Oxygen Triggered Switchable Polymerization for One-Pot Synthesis of CO2-Based Block Copolymers from Monomer Mixtures

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RESEARCH ARTICLE

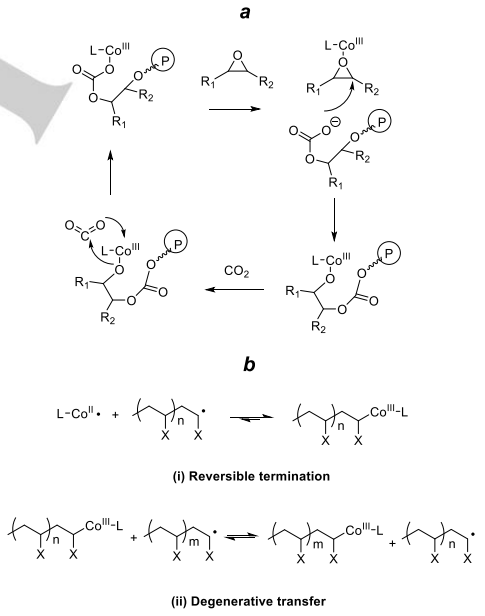
Oxygen Triggered Switchable Polymerization for One-Pot Synthesis of CO_2-Based Block Copolymers from Monomer Mixtures

Yajun Zhao, [a] Yong Wang,* [a] Xingping Zhou, [a] Zhigang Xue, [a] Xianhong Wang, [b] Xiaolin Xie[a] and Rinaldo Poli[c]

Abstract: Switchable polymerization affords a unique opportunity to regulate polymer sequence and structure in a one-pot process from mixtures of monomers. Here we report a strategy that uses O_2 as an external stimulus to switch the polymerization mechanism from the organometallic mediated radical polymerization (OMRP) of vinyl monomers mediated by (Salen)Co^{III}-R [Salen=*N,N'*-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine; R = alkyl] to the ring-opening copolymerization (ROCOP) of CO_2/epoxides. A critical issue is the unprecedented mono oxygen insertion into the Co-C bond, as demonstrated by experimental results and rationalized by DFT calculations, leading to the formation of (Salen)Co^{III}-O-R as an active species to initiate ROCOP. Diblock poly(vinyl acetate)-*b*-polycarbonate could be obtained from ROCOP of CO_2/epoxides with preactivation of (Salen)Co end-capped poly(vinyl acetate). Furthermore, a poly(vinyl acetate)-*b*-poly(methyl acrylate)-*b*-polycarbonate triblock copolymer has been successfully synthesized via a (Salen)cobalt-mediated sequential polymerization with an O_2-triggered switch in a one-pot process.

Introduction

In nature, feedback loops and a variety of trigger-induced effects endow enzymes with necessary temporal and spatial control to ensure highly-ordered biological activities through extremely complex catalytic processes.[1] Such smart activities have evolved into an intriguing design principle for catalysis systems to simplify the procedures for obtaining a high degree of structural complexities.[2] Specifically, switchable catalysts that display different polymerization activities in response to stimuli provide a unique opportunity to regulate polymer sequence and architecture from mixtures of monomers for fine tuning the material properties at the molecular scale.[3] Typically, modulating the polymerization activity of a known catalyst is achieved by incorporation of stimulus-responsive functional group into the ligand as well as by direct alternation of the oxidation state of the metal center.[4] For example, Diaconescu pioneered a redox switch that allowed the one-pot synthesis of polylactide-*b*-polycaprolactone.[5] Byers demonstrated that controlling the oxidation state of Fe catalysts by redox or electrochemical triggers enabled the facile discrimination of lactide and epoxide in the ring-opening polymerization (ROP).[6] Long and coworkers have successfully tailored the polyethylene branching via a redox switch.[7] Recently, Williams and Rieger achieved switchable ROCOP of CO_2/anhydrides/epoxides and ROP of cyclic esters by controlling the chemistry of metal-chain end-group, demonstrating the possibility to switch the reactivity of a single-site catalyst between different polymerization mechanisms [8] However, the limitation is that ROP and ROCOP share the metal-alkoxide active species.



Scheme 1. Mechanistic aspects for ROCOP and OMRP mediated by (Salen)Co complex. **a** Chain propagation process for cobalt(III) complex mediated ROCOP of CO_2/epoxides. **b** Reversible termination (RT) and degenerative transfer (DT) mechanisms occurring in cobalt(II)/cobalt(III) complex mediated OMRP.

