

Review

Terpolymerization of CO₂ with Epoxides and Cyclic Organic Anhydrides or Cyclic Esters

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Abstract: The synthesis of polymeric materials starting from CO₂ as a feedstock is an active task of research. In particular, the copolymerization of CO₂ with epoxides via ring-opening copolymerization (ROCOP) offers a simple, efficient route to synthesize aliphatic polycarbonates (APC). In many cases, APC display poor physical and chemical properties, limiting their range of application. The terpolymerization of CO₂ with epoxides and organic anhydrides or cyclic esters offers the possibility, combining the ROCOP with ring-opening polymerization (ROP), to access a wide range of materials containing polycarbonate and polyester segments along the polymer chain, showing enhanced properties with respect to the simple APC. This review will cover the last advancements in the field, evidencing the crucial role of the catalytic system in determining the microstructural features of the final polymer.

Keywords: CO₂; epoxides; cyclic esters; cyclic anhydrides; ROCOP; ROP



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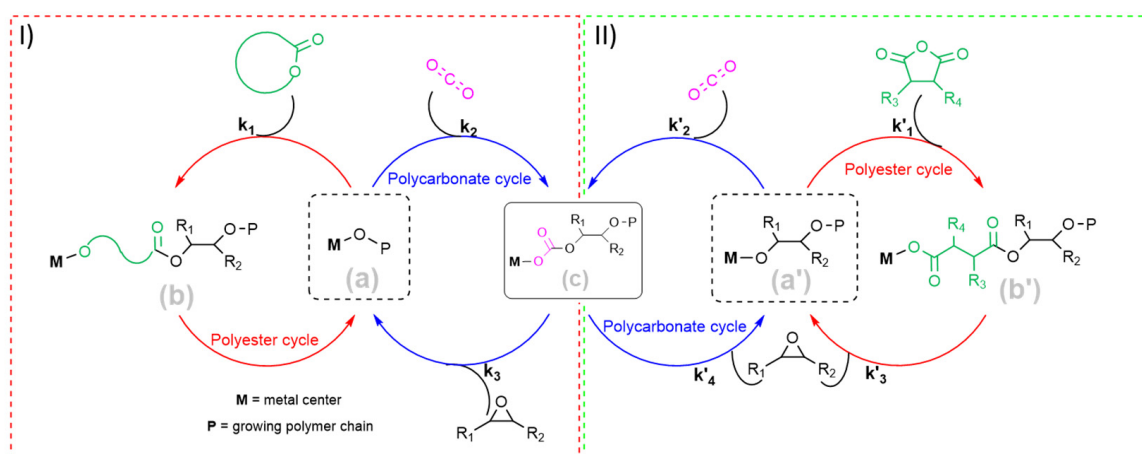


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1. Introduction

The pervasiveness of polymers in our daily life is a consolidated reality in recent decades. Indeed, the reason for the fortune of polymeric materials is due to both their unique physical and chemical properties and their cheapness compared to other structural materials. In the last few years, however, there is a growing body of evidence that the large success of these materials has determined a negative effect on terrestrial and marine ecosystems with the presence of microplastics that have become ubiquitous on our planet [1]. This situation has engendered the growing attention of the polymer industries and the scientific community to find biodegradable, more sustainable polymeric materials. Parallel to this trend, the use of CO₂ as a carbon feedstock has also gained momentum due to the rising interest in using such an inexpensive, non-toxic molecule as a starting material for the synthesis of polymers [2,3].

In particular, the alternating ring-opening copolymerization (ROCOP) of CO₂ with epoxides has offered a conceptually simple route for the synthesis of aliphatic polycarbonates (APC), which show a clear advantage in terms of biodegradability with respect to polyolefins [4–6]. APC, however, often display poor chemical and mechanical properties compared to aromatic polycarbonates, and the incorporation of epoxides with various structural features does not always result in an improvement in the final properties of APC [7–9]. Aliphatic polyesters are another important class of biopolymers that can be conveniently obtained by the ring-opening polymerization (ROP) of cyclic esters [10–13] or by the ROCOP of epoxides with cyclic anhydrides [14–17]. Transition metal complexes generally catalyze all these polymerization processes through a coordination–insertion mechanism. Actually, taking a closer look at the polymerization mechanism of the ROCOP of epoxides with CO₂ or cyclic anhydrides depicted in Scheme 1, it is evident that the formation of the metal-alkoxo bond (a' in Scheme 1) is a key intermediate in the propagation process. In analogy, the ROP of cyclic esters proceeds via the formation of a metal-alkoxo bond (a in Scheme 1) that allows the ring-opening of the following monomer unit.



Scheme 1. Representative mechanisms of the copolymerization of epoxides, CO₂, and cyclic esters (I) and the ROCOP of CO₂ or cyclic anhydrides with epoxides (II).

Given this mechanistic scenario, it is easy to imagine that it is possible to design a metal complex able to promote both types of polymerization, allowing us to obtain various block-copolymers. In principle, it is possible to obtain copolymers with polycarbonate and polyester segments and modulate the nature of the polycarbonate and polyester blocks, permitting the synthesis of new materials with tailored properties.

Notwithstanding the potential of such an approach, the efforts to develop efficient catalytic systems that cannot only incorporate CO₂ but also give rise to unprecedented new materials have raised good results only recently.

This review will cover the last advancements (since 2003) in the metal-catalyzed and metal-free terpolymerization of CO₂ with epoxides and cyclic esters or cyclic organic anhydrides for the obtaining of polycarbonate–polyester copolymers.

2. Terpolymerization of CO₂ with Epoxides and Cyclic Anhydrides

Polymeric materials containing ester and carbonate linkages have shown potential as biodegradable implants and, in addition, it is possible to adjust the degradation rate by regulating the length of the polyester and polycarbonate blocks. The first approach to synthesize poly(ester-block-carbonate)s in a one-pot reaction was the copolymerization, via ROP, of cyclic esters and cyclic carbonates promoted by stannous octanoate [18]. This conceptually simple approach has some limitations because six or seven-membered cyclic carbonates suitable for ROP must be synthesized through time-consuming multistep protocols [19,20].

2.1. Zinc Complexes

Only in 2006, Liu and coworkers reported on the terpolymerization of propylene oxide (PO) with CO₂ and maleic anhydride (MA) catalyzed by polymer-supported bimetallic catalyst (PBM) **1** of general formula P-Zn[Fe(CN)₆]_aCl_{2-3a}(H₂O)_b, with P being the polyether type chelating agent and a ≈ 0.5 and b ≈ 0.76 [21]. Notably, the catalyst was inactive in the PO/MA copolymerization whereas it gave the poly(propylenecarbonate) (PPC) from PO/CO₂. In the terpolymerization experiments (pCO₂ = 4.0 MPa, T = 60 °C, t = 24 h), the polymer yield increased up to a 5:3 ratio between PO and MA, and a further increase in the MA content was detrimental for the polymerization activity. ¹H and ¹³C NMR and IR spectroscopy revealed a random microstructure characterizing the resulting copolymers (Figure 1). The DSC thermograms showed a single transition with T_g values (29.1–56.1 °C) increasing by increasing the MA content in agreement with the microstructure revealed by NMR spectroscopy.

