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# Tandem Metal-Coordination Copolymerization and Organocatalytic Ring-Opening Polymerization via Water To Synthesize Diblock Copolymers of Styrene Oxide/$CO_2$ and Lactide

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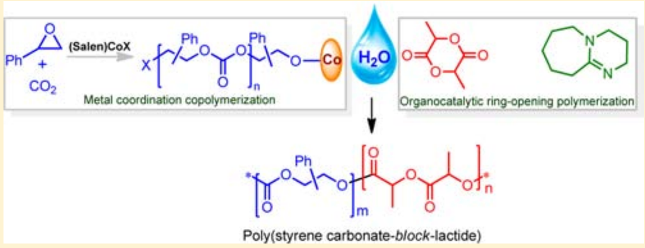
Ⓢ *Supporting Information*



**ABSTRACT:** Selective transformation of carbon dioxide and epoxides into degradable polycarbonates ($CO_2$-based copolymer) has been regarded as a most promising green polymerization process. Although tremendous progress has been made during the past decade, very few successful examples have been reported to synthesize well-defined block copolymers to expand the scope of these green copolymers. Herein, we report a tandem strategy combining two living polymerization techniques, salenCo(III)X-catalyzed styrene oxide SO/$CO_2$ copolymerization and ring-opening polymerization of lactide with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), for the synthesis of poly(styrene carbonate-*block*-lactide) copolymers. The key to the success of this tandem strategy is the judicious choice of water as the chain transfer and/or chain terminator reagent, which is added at the end of the salenCo(III)X-catalyzed SO/$CO_2$ copolymerization to in situ generate hydroxyl groups at the end of the polymer chains. The resulting polycarbonates with −OH end groups can thus be directly used as macroinitiators to subsequently initiate ring-opening polymerization of lactide to synthesize the diblock copolymers. Because of the living polymerization nature of both steps in this tandem strategy, we have demonstrated that the diblock copolymers synthesized possess well-defined structures with narrow molecular weight distributions and controllable lengths of both styrene carbonate and lactide blocks.

## ■ INTRODUCTION

The exclusive utilization of petroleum-based feedstocks for the synthesis of useful plastic materials will ultimately become an issue as the global oil supply is depleted. Hence, there is a need to pursue effective catalytic processes for the production of polymers from renewable resources.[1] One such process that incorporates the abundant, easy to transport/store, and nontoxic biorenewable carbon source, $CO_2$, is the production of degradable polycarbonates by the coupling of epoxides and $CO_2$. This process was first discovered by Inoue and co-workers in 1969[2] and is an alternative route to the polycondensation pathway involving the use of phosgene or its derivatives and diols.[3] This environmentally more benign approach for the synthesis of polycarbonates has received much attention recently by both industrial and academic researchers.[4] Importantly, some of these polycarbonates have been shown to be useful as ceramic binders, adhesives, coatings, and packaging materials, as well as in the synthesis of engineering thermoplastics and resins.[5] A wide variety of catalytic systems, both homogeneous and heterogeneous, have been developed for this transformation.[6] Although tremendous progress has been made over the past decade in suppressing ether linkages, increasing polymer selectivity, and controlling molecular weight for $CO_2$/epoxide copolymerization, further development of this green technology is needed to improve material performance as well as product type.[7] Hence, the synthesis of more diverse $CO_2$-based copolymers is an important and challenging theme for research and development.

A practical method for modifying the properties of manufactured plastics in order to meet specific needs is to link two or more distinct homopolymers through covalent bonds to provide di- or multiblock polymers.[8] On the basis of this methodology, two main strategies have been explored for the synthesis of block copolymers incorporating $CO_2$/epoxides and other monomers.[9] One synthetic method involves a polymer with a terminal initiating site that can be used as a chain transfer agent during the copolymerization of $CO_2$/epoxides to prepare block copolymers. On the basis of this method, the research groups of Lee and of Williams have synthesized some diblock and triblock copolymers.[10] An alternative approach involves the addition of a monomer that copolymerizes with epoxides at a much faster rate than $CO_2$. Accordingly, polyester-*block*-polycarbonate polymers have been prepared in a one-pot terpolymerization reaction of epoxides, cyclic acid anhydrides, and $CO_2$ using a variety of catalyst