Derived from the ROCOP of CO_2/epoxides, CO_2-based polycarbonates have been drawing increasing attention owing to their biodegradable and biocompatible properties as well as to the stringent demand for CO_2 utilization and sustainable chemistry.[9] Although CO_2-based polycarbonates may suffer from poor mechanical/thermal properties and limited functionalities, the living nature of ROCOP in the presence of various metal complexes enables the facile synthesis of CO_2-based block copolymers as a possible solution.[10] Current achievements have been mainly focused on the sequential addition of epoxide

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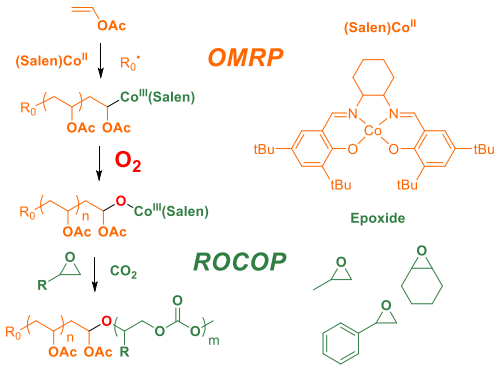
monomers to afford polycarbonate-*b*-polycarbonate or on the preparation of polyester-*b*-polycarbonate by combining the ROCOP of CO_2/epoxides and the ROP of cyclic esters.[8] However, the possibility to switch polymerization mechanism gives access to block copolymers with mechanistically incompatible monomers, therefore providing facile access to a wider array of high-value-added nanomaterials with attractive phase separation behavior.[11] To address this, we have recently reported a one-step route to CO_2-based block copolymers with tailorable functionalities and compositions by concurrent RAFT polymerization of conjugated vinyl monomers and ROCOP of CO_2/epoxides using a bifunctional chain transfer approach.[12] Yet, new methods need to be developed to further expand the structural diversity of CO_2-based block copolymers.



Scheme 2. O_2-triggerd switch from cobalt mediated OMRP to ROCOP for the synthesis of CO_2-based diblock copolymers.

Among all the effective catalysts for ROCOP, (Salen)Co^{III}X (X = Cl, OAc etc.) complexes, first employed by Coates, have displayed the most ideal activities, wherein the reversible formation and dissociation of polar Co-O bonds are crucial for the chain propagation process (Scheme 1a).[13] Relative to Co-O bonds, Co-C bonds are less polar and tend to break homolytically, which is key to various enzymatic reactions mediated by vitamin B_{12}.[14] Recently, cobalt complexes have allowed the well-controlled organometallic mediated radical polymerization (OMRP) of challenging non-conjugated monomers such as vinyl acetate (VAc),[15] vinyl chloride,[16] N-vinyl amides[17] and vinylidene fluoride (VDF)[18] (Scheme 1b). In particular, the radical polymerization of VAc was shown to be well-controlled also when mediated by the (Salen)Co^{II} system through a degenerative transfer mechanism with AIBN initiation at 60 °C, leading to the generation of (Salen)Co^{III}-PVAc as dormant species.[19] Herein, we report the switch of polymerization mechanism from OMRP to ROCOP using O_2 as a trigger and cobalt Salen complexes as mediators (Scheme 2). Key to this protocol is the unprecedented mono oxygen insertion into Co^{III}-C bonds, which generates (Salen)Co^{III}-O-R as an active species for the ROCOP of CO_2/epoxides.

Results and Discussion

The first step of the polymer synthesis consisted of the OMRP of VAc mediated by (Salen)Co^{II}, with initiation by AIBN at 60 °C in bulk, following the protocol of Peng et al.[20] The only difference consisted in running the polymerization in an autoclave rather than in regular glassware, in order to facilitate the one-pot switch to the ROCOP step, which requires work under CO_2 pressure. This also allowed the reaction to occur under exclusion of light.[21] Various (Salen)Co^{III}-PVAc products were obtained under different conditions (Table 1), confirming the results reported by Peng *et al.* and also demonstrating the purely thermal nature of this OMRP system. Indeed, comparative experiments conducted in ampules without protection from light displayed faster polymerization rates but inferior control (Table 1, entries 3-6). Moreover, higher AIBN loading significantly accelerated the polymerization but gave products with broader molecular weight distributions. An [AIBN]/[Co^{II}] ratio of 7/1 could well balance the efficiency and polymerization control (Figures S1-S2). The kinetic plots for the OMRP displayed good linearity and an initiation period of 310 min, which is typical for this system.[20] Also, repeat experiments showed excellent reproducibility. Electrospray ionization (ESI) mass analysis of low molecular weight (Salen)Co^{III}-PVAc (M_n = 2.1 kDa, $Đ$ = 1.05) was performed in methanol, wherein two main series of signals were observed in accordance with $[CN(CH_3)_2C(VAc)_n]Na^+$ and $[CN(CH_3)_2C(VAc)_n]H^+$, respectively (Figure. 1a). This suggests that the cyanoisopropyl radical generated from AIBN [$^{\bullet}C(CH_3)_2CN$] predominantly adds to VAc and generates (Salen)Co^{III}-$(VAc)_n$-$C(CH_3)_2CN$ dormant species (Figure 2). In this respect, this controlling system differs from (TMP)Co^{II} (TMP = tetramesityl porphyrin), which was shown by Wayland *et al.* to abstract a β-H atom from $^{\bullet}C(CH_3)_2CN$ and ultimately generate the (TMP)Co^{III}-$(VAc)_n$-H dormant species.[22]