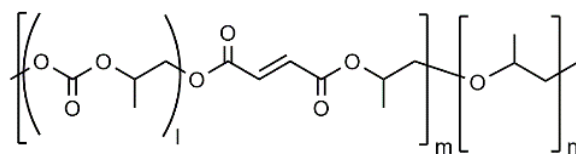


Figure 1. The structure of CO₂/PO/MA terpolymer obtained by Liu using complex **1** [21].

Later on, in 2008, the development of an efficient homogeneous catalytic system by Coates based on β -diimine (bdi) zinc complex **2** (Figure 2) allowed the synthesis of a poly(ester-*block*-carbonate) by the terpolymerization ($p\text{CO}_2 = 0.3\text{--}5.4$ MPa, $T = 50$ °C, $t = 0.2\text{--}3$ h) of cyclohexeneoxide (CHO) with diglycolic anhydride (DGA) and CO₂ [22].

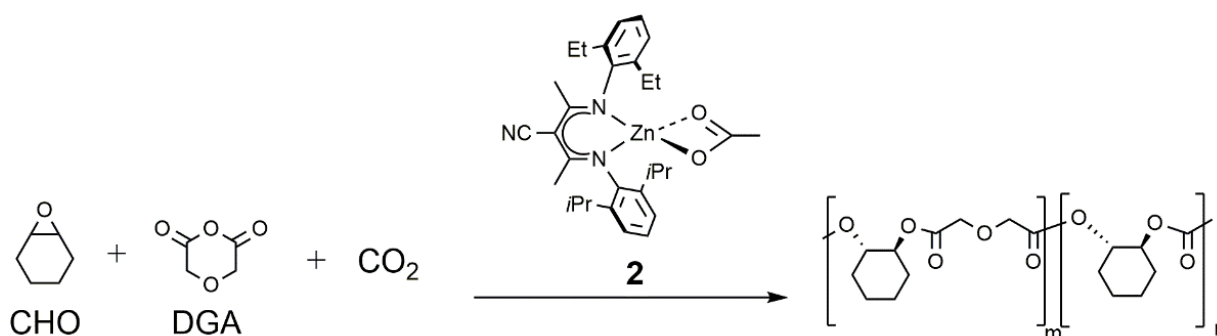
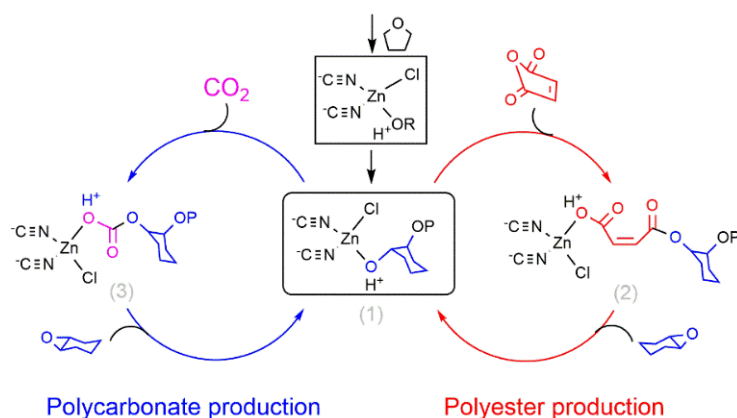


Figure 2. Terpolymerization of CHO, DGA and CO₂ with β -diimine zinc complex **2** by Coates. Reproduced with modification and permission from ref. [22]. Copyright (2008) John Wiley and Sons.

Notably, in spite of the polymerization feed simultaneously containing all three monomers, the final polymer was a diblock copolymer with a polyester block followed by a poly(cyclohexenecarbonate) (PCHC) block. Indeed, by following the polymerization reaction by in situ IR spectroscopy, the exclusive formation of the polyester block up to the total consumption of DGA was evident. From the mechanistic point of view, it was clear that the first step was the formation of zinc alkoxide by the ring-opening of CHO followed by the preferential and irreversible insertion of DGA until this monomer was completely consumed and only after the zinc alkoxide can allow the insertion of CO₂ with the growth of the polycarbonate block. The polymerization of succinic anhydride (SA), albeit with lower reactivity, and vinyl-CHO was also accomplished.

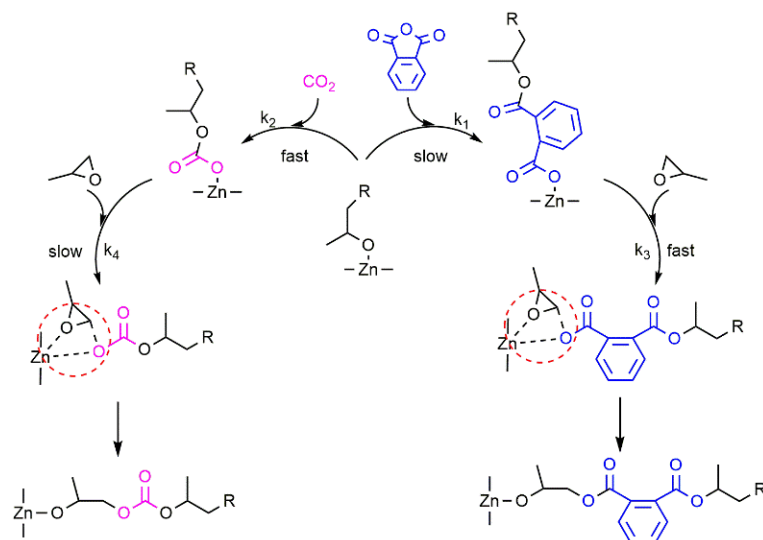
In 2010, Zhang and coworkers showed that the heterogeneous double metal cyanide complex (DMCC) **3** obtained by the reaction of K₃Co(CN)₆ with ZnCl₂ promotes the terpolymerization of CO₂ with CHO and MA [23]. The proposed active site for this catalyst is a Zn atom in a tetrahedral structure with the Co atom playing a spectator role. The catalyst was highly active and selective, giving a complete conversion of CHO ($p\text{CO}_2 = 4.0$ MPa, $T = 90$ °C, $t = 5$ h) and a complete selectivity toward the polymeric product. Notably, the resulting polymer was poly(ester-*block*-carbonate), but it also contained a variable amount of polyether linkages (2.9–11.7%) depending on the reaction conditions. In particular, the use of THF as a solvent inhibits the formation of polyether linkages due to the coordination of the THF molecule to the Zn²⁺ center. The mechanism proposed for CO₂/CHO/MA terpolymerization catalyzed by a Zn–Co(III) DMCC catalyst is depicted in Scheme 2.