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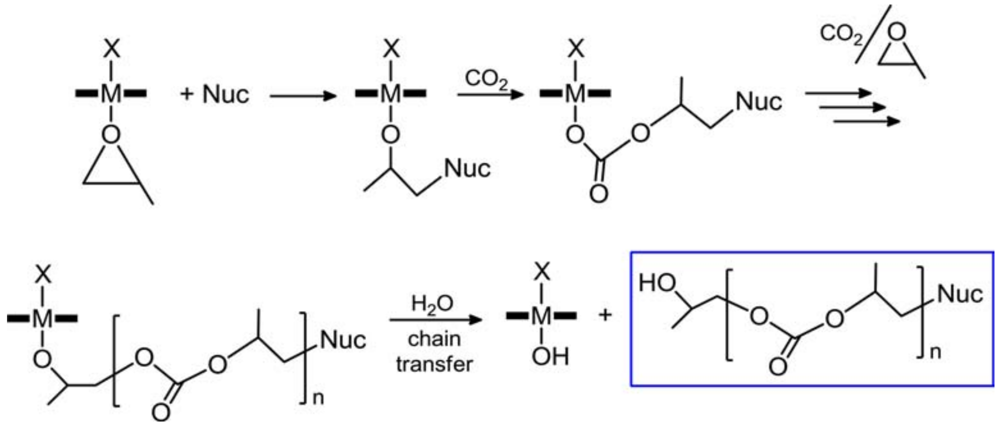
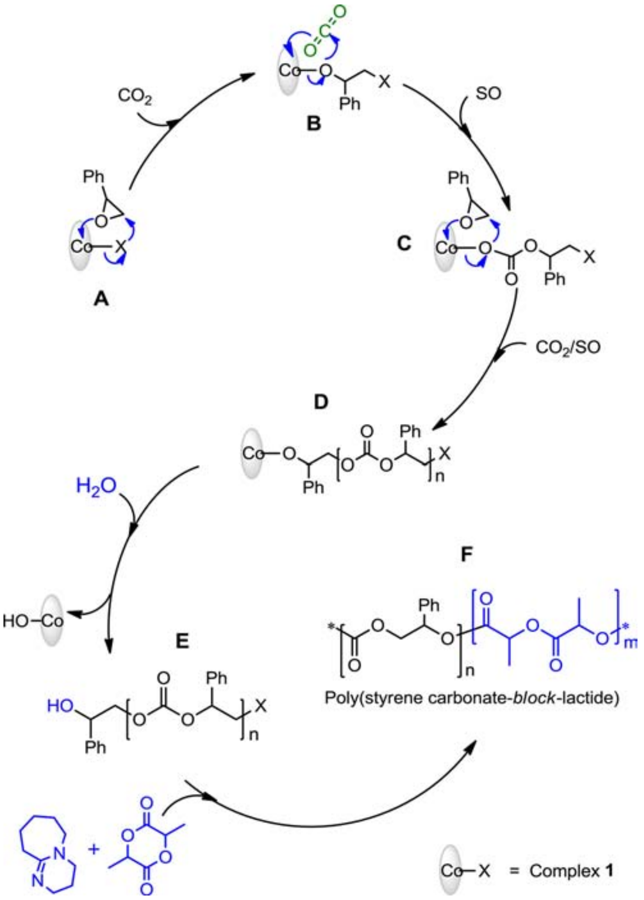
Scheme 1



systems.[11−13] Unfortunately, this strategy is particularly suitable for cyclic anhydride monomers, since few monomers are more reactive for copolymerization with epoxides than $CO_2$. For example, when lactone,[14] lactide,[15] or maleic anhydride[16] is introduced as the third monomer with epoxides and $CO_2$, polymers with random structures are generally produced. In addition, most of these processes involve high pressures of carbon dioxide and afford polymers with ether linkages and relatively broad molecular weight distributions.

Hence, there is a need for more facile and straightforward means for conveniently synthesizing block copolymers with controllable, narrowly distributed molecular weights. Herein, we have demonstrated a tandem catalytic approach for the synthesis of poly(styrene carbonate-*block*-lactide) by combining two living polymerization techniques, i.e., (salen)CoX-catalyzed styrene oxide/$CO_2$ copolymerization and organocatalytic lactide ring-opening polymerization. The key to this strategy is the utilization of $H_2O$ as a chain-transfer or chain-terminating agent that enables the direct synthesis of narrow molecular weight distributed poly(styrene carbonate) end-capped with a hydroxyl group. These hydroxyl end-capped poly(styrene carbonate)s serve as macroinitiators that allow direct chain extension via organocatalytic lactide ring-opening polymerization to obtain well-defined diblock copolymers.