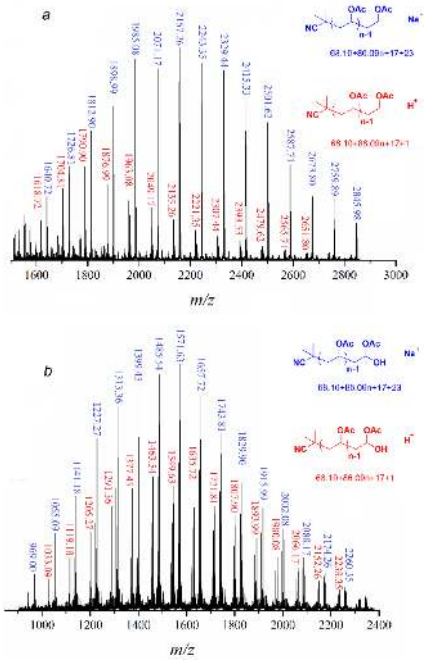


Figure 1. Polymer chain end group analysis using ESI spectra. **a** (Salen)Co^{III}-PVAc ($M_{n,GPC}$=2.1 kDa, $Đ$=1.05). **b** The acidolysis product of (Salen)Co^{III}-PVAc ($M_{n,GPC}$=1.8 kDa, $Đ$=1.07) in the presence of 3.0 MPa O_2 and acetic acid.

Table 1. Polymerization of VAc mediated by (Salen)Co^{II} in bulk under different conditions.[a]

Entry	[AIBN]/[Co]	Time (min)	Conv.[b] (%)[b]	$M_{n,GPC}$ (kDa)[c]	$M_{n,NMR}$ (kDa)[d]	$Đ$[c]
1	5/1	600	34	15.3	14.7	1.06
2	10/1	120	20	9.9	8.6	1.35
3[e]	7/1	300	16	9.5	6.9	1.13
4[e]	7/1	360	29	17.5	12.3	1.11
5	7/1	360	4	1.8	1.9	1.07
6	7/1	365	5	2.1	2.3	1.05
7[f]	7/1	395	15	5.6	5.5	1.06
8[f]	7/1	430	25	10.5	10.2	1.07
9	7/1	500	38	16.1	15.7	1.14

[a]Reaction conditions: 60 °C in 5 mL VAc with [Co]/[VAc]=1/500. [b]Conversion values detected by ^{1}H NMR. [c]Determined by gel permeation chromatography (GPC) with polystyrene as standard. [d] Number-average molar mass calculated from ^{1}H NMR spectra. [e]Comparative reactions carried out in ampule, which was exposed to natural light. [f]Conducted in 20 mL VAc with [Co]/[VAc]=1/500.

To switch from the VAc OMRP to the CO_2/epoxide ROCOP, a selective transformation of (Salen)Co^{III}-PVAc into (Salen)Co^{III}-O-PVAc is needed. Although the ROCOP process catalyzed by an alkoxide derivative of cobalt(III) appears unprecedented, metal alkoxide complexes (L-M-OR) are generally regarded as the active species when the reaction is initiated by related L-M-X complexes (X = halides or carboxylic groups),[13b, 23] which are preferred precatalysts given their lower tendency to decompose by hydrolysis. During the initiation periods, nucleophilic attack by X facilitates the ring-opening of an epoxide and results in the L-M-OR active species.

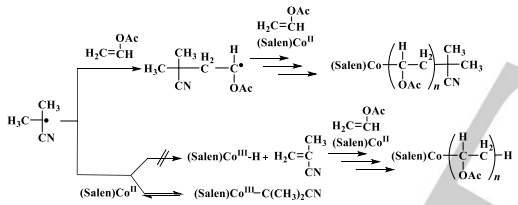


Figure 2. Plausible pathway for PVAc with cyanoisopropyl chain end group. Reactions of the cyanoisopropyl radical with (Salen)Co^{II} and VAc.

Therefore, we have investigated the reaction of the (Salen)Co^{III}-PVAc product of the (Salen)Co^{II}-mediated VAc polymerization (M_n = 16.1 kDa, $Đ$ = 1.09) with O_2 under different conditions. An initial study with O_2 bubbling at atmospheric pressure in the presence of acetic acid (HOAc) yielded a colorless polymer by precipitation in hexane, confirmed to be PVAc by ^{1}H NMR spectroscopy (Figure S4). The FT-IR investigation of this polymer revealed a broad absorption band around 3400 cm^{-1}, indicative of the substitution of the cobalt chain-end by an OH group (Figure S5). This conclusion was confirmed by the ESI-MS spectrum (Figure 1b), which exhibited two main series of signals in accordance with $[CN(CH_3)_2C(VAc)_nOH]Na^+$ and $[CN(CH_3)_2C(VAc)_nOH]H^+$. This result suggests the predominance of oxidation over acidolysis, because the latter should yield PVAc-H. On the basis of the known aptitude of (Salen)Co^{III}-OR to be readily hydrolyzed by protonic reagents to yield ROH,[24] we propose that the observed PVAc-OH results from the acidolysis of a (Salen)Co^{III}-O-PVAc intermediate by HOAc, with the concomitant formation of (Salen)Co^{III}-OAc (Figures S6-S7). Moreover, the GPC curve of the polymer exhibited a bimodal distribution with a main component at 14.9 kDa and a minor one at 31.2 kDa (Figure 3a). Given the monomodal distribution and low $Đ$ of the original (Salen)Co^{III}-PVAc, we reasoned that a side process involving some kind of irreversible radical coupling might have occurred. A comparative reaction, carried out in the autoclave under 3.0 MPa O_2, yielded a chemically similar polymer, except that the GPC curve displayed this time a monomodal distribution ($Đ$ = 1.15) (Figure 3b). The radical nature of this reaction is indicated by an experiment run in the presence of TEMPO [2,2,6,6-tetramethylpiperidine-1-oxyl], leading only to the generation of (Salen)Co^{II} (Figure S10) and TEMPO-capped PVAc (Figure S11). Thus, the reaction appears to take place by initial Co^{III}-C bond cleavage to produce (Salen)Co^{II} and PVAc• intermediates.