Notably, notwithstanding the heterogeneous nature of the catalyst, the dispersity was narrow ($D = 1.4\text{--}1.7$) and the M_n was up to 14.1 kg mol^{−1}.



Scheme 2. Proposed mechanism for CHO, MA and CO₂ terpolymerization using Zn-Co(III) DMCC catalyst 3. Reproduced with modification and permission from ref. [23]. Copyright (2010) Elsevier.

Zinc glutarate (ZnGA) 4 was also found to be a versatile catalyst for the terpolymerization of CO₂ with PO and various cyclic anhydrides. Indeed, in 2014, Meng reported on the synthesis of PO/phthalic anhydride (PA)/CO₂ copolymers ($p\text{CO}_2 = 5.0 \text{ MPa}$, $T = 75 \text{ }^\circ\text{C}$, $t = 15 \text{ h}$) using toluene as a solvent [24]. Notably, in this case the formation of polycarbonate is favored over the polyester formation; consequently, the resulting terpolymers (M_n up to 221 kg mol^{-1} , $D = 2.1\text{--}3.9$) consist of a polycarbonate chain randomly interrupted by PA units (4.8–10.5%) and a lower amount of polyether linkages (2.7–7.1%). On one hand, the lower reactivity of PA vs. CO₂ was explained with the slower insertion of the PA into the Zr-alkoxo bond; on the other hand, the increase in the polymer yield and M_n observed when PA is present in the feed was explained with a faster insertion of PO into the zinc benzoate growing chain with respect to the zinc carbonate chain (Scheme 3).



Scheme 3. Mechanism for terpolymerization of PA, PO and CO₂ with ZnGA 4 [24].

These opposite effects determine an ideal value for the PA/PO ratio giving the maximum activity and highest molecular weight, and this ratio in the feed was experimentally found to be 1:8. However, the observed decrease in the M_n could also be explained considering the presence of diacid impurities in the anhydride that acts as a chain-transfer agent.

DSC thermograms show that the introduction of an aromatic ter-monomer in the polymer sensibly enhances the T_g with respect to the corresponding polycarbonate with an increase of $6 \text{ }^\circ\text{C}$ incorporating 5.6% of PA.

The same catalytic system 4 was also used for the synthesis of pseudo-interpenetrating poly(propylenecarbonate) by the terpolymerization ($p\text{CO}_2 = 5.4 \text{ MPa}$, $T = 70 \text{ }^\circ\text{C}$, $t = 36 \text{ h}$) of

CO₂ with PO and pyromellitic dianhydride (PMDA) up to 4% (in this case, M_n increased up to 862 kg mol⁻¹), resulting in a noticeable improvement in the mechanical and thermal properties with respect to the corresponding polycarbonate [25].

More recently, Williams et al. described the synthesis of a new dinuclear zinc complex **5** (Figure 3) that promotes the terpolymerization of CHO/PA/CO₂ ($p\text{CO}_2 = 3.0$ MPa, $T = 100$ °C, $t = 18$ h) [26].

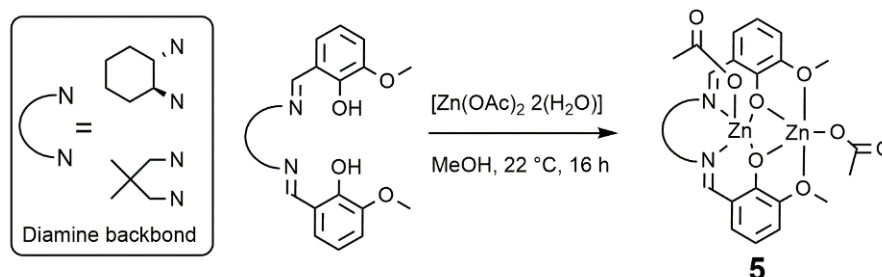


Figure 3. Synthesis of dinuclear zinc complex **5** by Williams et al. Reproduced with modification and permission from ref [26]. Copyright (2015) American Chemical Society.

By monitoring the reaction after 2 h, it was evident that there was the exclusive formation of polyether linkages and no formation of PCHC, and after 18 h the formation of a poly(ester-*block*-carbonate) (M_n up to 7 kg mol⁻¹, $D = 1.20$) was evident and confirmed by size-exclusion chromatography (SEC) analysis and diffusion-ordered spectroscopy (DOSY) experiments.

Similar results were also obtained by Castro-Osma and coworkers by using dinuclear zinc complexes **6–8** supported by heteroscorpionate ligands (Figure 4) [27].

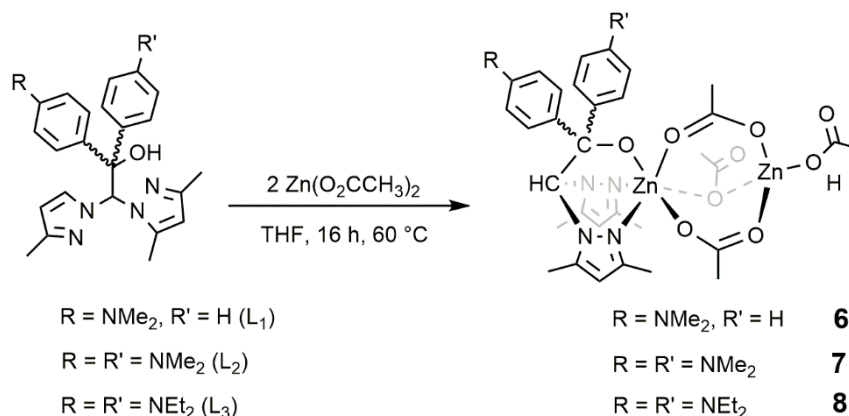


Figure 4. Synthesis of bimetallic zinc acetate catalysts **6–8** supported by heteroscorpionate ligands [27].

The complexes **6–8** were active, in the presence of DMAP, in the terpolymerization of CHO/PA/CO₂ ($p\text{CO}_2 = 4.0$ MPa, $T = 80$ °C, $t = 16$ h), giving a poly(ester-*block*-carbonate) material (M_n up to 3.9 kg mol⁻¹, $D = 1.41–1.64$).

2.2. Chromium and Cobalt Complexes

In 2011, Duchateau and coworkers reported on the terpolymerization ($p\text{CO}_2 = 5.0$ MPa, $T = 80$ °C, $t = 18$ h) of CHO with CO₂ and various anhydrides (SA, cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA) or PA) promoted by two chromium complexes (Figure 5): tetraphenylporphyrinato chromium chloride **9** and salophen chromium chloride **10** (where salophen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine) activated by DMAP (4-(*N,N*-dimethylamino)pyridine) [28].