Scheme 2



## ■ RESULTS AND DISCUSSION

The $CO_2$/epoxide copolymerization process catalyzed by bifunctional (salen)CoX or binary (salen)CoX/onium salt catalyst systems can be described by the series of steps summarized in Scheme 1. That is, chain propagation is initiated by ring-opening of the coordination/activation of epoxide by an external nucleophile to provide a metal−alkoxide intermediate that undergoes an insertion reaction with $CO_2$ to afford a metal−carbonate. Successive alternating incorporation of epoxide and carbon dioxide produces linear polycarbonates. In the presence of adventitious water rapid reversible chain transfer reactions can occur in which the anion of the growing polymer chain end is protonated by water to afford a copolymer with an −OH end group. Indeed, chain transfer by water has been observed in most systems catalyzed by (salen)MX/onium salt catalysts, resulting in a bimodal molecular weight distribution, where one copolymer has −X and −OH end groups and the second copolymer has two −OH end groups.[17] This particular role of water noted during numerous epoxide/$CO_2$ copolymerization processes inspired us to study the feasibility of incorporating this phenomenon in a tandem catalytic process to synthesize diblock copolymers.

Herein we propose to employ the tandem catalyst strategy illustrated in Scheme 2 to synthesize diblock copolymers of polycarbonates-*block*-polylactides. In recent publications we have presented results on the alternating copolymerization of $CO_2$ and styrene oxide using bifunctional cobalt-based catalysts as depicted in Figure 1, wherein a living polymerization process was observed.[18] Of importance, the isolated copolymers exhibited monomodal molecular weight distributions, which is quite different from the bimodal molecular weight distributions generally found in the copolymerization of $CO_2$ with other epoxides using these and closely related catalyst systems.

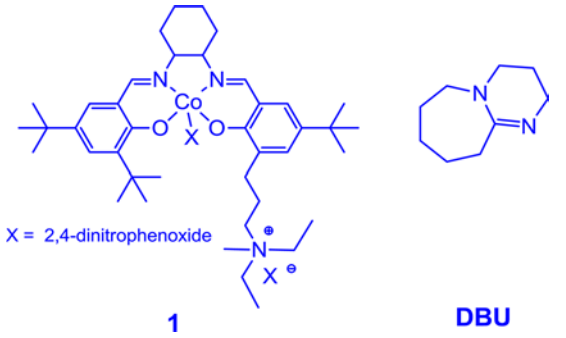


**Figure 1.** Complex **1** used for SO/$CO_2$ copolymerization and organocatalyst DBU for ROP of lactides.

Furthermore, mechanistic studies have shown that the use of these bifunctional cobalt(III) catalysts effectively suppress formation of cyclic carbonate byproducts, while increasing reaction rates as compared to their binary analogs.[19,20] Hence, the copolymerization of styrene oxide (SO) and $CO_2$ in the presence of complex **1** is the ideal process for the model study described in Scheme 2, since SO does not readily form poly(styrene carbonate) polyols. In addition, due to the efficacy of quinidine organocatalysts for the ring-opening polymerization of cyclic esters, ring-opening polymerization (ROP) of lactides with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU in Figure 1) was selected for the feasibility study outlined in Scheme 2.[21] These catalysts have been found to provide excellent control of molecular weight and polydispersity.

As indicated in Scheme 2, the first process involves the copolymerization of SO/$CO_2$ in the presence of complex **1**, where the process is initiated when the nucleophilic anion 2,4-dinitrophenoxide ring opens the styrene oxide to afford a cobalt alkoxide intermediate (**B**).[22] Rapid $CO_2$ insertion into the cobalt alkoxide occurs to provide the carboxylate species (**C**) with subsequent $CO_2$/SO enchainments to alternately yield the poly(styrene carbonate) (**D**). In a second process, upon complete consumption of styrene oxide, a carefully measured quantity of water was added to the reaction solution to in situ generate a hydroxyl group at the end of the copolymer chains to give **E**. The polycarbonate (**E**) facilitates the ring-opening polymerization of lactides in the presence of DBU to synthesize the diblock terpolymer (**F**) in one pot.