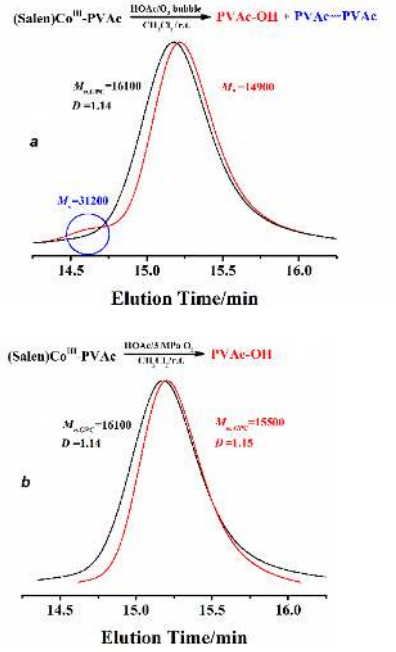


Figure 3. GPC curves of (Salen)Co^{III}-PVAc ($M_{n,GPC}$ = 16.1 kDa, $Đ$ = 1.14) (black) and of the corresponding oxidation/acidolysis product (red). **a** Comparison of (Salen)Co^{III}-PVA and the acidolysis product obtained with O_2 bubbling at atmospheric pressure. **b** Comparison of (Salen)Co^{III}-PVA and the acidolysis product obtained under a high O_2 pressure (3.0 MPa).

Furthermore, an isotopic labeling experiment was conducted by reaction of (Salen)Co^{III}-PVAc with $^{18}O_2$ in the presence of HOAc. In this case, the hydrolysis product was confirmed as PVAc-^{18}OH according to the ESI-MS spectrum (Figure S12), suggesting that the single O inserted into the Co-C bonds comes from O_2 instead of other reagents.

On the basis of the above results, the two following points are worthy of note: (i) the unexpected insertion of a single O atom between Co and the polymer chain upon oxidation with O_2; (ii) the increase of selectivity, relative to the chain-chain coupling side products, upon increasing the O_2 pressure. In previous investigations of alkylcobalt(III) oxidation, using a variety of ligands such as porphyrins,[25] dimethylglyoximates,[26] and other substituted glyoximates,[27] alkylperoxocobalt(III) derivatives were generated via a radical mechanism that consists of three steps (Scheme 3): homolytic cleavage Eq. (1), dioxygen addition to the alkyl radical to generate a peroxyl radical Eq. (2) and radical recombination Eq. (3). A few of these alkylperoxo derivatives,[25b, 27b] as well as others made by other methods,[28] have been isolated and structurally characterized. To the best of our knowledge, the insertion of a single O atom from O_2 into a Co^{III}-C bond or the rearrangement of a Co^{III}-OOR derivative into the corresponding Co^{III}-OR system is unprecedented.

$$LCo^{III}\text{-}R \longrightarrow LCo^{II} + R\bullet \quad (1)$$
$$R\bullet + O_2 \longrightarrow ROO\bullet \quad (2)$$
$$LCo^{II} + ROO\bullet \longrightarrow LCo^{III}\text{-}OOR \quad (3)$$

Scheme 3. Mechanistic aspects referring to the formation of LCo^{III}-OOR via dioxygen insertion into Co-C bonds.