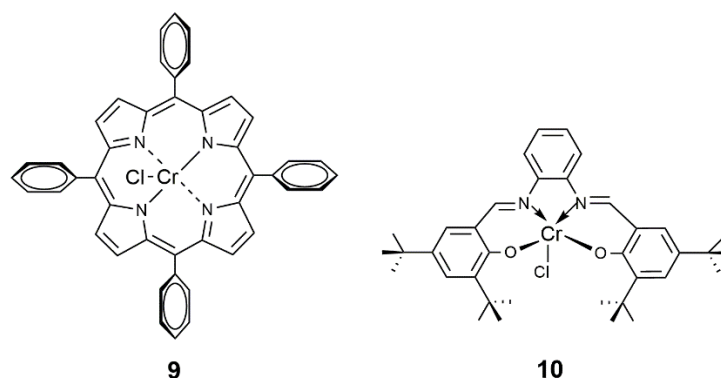
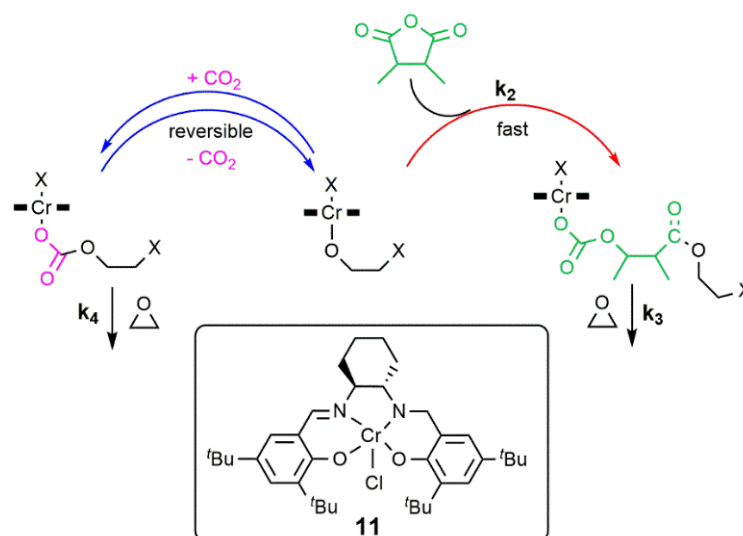


Figure 5. Catalysts **9** and **10** used by Duchateau in the terpolymerization of CO_2 , CHO and dicarboxylic acid anhydrides (SA, CPrA, CPA, PA) [28].

In analogy to the polymerization process observed by Coates in the case of the (bdi)Zn complexes, the formation of the polyester is favored over the formation of the polycarbonate, resulting in the formation of a poly(ester-*block*-carbonate). Notably, the authors also showed that DSC of poly(ester-*block*-carbonate) is inconclusive in giving information about the blocky microstructure of the copolymer because the polyester and polycarbonate phases are completely miscible, giving a single value for the T_g . Furthermore, in the case of complex **10**, the authors noticed that the presence of CO_2 in the polymerization feed completely suppresses the formation of polyether linkages. In particular, by copolymerizing the equimolar amount of CHO and CPrA in the presence of CO_2 , the pure polyester was obtained, while without CO_2 an amount of 15–30% of polyether linkages was observed. For all terpolymerizations, M_n (up to 19.2 kg mol^{-1}) showed a linear correlation with conversion and the D was ≤ 1.6 , indicating controlled behavior.

Soon after, Darensbourg, using a related (salan) CrCl complex **11** activated by PPNN_3 in the terpolymerization of CHO/PA/ CO_2 , observed similar results (M_n up to 18 kg mol^{-1} , $D = 1.07\text{--}1.13$) [29]. In this case, the poly(ester-*block*-carbonate) showed two distinct T_g values ($48 \text{ }^\circ\text{C}$ and $115 \text{ }^\circ\text{C}$). Intriguingly, the major reactivity of the anhydride vis à vis CO_2 was explained in terms of a slower ring-opening step of the metal-carbonate intermediate with the epoxide monomer instead of a faster insertion of the anhydride in the metal-alkoxo bond (Scheme 4).



Scheme 4. CO_2 insertion vs. cyclic anhydride insertion into the metal alkoxide intermediate. Reproduced with modification and permission from ref [29]. Copyright (2012) American Chemical Society.

Chromium(III) complex **12** (TPPCrCl, Figure 6) with a porphyrin ligand in combination with PPNCl was successfully used by Chisolm and coworkers for the terpolymerization of CO₂/PO/SA ($p\text{CO}_2 = 4.0\text{--}5.0$ MPa, $T = 25$ °C, $t = 3\text{--}18$ h) [30]. It is worth noting that the PPNCl/Cr ratio is crucial to avoid the formation of polyether linkages; indeed, when 0.5 equiv. of PPNCl have been used, the formation of polyether linkages is favored (up to 42%) over the polyester and polycarbonate linkages, whereas with 1.0 equiv. of PPNCl the amount of polyether linkages is drastically reduced (<2%). In analogy to other chromium systems, for this system the polyester formation is also faster than the polycarbonate one, leading to copolymers with a tapered/diblock microstructure. The authors attributed the higher reactivity of SA over CO₂ to the higher solubility of the anhydride in the reaction medium.

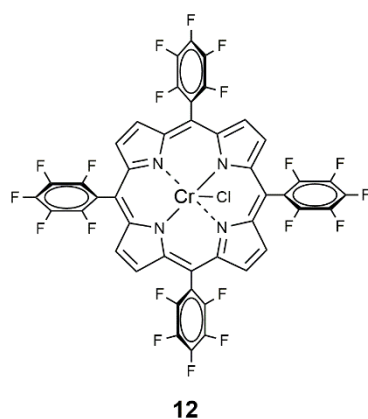


Figure 6. The (porphyrin)Cr(III)Cl complex **12** employed by Chisolm and coworkers [30].

A major breakthrough in this field was the use of the single component Co(III) complex **13** (Figure 7) tethering four quaternary ammonium salts [31].

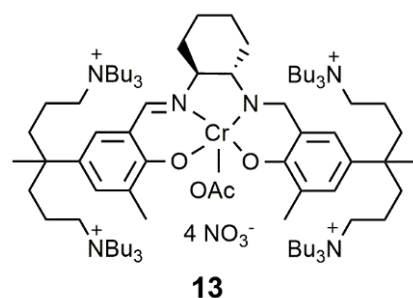


Figure 7. The (salen)Co(III) complex **13** with quaternary ammonium salts in a molecule [31].

This complex displayed one of the highest activities in the CO₂/PO copolymerization, reaching TOF up to 16,000 h⁻¹. In the presence of CO₂/PO/PA, this complex also shows high reactivity with a total conversion of PO only after 3.0 h ($p\text{CO}_2 = 3.5$ MPa, $T = 80$ °C) and a calculated TOF = 12,000 h⁻¹. The resulting copolymers have a gradient poly(1,2-propylene carbonate-co-phthalate)s microstructure since, due to the highest reactivity of PA compared to CO₂, the polymeric chains formed in the initial stages are richer in PA, but the consumption of this comonomer favors the formation of polycarbonate chains in the last stages. The resulting copolymers have a very narrow dispersity ($D = 1.03\text{--}1.22$) and high molecular weight (M_n up to 354 kg mol⁻¹). As previously observed, the incorporation of PA in the polymeric chain enhances the thermal properties of the final polymer with respect to the corresponding PPC.