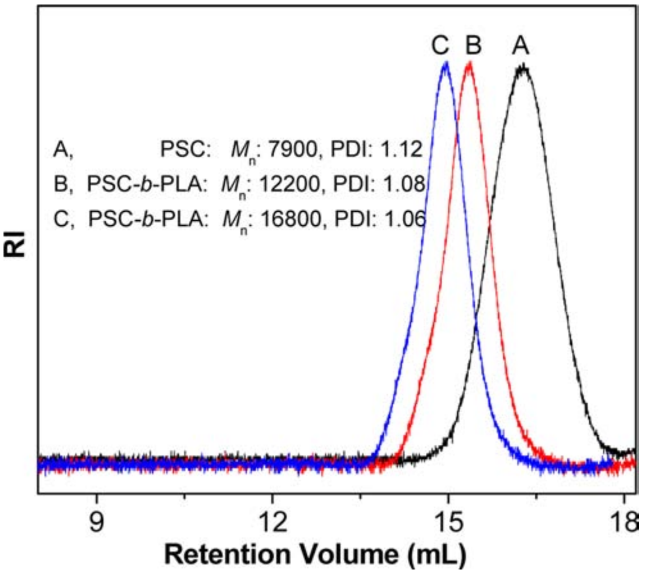


**Figure 2.** GPC analysis of hydroxy-functionalized PSC macroinitiator prepared by SO/$CO_2$ copolymerization (A, Table 1, entry 1) and PSC-*b*-PLA block copolymers (B, Table 1, entry 2; C, Table 1, entry 3).

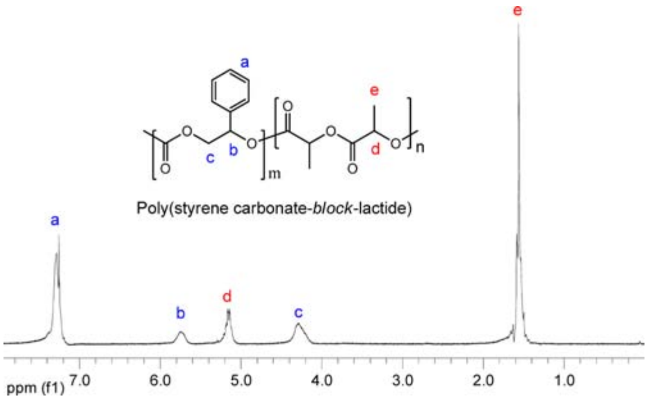


**Figure 3.** $^1H$ NMR spectroscopy of the obtained PSC-*b*-PLA in $CDCl_3$.

To demonstrate the feasibility of the pathways proposed in Scheme 2, the copolymerization of SO/$CO_2$ in the presence of

**Table 1. Tandem Metal-Coordination Styrene Oxide/$CO_2$ Copolymerization and Organocatalytic Ring-Opening Lactide Polymerization To Prepare Poly(styrene carbonate-*block*-lactide)[a]**

| | | Lactide | | | | | $M_n$ (g/mol) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | [SO]/**1** | mmol | stereo | *t* (h) | convn[b] (%) | PSC/PLA[b] (molar ratio) | theoretical | expl[c] | PDI[c] | $T_g/T_m$[d] (°C) | $\Delta H_m$[d] (J/g) |
| 1 | 100/1 | 0 | – | – | – | 1/0 | 8200 | 7900 | 1.12 | 80 | – |
| 2 | 100/1 | 1.5 | rac | 2 | 99 | 1/0.75 | 13600 | 12200 | 1.08 | 65 | – |
| 3 | 100/1 | 3.0 | rac | 6 | 95 | 1/1.42 | 18400 | 16800 | 1.06 | 60 | – |
| 4 | 200/1 | 1.5 | rac | 3 | 98 | 1/0.36 | 21600 | 19800 | 1.04 | 72 | – |
| 5 | 100/1 | 1.5 | D | 2 | 97 | 1/0.73 | 13400 | 12800 | 1.06 | 63/133 | 0.3 |
| 6 | 100/1 | 3.0 | D | 6 | 95 | 1/1.42 | 18400 | 17200 | 1.09 | 74/137 | 25.0 |

[a] Experimental procedure: Complex **1** (20 μmol), styrene oxide, and 1.0 mL of toluene/$CH_2Cl_2$ (1/1, volume ratio) were added into a 15 mL predried autoclave in a glovebox that was pressurized to 1.5 MPa $CO_2$. After 12 h, the $CO_2$ pressure was slowly released and a small amount of the resultant polymerization mixture was removed from the autoclave for $^1H$ NMR analysis, to determine the conversion of SO, the selectivity of polycarbonates to cyclic carbonate, the number of carbonate linkages, and also for GPC analysis. The results showed that the conversion of SO, polymer selectivity, and polycarbonates linkages were all >99%. One milliliter of $CH_2Cl_2$ containing 40 μmol of $H_2O$ was added to the reaction solution, and after 5 min, a certain amount of lactide and DBU (40 μmol) in 2 mL of $CH_2Cl_2$ was in situ added to prepare the diblock polymers. [b] Determined by $^1H$ NMR spectroscopy. [c] Measured values by GPC and $^1H$ NMR. [d] Determined by DSC.

