL, 2.1 mmol), and deionized water (0.59 mL, 5.9 mmol) was transferred to the reaction mixture and stirred for 10 min. The reactor was taken out of the glove box, and about 10 mL of THF was added, upon centrifugation of the collected reaction medium PDMA-S was isolated as a precipitate. This PDMA-S was washed again with THF, and then dried to get pure PDMA-S as an initiator. The collected THF fractions were concentrated and precipitated using 30 mL of hexane; the precipitated polymer was separated by centrifugation. The copolymer was collected and dried in a vacuum. The organic hexane fraction was evaporated under reduced pressure on a rotary evaporator to get TEB-butyl amine adduct. In an inert atmosphere, the dried TEB-butyl amine adduct was diluted with THF (0.5 mL), and tosyl isocyanate (0.27 mL, 1.76 mmol) was added and stirred for 10 min; after the complete reaction, the freed TEB along with THF was distilled under reduced pressure to get pure TEB for next cycle of polymerization.

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Keywords: Recycling • Tetrabutylammonium • Triethylborane • Polycarbonate polyol • Polymeric initiator

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Entry for the Table of Contents

Ready for Industrialization: A cost-effective and environmentally friendly process is developed for the recycle of triethyl borane and the tetrabutylammonium cation that both enter in the composition of the initiators for preparation of PPC diols/polys. In addition, a polymeric support which carry ammonium carboxylate salts along its chain could obtain same polymerization results as soluble salts but be easily recovered by simple filtration.