In order to throw light onto the above two points, a DFT investigation was carried out using the short alkyl group -CH(Me)OCOMe as model for the PVAc chain (see the computational details in the SI). The results are shown in Figure 4 with the changes of each individual steps shown as ΔG° at 60 °C in kcal/mol. Energy profiles for the entire transformation at 25 and 60 °C are available in the SI. The starting point of the investigation is the structure of (Salen)Co^{III}-CH(Me)OCOMe and the sequence of Eq (1), (2) and (3) in Scheme 3. The starting complex is diamagnetic with a square pyramidal geometry, as experimentally found in several (Salen)Co^{III}X derivatives, e.g. with X = Cl, Br or I,[29] O-3,5-$C_6H_3F_2$,[30] COOMe,[19b] C(=CH_2)CH=CH_2,[31] and CONHR (R = CH(Me)Cy, CH_2C≡CH, CH_2-2-C_4H_3O).[32] Chelation by the acetate carbonyl group, to yield a 6-coordinated isomer is endoergic, contrary to what was found for the bis(acetylacetonate) analogue, $(acac)_2Co^{III}$-CH(Me)-OCOMe.[33] This is probably related to the cost of rearranging the Salen ligand to a non-planar coordination environment. The homolytic Co^{III}-C bond dissociation is 26.2 kcal/mol at 25 °C and 24.2 kcal/mol at 60 °C. Processes resulting in bond cleavage without spin state change (the antiparallel combination of the two S = ½ products yields an overall S = 0 system) have no electronic barrier for the reverse recombination process and may only have a small steric barrier related to the need to reorganize the metal coordination sphere. This was computationally verified for other similar metal-alkyl systems.[34] Therefore, the thermodynamic bond strength can be considered a reasonable lower limit approximation of the kinetic activation barrier. This bond strength is much greater than that of $(acac)_2$Co-CH(Me)OCOMe (recalculated as 9.2 kcal/mol at 25 °C at the same level of theory), in agreement with a more difficult polymerization by reversible termination for the (Salen)Co system. Using the Eyring equation and the bond strength at 60 °C as an approximation of the activation barrier yields a rate of homolytic bond cleavage of 3.4 h^{-1} and a half-life of 0.2 h (12 min). The O_2 addition to the alkyl radical to generate •OOCH(Me)OCOMe (Figure 4 Eq. (2)) is exoergic as expected and can be considered quantitative in the presence of a high O_2 concentration. The O_2 addition to (Salen)Co^{II}, on the other hand, is slightly endoergic, whether the adduct is calculated as a doublet or as a quartet. Trapping of the resulting alkylperoxyl radical by (Salen)Co^{II} (Figure 4 Eq. (3)) is also exoergic, but only by 10.8 kcal/mol (9.0 at 60 °C). This O-based radical trapping is another example of bond formation by antiparallel combination of two S = ½ products with no electronic barrier. Thus, the formation of the (Salen)Co^{III}-OOCH(Me)-OCOMe derivative is not an irreversible process under the experimental conditions used for the oxidation. Note that an alternative process for the alkyl radicals generated by Eq (1) is dimerization (Figure 4 Eq. (4)), which is a model for PVAc• termination by the combination. This process is calculated as thermodynamically very favorable (irreversible), more than the O_2 addition. Hence, this process may occur at low [O_2], whereas Eq. (2) prevails over Eq. (4) at high [O_2]. Dimerization by Eq. (4) (Figure S12) may explain at least in part the double molar mass distribution observed in the GPC trace of Figure 3a.

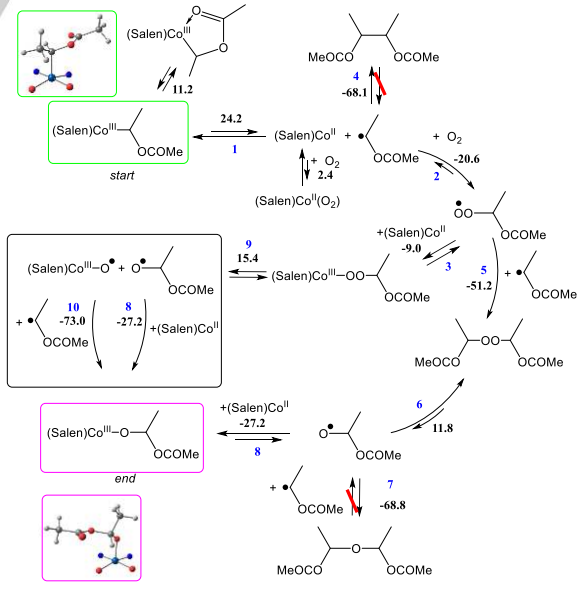


Figure 4. Mechanism for the oxidation of (Salen)Co^{III}-CH(Me)OCOMe to (Salen)Co^{III}-OCH(Me)-OCOMe under O_2. The bold blue numbers represent individual elementary steps. The bold black numbers are calculated standard Gibbs energy changes (ΔG°) at 60 °C in kcal/mol. In the geometry-optimized structures shown for starting and ending complexes, only the donor atoms of the Salen ligand are shown for clarity.

Table 2. ROCOP of CO_2/epoxides mediated by (Salen)Co^{III}-PVAc with pre-activation by O_2.[a]

Entry	Epoxide	(Salen)Co^{III}-PVAc M_n/kDa	Time/h	PPC yield/% [e,f]	PC yield/% [e,g]	TOF/h^{-1} [h]	$M_{n,GPC}$/kDa [i]	$M_{n,NMR}$/kDa [j]	$Đ$ [f]
1[b]	PO	10.5	48	--	2	0	--	--	--
2[c]	PO	10.5	48	--	6	0	--	--	--
3[d]	PO	10.5	48	--	5	0	--	--	--
4	PO	10.5	24	10	2	5	19.5	20.4	1.11
5[k]	PO	5.6	12	10	1	9	9.4	10.6	1.09
6[k]	CHO	5.6	24	12	1	3	12.5	14.2	1.16
7[k]	SO	5.6	24	10	1	2	12.2	13.8	1.15

[a]Reaction conditions: (Salen)Co^{III}-PVAc (from Table 1, entry 8) = 0.05 mmol, PO=3.5 mL, [Co]/[MTBD]/[epoxide] = 1/0.5/1000; pre-activated by 3.0 MPa O_2 at 60 °C for 12 h before the ROCOP was conducted under 3.0 MPa CO_2 at 30 °C. [b]Comparative experiment by (Salen)Co^{III}-PVAc without pre-activation. [c]Comparative experiment in the presence of AIBN, [Co]/[AIBN]=1/2. [d]Comparative experiment in the presence of TEMPO, [Co]/[TEMPO]=1/2. [D]etermined by ^{1}H NMR spectra. [f]PPC = poly(propylene carbonate). [g]PC = propylene carbonate. [h]Turnover frequency (TOF) = moles of product (PPC) per mole of catalyst per hour. [i]Number-average molar mass calculated from the ^{1}H NMR spectra. [j]Determined by GPC in THF, calibrated by polystyrene standards. [k](Salen)Co^{III}-PVAc (from Table 1, entry 7) = 0.1 mmol, PO=3.5 mL, [Co]/[MTBD]/[epoxide] = 1/0.5/500.