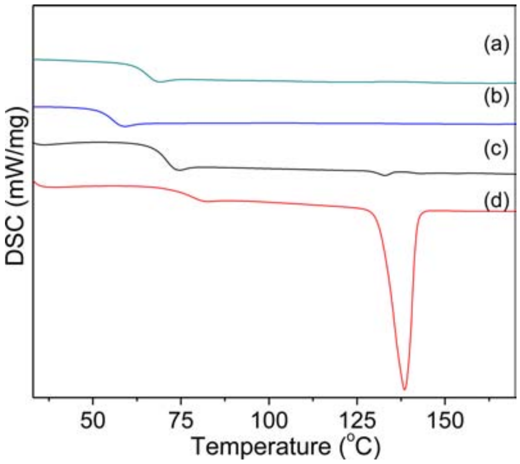


**Figure 4.** DSC thermograms for the set of PSC-*b*-PLA and PSC-*b*-PDLA copolymers synthesized in Table 1. (a) PSC:PLA = 1:0.75, (b) PSC:PLA = 1/1.42, (c) PSC:PDLA = 1:0.73, and (d) PSC:PDLA = 1/1.42. Samples from c and d were crystallized isothermally at 125 °C for 10 h; the second plot, 10 °C/min.

catalyst **1** (0.01 mol % loading) was carried out at 1.5 MPa $CO_2$ pressure and ambient temperature in toluene/$CH_2Cl_2$ (1/1 ratio by volume). The polymerization conversion reaction was performed for 12 h to ensure the quantitative conversion of styrene oxide. Upon releasing the excess $CO_2$, complete quenching of the polymer solution was achieved by injection of 2 equiv of water (relative to catalyst **1**). On the basis of NMR analysis of a small quantity of the resulting copolymer, it was clearly shown that the polymer selectivity and polycarbonate linkages were greater than 99%. The GPC analysis revealed a unimodal distribution of molecular weights with a $M_n$ value of 7900 g $mol^{-1}$ and PDI of 1.12 (Table 1, entry 1). The observed $M_n$ value is in excellent agreement with the theoretical value based on both phenoxide anions initiating chain growth. This is a consequence of chain transfer from adventitious water and the apparent inability of the resulting Co−OH unit to initiate the ring-opening of styrene oxide. It is noteworthy that if efforts are not made to carefully exclude water, no copolymerization of styrene oxide and $CO_2$ occurs; nevertheless, trace quantities of moisture are virtually impossible to eliminate. An analysis of the MALDI-TOF data provided only one series of signals with a regular interval of 164.1 *m*/*z* being observed, and each signal matches [183.3 (2,4-dinitrophenoxide) + (164.1 × *n*) (SO-*alt*-$CO_2$) + 164.1 (SO) + 1.0 (H) + 39.0 ($K^+$)]. See Figure S1 in Supporting Information. This experiment clearly indicated that the SO/$CO_2$ copolymerization was initiated by the 2,4-dinitrophenoxide anion from catalyst **1** and terminated by protolysis by the injected water, verifying the sequence **A**−**E** in Scheme 1.

In subsequent experiments following the removal of the polymer chain from the metal center by water, certain quantities of *rac*-lactide and DBU were added in situ into the reaction solution to prepare predesigned PSC-*b*-PLA diblock copolymers (Table 1, entries 2 and 3). The GPC traces of the resultant copolymers are shown in Figure 2, where it is apparent that an increase in reaction time and lactide loading leads to an increase in the copolymer's molecular weight. More importantly, the copolymers display monomodal weight distributions with very narrow PDI values (<1.10), demonstrating the successful chain extension from the chain end of poly(styrene carbonate) to afford the predesigned PSC-*b*-PLA diblock copolymer. The structure of the diblock copolymer is readily revealed by $^1H$ NMR spectroscopy. That is, as illustrated in Figure 3, the blocks derived from SO/$CO_2$ copolymerization (resonance at 5.8 ppm) and from lactides ROP (resonance at 5.2 ppm) are clearly seen. By altering the quantities of SO and lactides, the molecular weight and composition of the corresponding polymer chains can be easily adjusted and controlled (Table 1, entries 2−4). In addition, using D-lactide (D-LA) as the substrate (Table 1, entries 5 and 6) PSC-*b*-PDLA diblock copolymers were produced of varying molecular weight and composition. Meanwhile, the very narrow PDI values after chain extension and the carbonyl region of $^{13}C$ NMR spectra of the obtained PSC-block-PDLA at 169.5 ppm (Figure S2, in Supporting Information) both showed that little transesterification had occurred in the reaction.