A dinuclear Cr(III) salen complex **14** (Figure 8) was reported by Lu and coworkers to promote, in the presence of 2 equiv. PPNCl, the terpolymerization of CO₂/CHO/PA ($p\text{CO}_2 = 1$ MPa, $T = 80$ °C, $t = 0.5\text{--}6$ h) [32]. In the first 2 h, the system only produced the

polyester segment with no incorporation of CO₂, and only after the total consumption of PA the polycarbonate block was formed, also giving, in this case, a diblock polymer. The produced copolymers have a very narrow dispersity ($D = 1.19\text{--}1.22$) and the molecular weight increases with the polymerization time (M_n up to 21.2 kg mol^{-1}).

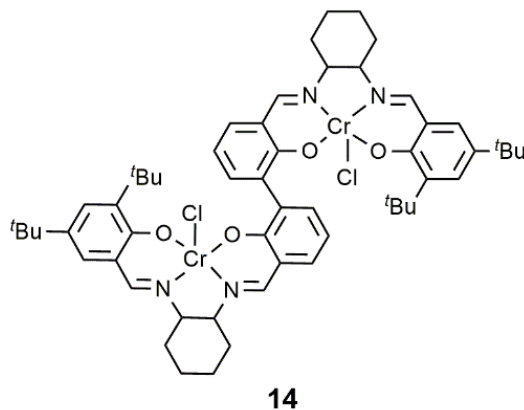


Figure 8. Dinuclear chromium catalyst **11** developed by Lu et al. [32].

2.3. Metal-Free Catalysts

Since the discovery by Feng and coworkers that triethyl borane (TEB) in combination with onium halides or alkoxides promotes the formation of polycarbonates by coupling CO₂ with PO or CHO, the efforts to extend the use of this metal-free system to the terpolymerization of CO₂ with epoxides and anhydrides resulted in the synthesis of terpolymers having various microstructural features [33].

In 2020, Meng reported the quadripolymerization of CO₂ with PA, PO and CHO in the presence of TEB and PPNCl, resulting in the formation of the copolymer ($p\text{CO}_2 = 1 \text{ MPa}$, $T = 70 \text{ }^\circ\text{C}$, $t = 24\text{--}96 \text{ h}$) with good selectivity (94%) with respect to the cyclic product [34,35]. The microstructure of the resulting quadripolymer was clarified by ¹H and ¹³C NMR showing the presence of four main blocks, i.e., poly(PA-*alt*-CHO), poly(PA-*alt*-PO), poly(propylene carbonate) (PPC), and poly(cyclohexene carbonate) (PCHC), and a very low amount of polyether linkages (<1%). In addition, in this case the formation of the polycarbonate segments only starts after the complete PA conversion and thus after the formation of the polyester segments. The resulting polymers display narrow dispersity ($D = 1.14\text{--}1.21$) and a high molecular weight (M_n up to 77 kg mol^{-1}). Notably, the T_g can be easily tuned by regulating the feed ratio with a wide temperature range ($T_g = 82\text{--}116 \text{ }^\circ\text{C}$).

Afterward, Li and coworkers reported on the terpolymerization of CO₂ with PA and CHO, in the presence of TEB and PPNCl ($p\text{CO}_2 = 0.1 \text{ MPa}$, $T = 80 \text{ }^\circ\text{C}$, $t = 0.25\text{--}2 \text{ h}$) [36]. Additionally, in this case the polycarbonate block starts forming only after the complete consumption of PA in the feed, resulting in a poly(ester-*b*-carbonate) copolymer with little tapering, as shown by NMR spectra. The same catalytic system also allows the synthesis of poly(ester-*b*-carbonate) without tapering by sequential monomer addition. The resulting copolymers possess narrow dispersity ($D = 1.09\text{--}1.15$) and M_n up to 23.5 kg mol^{-1} .

Lately, Feng obtained similar results by using TEB in combination with Bu₄NN₃ ($p\text{CO}_2 = 0.1 \text{ MPa}$, $T = 60 \text{ }^\circ\text{C}$, $t = 0.75\text{--}18 \text{ h}$) for the terpolymerization of CO₂ with PO and SA/PA. The PO/SA/CO₂ terpolymerization clearly shows higher reactivity toward the oxoanion of SA over CO₂, leading to the preferential formation of the polyester resulting in tapered poly(ester-*b*-carbonate) [37]. Only at a low concentration of SA (SA:PO = 1:20), a random poly(ester-*co*-carbonate) copolymer was obtained with 51% of polyester and 49% of carbonate. Notably, the PO/SA/CO₂ terpolymerization leads to random copolymers also at PA:PO = 20:200, and only with the presence of 40% of PA in the feed the resulting copolymer displays a blocky nature. The terpolymerization of CHO/PA/CO₂ activating TEB with PPNCl ($p\text{CO}_2 = 0.1 \text{ MPa}$, $T = 80 \text{ }^\circ\text{C}$, $t = 17\text{--}18 \text{ h}$) shows the analogous behavior of PO preferentially producing copolymers with a random microstructure and blocky

copolymers only with a high content of PA in the feed. Genuine poly(ester-*b*-carbonate)s can be obtained by sequential monomer addition both in the case of PA/PO and CHO/PA followed by feeding CO₂. The T_g of the resulting copolymers can be tuned by regulating the PA content in the final copolymer with values ranging from 32.5 °C to 46.2 °C in the case of the PO/PA/CO₂ copolymers and from 121 °C to 135.1 °C in the case of the CHO/PA/CO₂ copolymers.

In Table 1, the results obtained in the CO₂/epoxide/cyclic anhydrides' terpolymerization discussed in this first part are summarized.

Table 1. Summary of terpolymerization of CO₂ with epoxides and cyclic organic anhydrides.