Since the alkylperoxyl radical is not irreversibly trapped by Eq. (3), it accumulates in the medium. At a certain point, reaction 5, which is thermodynamically quite favorable, becomes possible. Its rate law is k_5[•CH(Me)OCOMe][•OOCH(Me)-OCOMe]. It can prevail over reaction 2 (rate law: k_2[•CH(Me)OCOMe][O_2]) because of a presumably lower activation barrier (as expected from Hammond's principle) and also over reaction 4 (k_4[•CH(Me)OCOMe]^2) because [•OOCH(Me)OCOMe] >> [•CH(Me)OCOMe]. Therefore, the peroxo product of Eq. (4) may form quantitatively before all •CH(Me)OCOMe is consumed by O_2 in reaction 2. Note, however, that reaction 2 has a slight degree of reversibility at 60 °C (ΔG = -20.6 kcal/mol) and can therefore serve as a form of moderating equilibrium for the active •CH(Me)-OCOMe radical. In turn, the peroxide generated by Eq. (5) can homolytically break in Eq. (6) to generate two alkoxyl radicals, •OCH(Me)OCOMe, with a relatively low energy cost (ΔG = 7.4 kcal/mol at 60 °C). The latter can now be trapped either by an additional •CH(Me)OCOMe radical (Figure 4 Eq. (7)), to yield an ether product, MeCOOCH(Me)-O-CH(Me)-OCOMe, in a very favorable (irreversible) step, or by (Salen)Co^{II} to yield the observed (Salen)Co^{III}-O-CH(Me)-OCOMe by Eq. (8). Eq. (7) may also be responsible for the generation of the double molar mass polymer at low O_2 pressure.

It is also possible to envisage an alternative pathway leading to the final (Salen)Co^{III}-O-CH(Me)OCOMe product, which involves a homolytic O-O bond cleavage for the intermediate alkylperoxo complex (reaction 9). This generates the (Salen)Co^{III}-O• and •OCH(Me)OCOMe radicals, and the process is completed by reactions 10 and 8 as indicated in Figure 4. Indeed, there is precedent for the O-O bond cleavage in alkylperoxo-cobalt(III) compounds.[28b, 35] The calculations suggest that the metal complex is a Co^{III} complex with an oxyl radical, rather than a Co^{IV}=O complex: the system has lower energy as S = 3/2 with two unpaired electrons on Co and one on the O atom (spin densities of 1.893 and 0.910, respectively). There is also an excited S = ½ state at 8.9 kcal/mol higher in G that can also be described as an oxyl radical (spin densities of 0.161 on Co and 0.816 on O). The O-O bond cleavage of Eq. (9) is quite facile at 60 °C (ΔG° = 15.4 kcal/mol) and is followed by thermodynamically favorable processes. However, the competition between Eq. (5) and (3), which is much in favor of the former at 60 °C, leads us to prefer the scheme involving the sequence of reactions 1-2-5-6-8. In fact, there is also a third possible pathway, which involves a bimolecular reaction between two PVAc-OO• radicals to produce two PVAc-O• radicals and O_2. This is equivalent to the sequence of Eq. (5) and (6) and would still be followed by trapping of the product PVAc-O• radical by the (salen)Co^{II} complex (Figure 4 reaction 8). However, the second order rate law and especially the much lower calculated exergonicity of this reaction (ΔG = -18.70 kcal/mol) vs. trapping by PVAc• (Figure 4 reaction 5) makes us believe that the latter will be much faster (by application of Hammond's postulate) and prevail for the transformation of 2 PVAc• + O_2 to 2 PVAc-O•.

The most important contribution of the computational study is to show that the putative alkylperoxo complex, which is not observed in this work but is amply documented in the literature for other ligand systems, is thermally fragile and not thermodynamically stable at high temperatures. It evolves to the more stable alkoxo derivative in an environment where additional alkyl radicals are present. In all the previous work dealing with alkylperoxo derivatives of Co^{III}, these complexes were generated by either ligand exchange using hydroperoxides, ROOH (no O atom acceptors were present to produce alkoxo derivatives) or by autoxidation of alkylcobalt(III) derivatives as in the present case, but the processes were carried out at low temperatures where trapping by Eq. (3) becomes favorable and allows completions of the primary alkyl radical oxidation by Eq. (2).