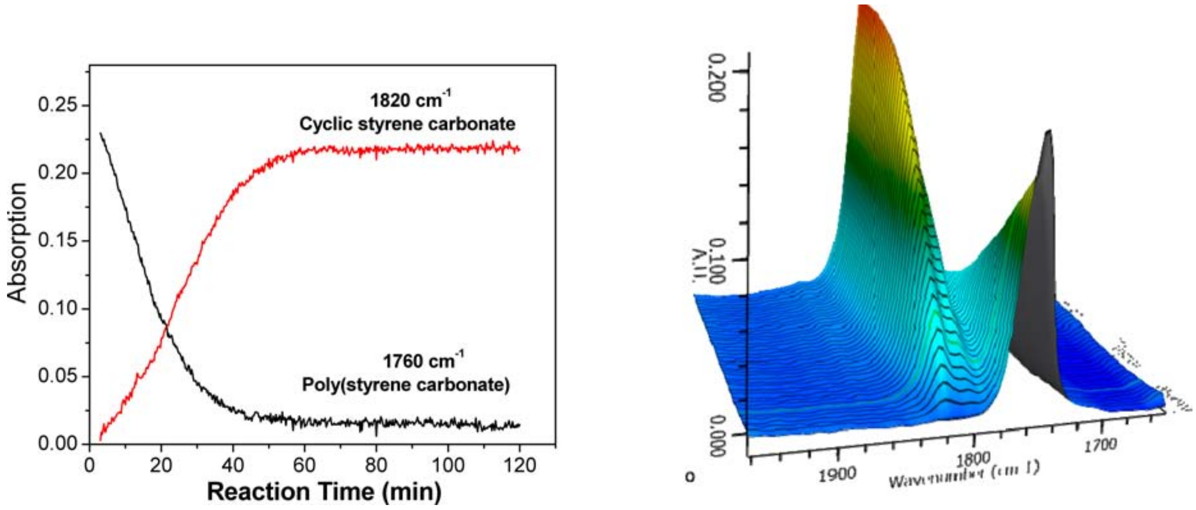
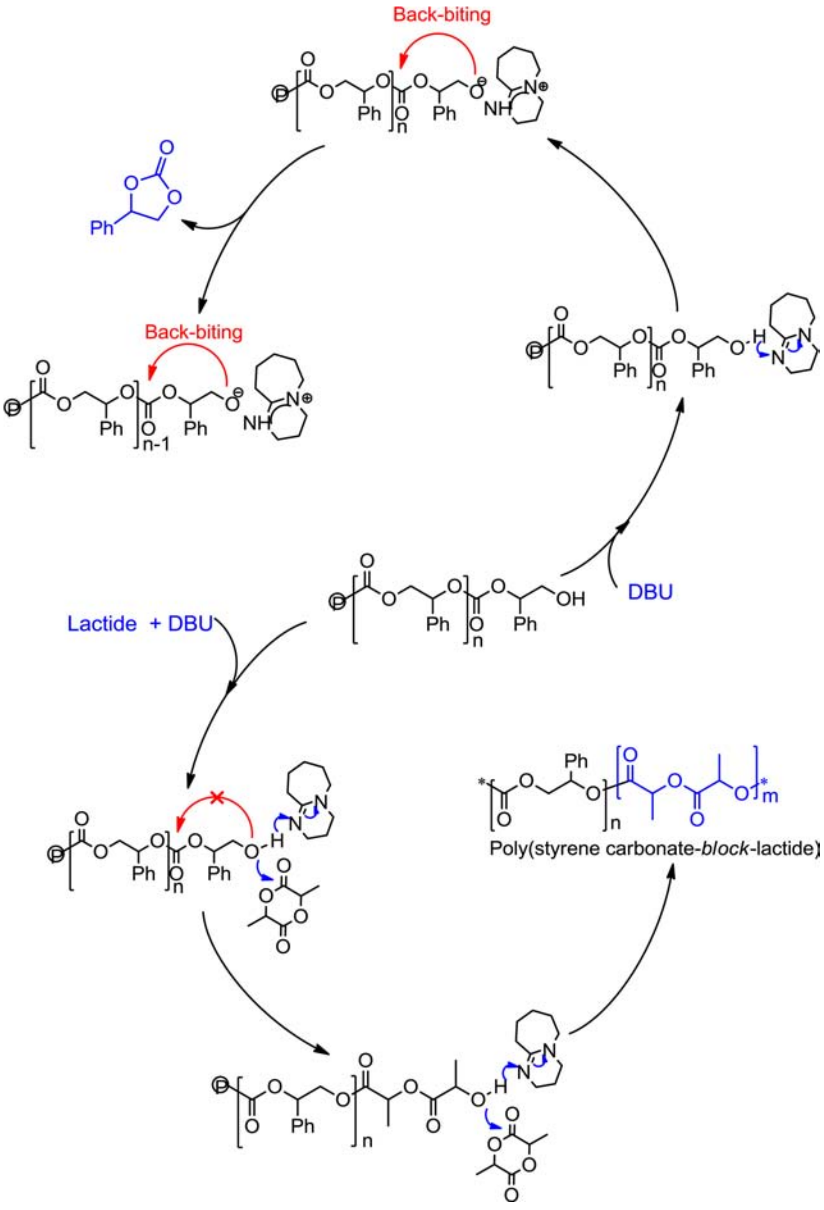