Catalyst	Monomers	Polymerization Conditions $p\text{CO}_2$, T, t	M_n * (\bar{D}) kg mol ⁻¹	Polymer Microstructure	Ref.
1	CO ₂ , PO, MA	4.0 MPa, 60 °C, 24 h	-	random	[21]
2	CO ₂ , CHO, DGA	0.3–5.4 MPa, 50 °C, 0.2–3 h	37 (1.2–1.4)	block	[22]
3	CO ₂ , CHO, MA	4.0 MPa, 90 °C, 5 h	14.1 (1.4–1.7)	block	[23]
4	CO ₂ , PO, PA	5.0 MPa, 75 °C, 15 h	221 (2.1–3.9)	random	[24]
4	CO ₂ , PO, PMDA	5.4 MPa, 70 °C, 36 h	862 (2.0–3.8)	random	[25]
5	CO ₂ , CHO, PA	3.0 MPa, 100 °C, 18 h	7 (1.20)	block	[26]
6–8	CO ₂ , CHO, PA	4.0 MPa, 80 °C, 16 h	3.9 (1.41–1.64)	block	[27]
9–10	CO ₂ , CHO, SA/CPrA/CPA/PA	5.0 MPa, 80 °C, 18 h	19.2 (1.1–1.6)	block	[28]
11	CO ₂ , CHO, PA	3.5 MPa, 80 °C, 12 h	18 (1.07–1.13)	block	[29]
12	CO ₂ , PO, SA	4–5.0 MPa, 25 °C, 3–18 h	-	tapered/block	[30]
13	CO ₂ , PO, PA	3.5 MPa, 80 °C, 3 h	354 (1.03–1.22)	gradient	[31]
14	CO ₂ , CHO, PA	1 MPa, 80 °C, 0.5–6 h	21.2 (1.19–1.22)	block	[32]
Metal-free catalyst					
TEB + PPNCI	CO ₂ , PO, PA, CHO	1 MPa, 70 °C, 24–96 h	77.7 (1.14–1.21)	alternated	[34,35]
	CO ₂ , CHO, PA	0.1 MPa, 80 °C, 0.25–2 h	23.5 (1.09–1.15)	block	[36]
TEB + Bu ₄ NN ₃	CO ₂ , PO, SA/PA	0.1 MPa, 60 °C, 0.75–18 h	17.3 (1.04–1.2)	tapered/random	[37]
TEB + PPNCI	CO ₂ , CHO, SA/PA	0.1 MPa, 80 °C, 16–17 h	22.7 (1.06–1.09)	tapered/block	[37]

* The highest reported value.

3. Terpolymerization of CO₂ with Epoxides and Cyclic Esters

The synthesis of polyester-*co*-polycarbonate was also attempted by the terpolymerization of CO₂ with epoxides and cyclic esters combining the ROCOP and ROP mechanisms [38]. This approach gives access to microstructures not accessible via ROCOP with organic anhydrides and has the advantage of using largely available monomers ϵ -caprolactone (CL), *DL*-lactide (LA) and β -butyrolactone (BBL) [14,16,36,38–40].

3.1. Zinc Complexes

ZnGA **4**, obtained by the reaction of zinc oxide and glutaric acid, was active in the terpolymerization of CO₂/PO/CL ($p\text{CO}_2 = 2.8$ MPa, T = 60 °C, t = 40 h), resulting in high molecular weight polymers (M_n up to 27.5 kg mol⁻¹) with narrow dispersity ($\bar{D} = 1.50$ –2.97) [41]. The catalytic activity decreases by increasing the content of CL beyond the 50% in mol in the feed. Notably, the system was inactive in the polymerization of CL alone and the production of cyclic carbonate contaminant was not observed. The ¹³C NMR analysis reveals a diblock microstructure with CL units directly linked to PC units and CL units in homosequences. Accordingly, the DSC thermograms display two transitions: one relative to the T_g of the PPC block ($T_g = 5.4$ –17.7 °C) and the T_m of the PCL block ($T_m = 51.0$ –57.2 °C). These polymers show excellent enzymatic biodegradability catalyzed by various lipases. The same catalytic system using glycidol terminated -PCL as a macromonomer produced the corresponding grafted copolymers in the presence of CO₂/PO ($p\text{CO}_2 = 1.0$ MPa, T = 60 °C, t = 6 h) [42].

In 2006, Doring reported the first example of the terpolymerization of CO₂/CHO/LA by using zinc acetate complexes **15**–**22** with aminoimidoacrylate (AIA) ligands (Figure 9) [43].

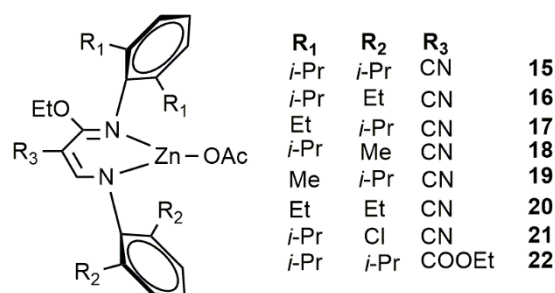


Figure 9. (AIA)Zn(OAc) complexes 15–22 [43].

In order to obtain a terpolymer with an appreciable amount of polycarbonate linkages, an excess of CHO in the feed was necessary (CHO:LA = 3:1, $p\text{CO}_2 = 4.0$ MPa, $T = 90$ °C, $t = 16$ h), giving high molecular weight polymers ($M_n = 11.3\text{--}41.6$ kg mol⁻¹) with narrow dispersity ($D = 1.09\text{--}1.96$). The copolymers obtained by using *L*-LA instead of *rac*-LA show crystallinity with a melting point around 167 °C. The authors also reported the terpolymerization by using the (bdi) Zn catalysts developed by Coates (see Figure 2), showing, in this case, even a major tendency to incorporate a higher amount of polycarbonate linkages (up to 80%).

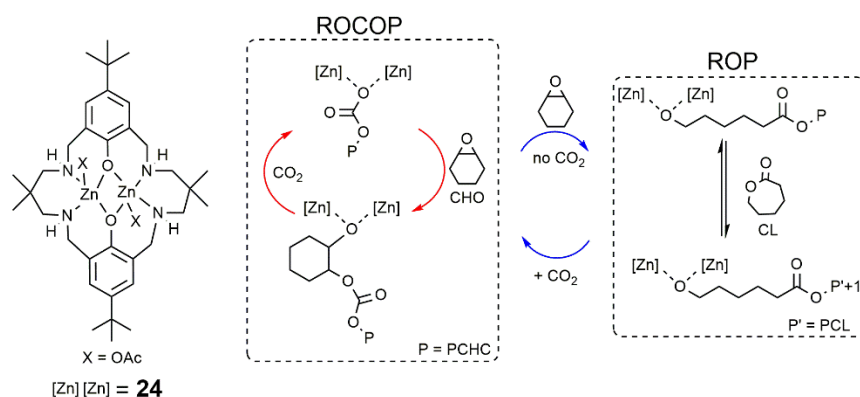
The polymer-supported bimetallic catalyst (PBM) **1** of general formula P-Zn[Fe(CN)₆]_aCl_{2-3a}(H₂O)_b ($a \approx 0.5$ and $b \approx 0.76$) developed by Liu was also effective in the terpolymerization ($p\text{CO}_2 = 4.0$ MPa, $T = 50\text{--}90$ °C, $t = 16$ h) of CO₂/PO/CL, giving materials also containing polyether linkages [44].