Finally, the (Salen)Co^{III}-O-PVAc product obtained by oxidation, in the absence of acetic acid, of (Salen)Co^{III}-PVAc was tested as the initiator for the ROCOP of CO_2/propylene oxide, targeting the synthesis of PVAc-*b*-PPC diblock copolymers. The results are collected in Table 2. When (Salen)Co^{III}-PVAc ($M_{n,GPC}$ = 10.5 kDa, Table 1, entry 8) and 0.5 equivalent of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) (cocatalyst for ROCOP), dissolved in propylene oxide (PO), were placed under 3.0 MPa of CO_2 and allowed to stir at room temperature for 48 h, no poly(propylene carbonate) (PPC) was detected by ^{1}H NMR (Table

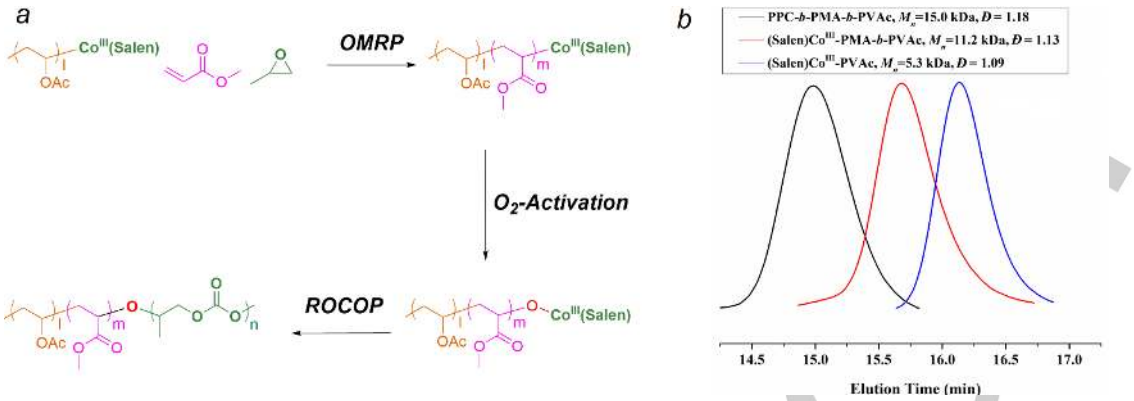


Figure 5. Synthesis of triblock copolymer. **a** Procedures for O_2-triggered switchable polymerization from mixture of (Salen)Co^{III}-PVAc macro-initiator, MA and PO under condition: [(Salen)Co^{III}-PVAc]/[MA]/[PO] =1/220/500, OMRP of MA within 10 h at 60 °C, conv.=30%; O_2-Activation within 12 h at 60 °C under 3.0 MPa O_2, ROCOP of PO/CO_2 within 8 h at 25 °C under 3.0 MPa CO_2, conv.=7.5%. **b** GPC traces of the (Salen)Co^{III}-PVAc macro-initiator, M_n=5.5 kDa, $Đ$=1.09; (Salen)Co^{III}- PMA-*b*-PVAc, M_n=11.2 kDa, $Đ$=1.13; PPC-*b*-PMA-*b*-PVAc, M_n=15.0 kDa, $Đ$=1.18.

2, entry 1). Also, no polymerization was observed when, either AIBN (Table 2, entry 2) or TEMPO (Table 2, entry 3) was deliberately added to the (salen)Co^{III}-PVAc macroinitiator before the O_2-triggered activation phase. It is important to note that the (Salen)Co^{III}-PVAc used as macroinitiator was isolated by precipitation before the O_2-triggered switch and subsequent ROCOP, thus eliminating any residual AIBN. When a switch was directly attempted starting from a one-pot mixture of (Salen)Co^{II}/VAc/PO/AIBN/MTBD, the reaction only produced PVAc and cyclic propylene carbonate (PC) according to the ^{1}H NMR spectrum of the reaction mixture (Figure S 34). Obviously, the presence of these reagents somehow blocks the transformation of (salen)Co^{III}-PVAc to (salen)Co^{III}-O-PVAc. However, a comparative reaction with (Salen)Co^{III}-PVAc pre-activated by 3.0 MPa O_2 led to a slight pressure drop (Table 2, entry 4). The formation of PPC with a perfectly alternating structure could be confirmed by ^{1}H NMR spectrum of the reaction mixture, while the GPC curve exhibited a monomodal distribution with a low $Đ$ (Figure S15). The ^{1}H DOSY NMR spectrum gave a single diffusion coefficient for all the PVAc and PPC resonances, whereas two diffusion coefficients were observed for a PVAc/PPC blend (Figures S16-17). We then evaluated the generality of the ROCOP step using other epoxides including cyclohexene oxide (CHO) and styrene oxide (SO) (Table 2, entries 6-7). In all cases, block copolymers with a completely alternating structure for the polycarbonate segments were obtained. It is notable that all the produced polymers displayed low $Đ$. Typically, salen catalysts have been shown to be highly active for ROCOP of epoxides/CO_2, especially in the presence of active co-catalysts, like MTBD.[36] However, significant decreases of catalytic activity were observed in our experiments (TOF ranging from 2 to 10 h^{-1}), which is attributed to the use of a macroinitiator.[37]