**Figure 5.** Reaction profile and the resulting three-dimensional stack plot of the IR spectra collected every 15 s during the decomposition of PSC ($M_n$ = 7900, PDI = 1.12) end-capped with −OH groups in the presence of DBU. Reaction conditions: 158 mg of PSC, 3.04 mg of DBU, PSC−OH/DBU = 1/1 (mole ratio), 3 mL of $CH_2Cl_2$, ambient temperature. Deconvolution was performed by ReactIR ic10 software; 1760 $cm^{-1}$ is the absorbance of the carbonyl group from PSC and 1820 $cm^{-1}$ is the absorbance of cyclic styrene carbonate.

**Scheme 3**



The thermal properties of the resulting diblock copolymers listed in Table 1 were determined by DSC. With the introduction of the LA block, a gradual decrease in the $T_g$ of the block copolymers was observed (Figure 4a,b). Only one glass transition temperature was observed for these PSC-*b*-PLA copolymers, indicating excellent compatibility between the PSC and PLA blocks. Curves c and d display the DSC thermograms of the two sets of block copolymers containing different lengths of the D-LA blocks. The block copolymer with the shorter D-LA block (PSC/PDLA = 1/0.73, c) exhibited a very small melting enthalpy at 133 °C with $\Delta H_m$ = 0.32 J/g and a $T_g$ at 63 °C. With the introduction of the D-LA block of increased length (PSC/PDLA = 1/1.42, d), a higher $T_g$ (74 °C) for the block copolymers and higher melting enthalpy at 137 °C with $\Delta H_m$ = 25.0 J/g was noted under the same crystallization conditions.

In order to directly monitor the synthesis of the LA block from the end hydroxyl group of PSC, we utilized in situ infrared spectroscopy. Initially, we were interested in the stability of PSC in the presence of the strong base DBU (p$K_a$ DBUH$^+$ = 24.3).[23] As shown in Figure 5, the absorbance at 1760 cm$^{-1}$ due to poly(styrene carbonate) decreases gradually, while the absorbance at 1820 cm$^{-1}$ due to styrene carbonate increases with time. Over a 1 h reaction period at ambient temperature PSC completely depolymerizes to cyclic styrene carbonate in the presence of DBU. The top catalytic cycle in Scheme 3 accounts for this depolymerization pathway in which the deprotonated hydroxyl chain end backbites upon itself to produce cyclic carbonate. A more detailed account of this backbiting mechanism for the depolymerization of poly(styrene carbonate) and other aliphatic polycarbonates has been published elsewhere.[24]

By way of contrast, Figure 6 represents the three-dimensional plot of the ring-opening polymerization of lactides initiated by PSC end-capped with a hydroxyl group in the presence of DBU. Except for the addition of the lactides monomer, all the reaction conditions are identical to those employed in Figure 5. From the infrared spectra shown in Figure 6, it is apparent that the carbonyl absorbance at 1771 cm$^{-1}$ for lactides gradually