A ternary system composed of Y(CCl₃COO)₃/ZnEt₂/glycerin **23** was used by Xi-anhong and coworkers to synthesize ($p\text{CO}_2 = 4.0$ MPa, $T = 70$ °C, $t = 10$ h) terpolymers CO₂/PO/*L*-LA with a high molecular weight ($M_n = 7.2\text{--}15.4$ kg mol⁻¹) and broad dispersity ($D = 4.2\text{--}9.9$), with the molecular weight increasing by decreasing the *L*-LA content in the feed [45]. It is worth noting that the presence of *L*-LA in the polymeric backbone even at a low content (2.4% mol) results in a considerable increase in the mechanical and thermal properties.

A major advance came in 2014 when Williams and coworkers reported that the dizinc complex **24** bearing a reduced Robson-type macrocyclic ligand promotes the ROCOP of CO₂/CHO and the ROP of CL ($p\text{CO}_2 = 0.1$ MPa, $T = 80$ °C, $t = 2\text{--}21$ h) only when activated by CHO, and intriguingly, a polymerization feed composed by a mixture of CO₂/CHO/CHO only leads to the exclusive formation of PCHC (Scheme 5) [46]. Indeed, the synthesis of PCL-*b*-PCHC was only possible by sequential monomer addition by introducing CO₂ after the consumption of CL in the presence of CHO or by reverse order completely removing CO₂ after the formation of the PCHC block. The molecular weight of the resulting polymers was rather low (M_n up to 4.8 kg mol⁻¹), with narrow dispersity ($D = 1.38\text{--}1.49$). This ability to selectively polymerize only one kind of monomer from a mixture and the ability to oscillate between the ROCOP and ROP mechanisms led to the definition of “switch catalysis” [47].

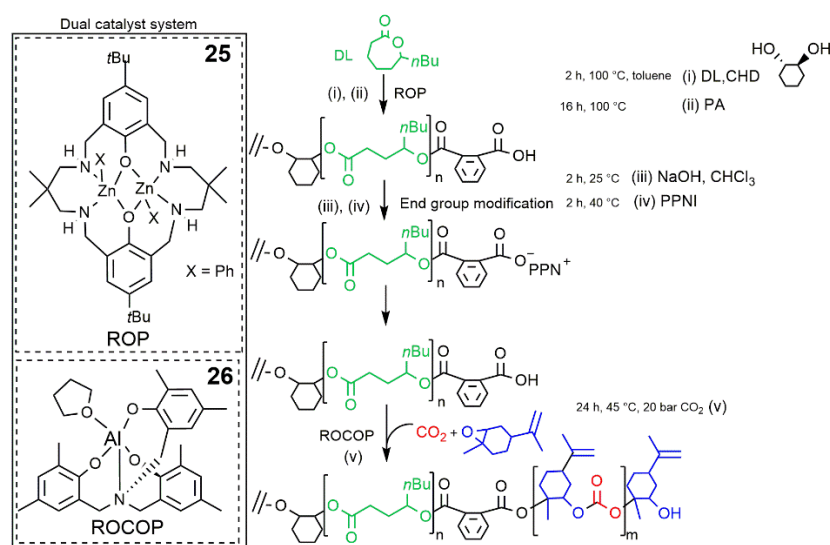
By performing the ROCOP of CO₂/CHO, it was also possible to obtain a polycarbonate polyol ($p\text{CO}_2 = 0.1$ MPa, $T = 80$ °C, $t = 16\text{--}25$ h) that, after removing CO₂, can be used for the synthesis of ABA triblock copoly(caprolactone-*b*-cyclohexene carbonate-*b*-caprolactone) by adding CL. Notably, from the thermal behavior, it was also evident that the presence of the PCHC block disturbs or, at a higher percentage, suppresses the crystallinity of the PCL blocks, allowing the preparation of amorphous polymer films with good transparency [48].

The same catalytic system **24** was also used to obtain pentablock copolymers by alternating ROCOP (anhydrides/epoxide), ROP (lactone) and ROCOP (CO₂/epoxide) by using various epoxides (CHO and VCHO), anhydrides (PA, NA), and DL (ϵ -decalactone). The resulting pentablock copolymers show a single T_g (from -35 to 20 °C), low molecular weight (10–16 kg mol⁻¹) [49] and $D = 1.06\text{--}1.16$.



Scheme 5. The switch catalysis mechanism, ROCOP and ROP promoted by **24**. Reproduced with modification and permission from ref [46]. Copyright (2014) John Wiley and Sons.

A more sophisticated technique was necessary to synthesize ABA block copolymers having poly(limonene-carbonate) (PLC) blocks because of the incapability of the dizinc complex to catalyze the polymerization of limonene oxide (LO) with CO_2 [50]. In order to circumvent this problem, a dual catalytic system was used: (1) the dizinc complex **25** promotes, in the presence of 1,2-cyclohexane diol (CHD), the formation of a hydroxyl-telechelic PDL by the ROP of DL. This macroinitiator was then used, after the modification of the end groups for the synthesis of the PLC blocks, by using a second catalytic system based on the Al aminotriphenolate complex **26** developed by Kleij [51], as shown in Scheme 6.



Scheme 6. Block polymer synthesis using a dual catalytic system. Reproduced with modification and permission from ref. [50]. Copyright (2020) Royal Society of Chemistry.

The resulting biopolymers PLC-*b*-PDL-*b*-PLC have molar masses M_n spanning from 50.700 to 114.6 kg mol^{-1} and narrow dispersity ($D = 1.38\text{--}1.49$). The thermal and mechanical properties are superior compared to PLC, and these terpolymers show good chemical recyclability through depolymerization with the same dizinc catalyst affording the starting monomers.

Lately, a heterodinuclear Zn/Mg catalyst **27** (Figure 10) with the same ligand framework promoted the formation of ABA triblock copolymers by using DL with high activity [52].