Synthesis of a PVAc-*b*-PMA-*b*-PPC triblock copolymer. (Salen)Co^{III}-PVAc proved to be a viable macroinitiator for thermally induced chain extension with methyl acrylate (MA) in the absence of additional radical source (RT pathway), yielding a (salen)Co^{III}-capped PVAc-*b*-PMA copolymer with increased molecular weight and narrow molecular wright distribution (Fig. 5b). In fact, this polymerization can be carried out in the presence of propylene oxide (but absence of CO_2) and only MA was incorporated in the polymer. Starting from the mixture of (Salen)Co^{III}-PVAc ($M_{n,GPC}$ = 5.3 kDa, Table S1, entry 2), MA and PO (Figure 5a), the first step of MA polymerization by OMRP gave (salen)Co^{III}-PMA-*b*-PVAc. Subsequent O_2 activation and pressurization with CO_2 allowed the chain extension by ROCOP with incorporation of CO_2/PO, while the residual MA from the previous step was no longer incorporated. This constitutes the synthesis of a PPC-*b*-PMA-*b*-PVAc triblock copolymer with monomodal and narrow molar mass distribution in a one-pot procedure (Figure 5b) and the ^{1}H DOSY NMR spectrum gave a single diffusion coefficient for all the PMA, PVAc and PPC resonances, whereas three diffusion coefficients were observed for a PMA/PVAc/PPC blend (Figures S32-33). This result demonstrates that an efficient one-pot switch from OMRP to ROCOP also occurs from a (salen)Co^{III}-capped PMA chain.

Conclusion

In summary, the first example of a switch from an organometallic mediated radical polymerization of vinyl monomers to ring-opening copolymerization of CO_2/epoxides has been described, using a (Salen)Co system as a common moderating agent/catalyst and O_2 as a trigger for the mechanistic switch. Mechanistic aspects concerning the activation of the OMRP dormant species (Salen)Co^{III}-R by O_2 have been reasonably proposed, as confirmed by experimental results and supported by DFT calculations. The key to the switch lies in an unprecedented single oxygen atom insertion into Co-C bonds, resulting in a ROCOP-active (Salen)Co^{III}-O-R species. Temporal control over the polymerization processes has been demonstrated, allowing for the facile synthesis of well-defined CO_2-based block copolymers in a one-pot procedure.

Experimental Section

Typical Procedure for OMRP of VAc in autoclave. In an argon filled glove box, (Salen)Co^{II} (260 mg, 0.432 mmol), AIBN (124 mg, 0.756 mmol)

and VAc (2 mL, 216 mmol) were charged into a pre-dried 25 mL autoclave equipped with a magnetic stir bar. The autoclave was then taken out of the glove box and allowed to stirred at 60 °C for periods of time before it was cooled down to room temperature. A small aliquot of the polymerization mixture was taken out for ^{1}H NMR spectroscopy. The remained crude mixture was diluted with CH_2Cl_2 and precipitated in hexane to yield a dark green powder.

Typical Procedure for ROCOP of CO_2/epoxide with pre-activation of (Salen)Co^{III}-PVAc by O_2. In an argon filled glove box, (Salen)Co^{III}-PVAc (525 mg, 0.05 mmol, $M_{n,GPC}$=10.5 kDa, $Đ$=1.07), MTBD (3.8 mg, 0.025 mmol) and PO (3.5 mL) were charged into a pre-dried 10 mL autoclave equipped with a magnetic stir bar. The autoclave was taken out of the glove box, pressurized with 3.0 MPa O_2 and allowed to stir at 60 °C for 12 h. After O_2 was slowly released, the autoclave was pressured with 3.0 MPa CO_2 and stirred at room temperature for 24 h. A small aliquot of the copolymerization mixture was taken out for ^{1}H NMR spectroscopy and the remained crude mixture was precipitated in cold methanol to yield a white powder.

Procedure for O_2 triggered switch from OMRP to ROCOP. In an argon filled glove box, (Salen)Co^{III}-PVAc (530 mg, 0.100 mmol, $M_{n,GPC}$=5.3 kDa, $Đ$=1.09), MTBD (7.6 mg, 0.05mmol), MA (1 mL) and PO (3.5 mL) were charged into a pre-dried 10 mL autoclave equipped with a magnetic stir bar. The autoclave was taken out of the glove box and allowed to stir at 60 °C for 10 h. After a sample was withdrawn for NMR spectra and GPC analysis, the autoclave was pressurized with 3.0 MPa O_2. The reaction mixture was further stirred at 60 °C for 12 h to activate the chain end before it was cooled down to room temperature. After O_2 was slowly released, the autoclave was pressurized with 3.0 MPa CO_2 and stirred at room temperature for 8 h. At the end of the reaction, a small aliquot of mixture was taken out for ^{1}H NMR spectroscopy and the remained crude mixture was precipitated in cold methanol to yield a white powder.

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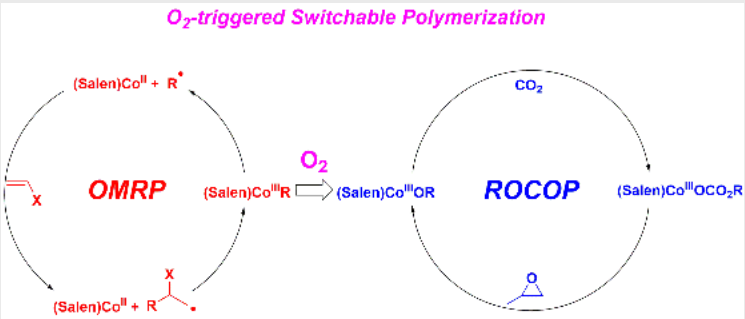

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Oxygen Triggered Switchable Polymerization for One-Pot Synthesis of CO_2-Based Block Copolymers from Monomer Mixtures