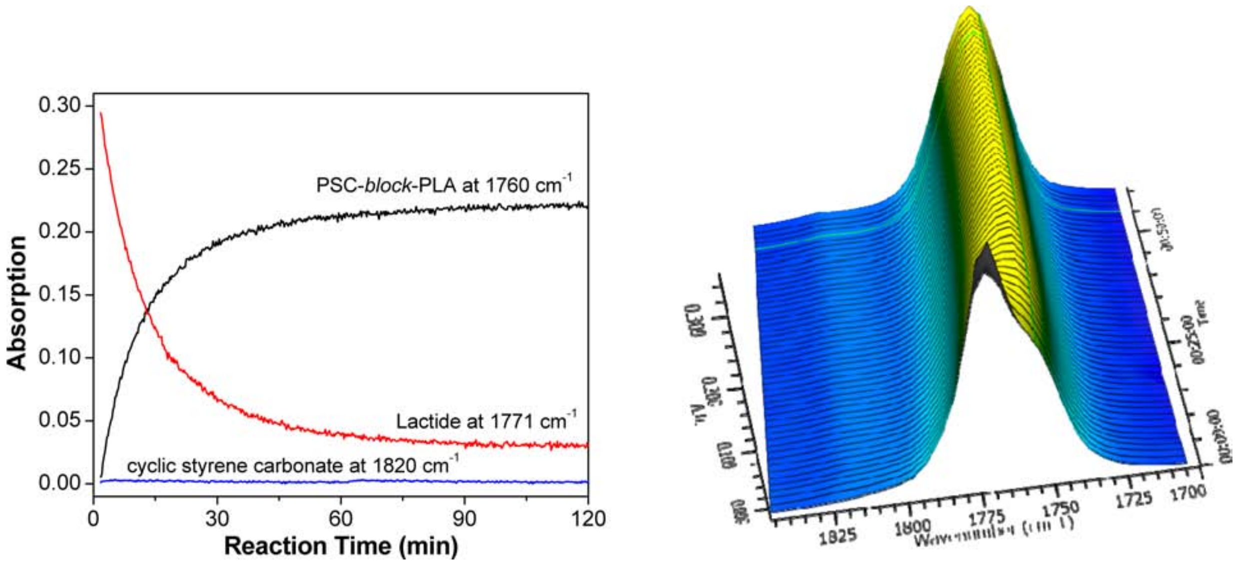


**Figure 6.** Reaction profile and the resulting three-dimensional stack plot of the IR spectra collected every 15 s during the ring-opening polymerization from the end-capped −OH of the PSC chain ($M_n$ = 7900, PDI = 1.12) in the presence of DBU. Reaction conditions: 158 mg of PSC, 3.04 mg of DBU, LA = 144 mg, PSC−OH/DBU = 1/1/50 (mole ratio), 3 mL of $CH_2Cl_2$, ambient temperature. Deconvolution was performed by ReactIR ic10 software; 1771 cm$^{-1}$ is the absorbance of the carbonyl group from lactide, and 1760 cm$^{-1}$ is the absorbance of the carbonyl groups from the resulting block copolymer.

decreases with a concomitant increase in the carbonyl absorbance at 1760 cm$^{-1}$ due to the diblock copolymer. Importantly, an absorbance at 1820 cm$^{-1}$ for styrene carbonate did not grow during this process, indicative of PSC being stabilized in the presence of 1 equiv of DBU and excess lactides monomer.

On the basis of the above observations, the catalytic cycle for the ROP of lactides catalyzed by DBU is depicted in the bottom portion of Scheme 3. Hence, in the presence of lactide substrate the deprotonated poly(styrene carbonate) chain initiates the ring-opening polymerization of lactide in preference to backbiting upon itself to produce styrene carbonate. This is probably a consequence of the lactide molecule possessing increased ring strain resulting from the presence of two ester moieties in a planar conformation, thereby making its carbonyl group more prone to nucleophilic attack than an adjacent carbonyl group on the PSC chain.[25] Thus, the capping of the poly(styrene carbonate) chain end by the ring-opening of the first lactide molecule stabilizes it toward depolymerization. This stabilizing effect was also observed upon end-capping the −OH chain end of PSC with an acetate group.[24]

## ■ CONCLUSIONS

We have demonstrated herein a novel in situ tandem catalytic strategy combining (salen)CoX-catalyzed SO/$CO_2$ copolymerization followed by DBU-initiated ring-opening polymerization of lactide to synthesize in one pot well-defined poly(styrene carbonate-*block*-lactide) copolymers. This approach is enabled by the judicious choice of water as a chain-terminating reagent, which when added at the end of the metal-catalyzed SO/$CO_2$ copolymerization process generates in situ the hydroxyl end group of the polymer chain. This −OH-terminated poly(styrene carbonate) in the presence of the organocatalyst, DBU, serves as a macroinitiator for subsequent ring-opening polymerization of lactide. Although other protic sources could be added at the end of the copolymerization process to further quench the reaction, e.g., the careful addition of benzoic acid, water is a renewable reagent. The addition of alcohols on the other hand could themselves initiate polymerization of lactide and prevent diblock polymer formation. Using this strategy, successful chain extension was achieved, and block copolymers having narrow polydispersities (<1.10) and lactide blocks of controllable lengths were conveniently prepared. The mild reaction conditions for the polymerization processes may make it possible to synthesize other $CO_2$-based functional copolymers to expand the scope of applications of these green copolymers. Such studies are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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