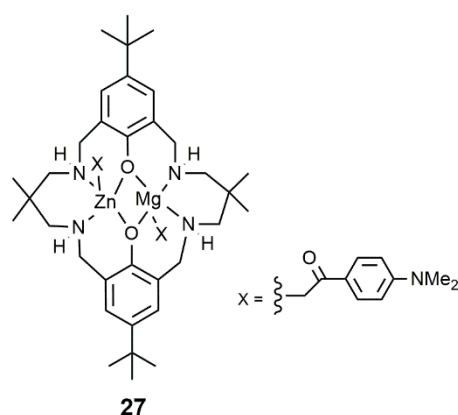


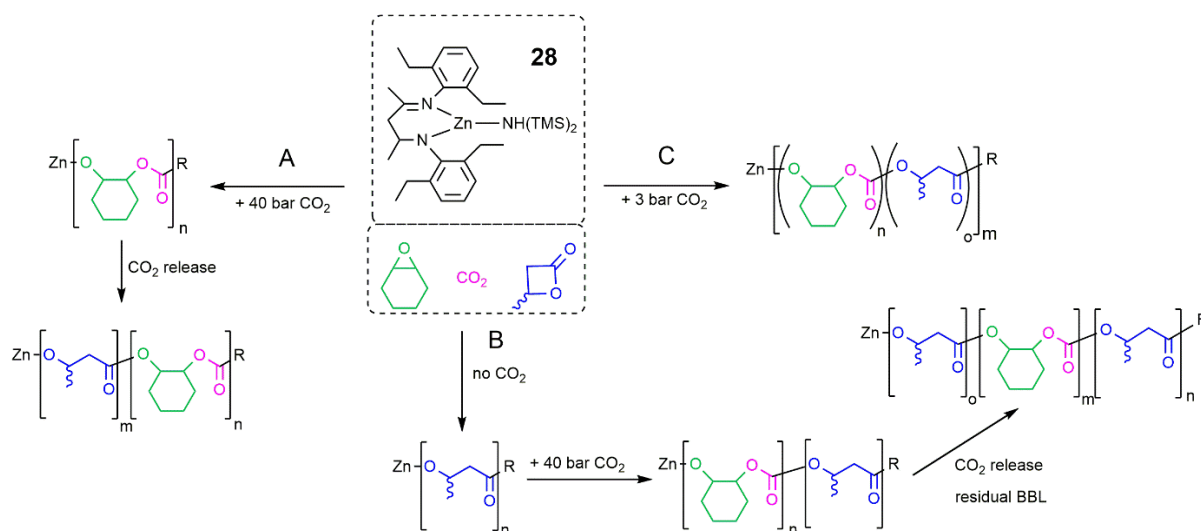
Figure 10. Heterodinuclear Zn/Mg catalyst **27** [52].

In particular, by performing the ROP of DL a dihydroxyl telechelic PDL was obtained that, in the presence of CO₂, undergoes the transformation into the ABA triblock copolymer PCHC-*b*-PDL-*b*-PCHC. The raw copolymers can incorporate a high amount of CO₂ (up to 23%) and possess a high molecular weight (38.0–71.9 kg mol⁻¹) with narrow dispersity ($\bar{D} = 1.07$ –1.16). These materials display a single T_g (from -44 to -50 °C), evidencing the amorphous nature of the blocks and their complete miscibility, and only the polymers with a higher content of PCHC (>50%) show a second transition at higher temperatures (81; 110 °C). These materials show promising thermal and mechanical properties compared to PCHC and the possibility to modulate them by regulating the length of the blocks in the final polymer, potentially giving a wide range of applications.

Rieger and coworkers were able, by using a (bdi)-zinc complex **28** (Scheme 7), to obtain copolymers by the terpolymerization of CO₂/BBL/CHO [53]. In particular, also in this case the CO₂ acts as a switching agent: (A) at $p\text{CO}_2 = 4.0$ MPa, the polymerization proceeds with the exclusive production of PCHC and the formation of the poly(hydroxybutyrate) (PHB) only starts after releasing CO₂ pressure, leading finally to a diblock copolymer PCHC-*b*-PHB. (B) In the absence of CO₂, obviously, the system evolves to the formation of PHB and before to the total consumption of BBL feeding CO₂ ($p\text{CO}_2 = 4.0$ MPa) with the formation of a PCHC block, finally releasing the CO₂ the “residual” BBL polymerizes, giving, at the end, an ABA triblock copolymer PCHC-*b*-PHB-*b*-PCHC. (C) By lowering the CO₂ pressure to $p\text{CO}_2 = 0.3$ MPa, the rates of the ROCOP and ROP processes are comparable and therefore a statistical copolymer was formed.

The copolymers’ molecular weights, in the case of the block copolymers, are higher ($M_n = 77.0$ –166 kg mol⁻¹) than those obtained in the case of statistical copolymers ($M_n = 34.0$ –69.0 kg mol⁻¹), in both cases showing narrow dispersity ($\bar{D} = 1.2$ –1.8). PCHC-*b*-PHB and PCHC-*b*-PHB-*b*-PCHC display two T_g values relative to the PHB and PCHC blocks, respectively ($T_{g1} = 1$ –2 °C and $T_{g2} = 116$ –118 °C), as a consequence of phase separation between the polycarbonate and polyester blocks, also confirmed by atom force microscopy (AFM). Conversely, the random copolymers display a single transition ($T_g = 36$ –91 °C) that increases by increasing the amount of carbonate linkages in the polymer chain. Similar results were obtained with cyclopenteneoxide (CPO), but in this case the polymerization at a higher pressure ($p\text{CO}_2 = 4.0$ –5.0 MPa) results in the formation of a gradient copolymer rather than a diblock copolymer. The kinetic study evidenced a change in the reaction order with respect to CO₂ with a zero order dependence at high pressure (between $p\text{CO}_2 = 0.5$ –1 MPa) and first-order at lower pressure ($p\text{CO}_2 < 0.5$ MPa), indicating that under the latter conditions the insertion of CO₂ became the rate-limiting step [54]. As expected, the incorporation of polyester segments in both the statistical and block copolymers leads to an improvement in the mechanical properties compared to the brittle PCHC with a decrease in the Young modulus and tensile strength and an increase in the elongation at break for polymers with a high molecular weight (>100 kg mol⁻¹). Efforts to terpolymerize CO₂/BBL/LO (limonene oxide) evidenced that due to the low

ceiling temperature (60 °C) of the polylimonencarbonate (PLC), the only way to obtain block copolymers is to first obtain the PHB block via the ROP of BBL and then feed CO₂ for the formation of the PLC block. Notably, the PHB-*b*-PLC copolymers possess a high molecular weight (M_n up to 233 kg mol⁻¹) and narrow dispersity ($D = 1.23$ – 1.39), showing two $T_g = 1$ – $3/26$ – 133 °C. Statistical copolymers were also obtained by adjusting the CO₂ pressure ($p_{\text{CO}_2} = 0.9$ MPa), resulting in low conversion (up to 22% LO and 26% BBL in 22 h) and low molecular weight polymers ($M_n = 9.0$ kg mol⁻¹).



Scheme 7. Different reaction pathway of **28** toward ROP of BBL, copolymerization of CPO with CO₂, and terpolymerization of CHO, CO₂ and BBL. Reproduced with modification and permission from ref [53]. Copyright (2017) American Chemical Society.

3.2. Cobalt Complexes

Salen cobalt complexes are highly active catalysts in the ROCOP of CO₂ with epoxides and therefore are, in principle, viable candidates for the terpolymerization of CO₂ with epoxides and lactones. Unfortunately, these complexes are inactive in the ROP of cyclic esters, and consequently, the implementation of an active catalytic system for obtaining polycarbonate-*b*-polyester copolymers requires the use of multi-component systems able to synthesize the desired polymeric product.

An elegant strategy was developed by Darensbourg and Lu that used a combination of the bifunctional Co(III) salen complex **29** and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (Figure 11) for the terpolymerization ($p_{\text{CO}_2} = 1.5$ MPa, $T = 25$ °C, $t = 2$ – 6 h) of CO₂/SO/LA [55].

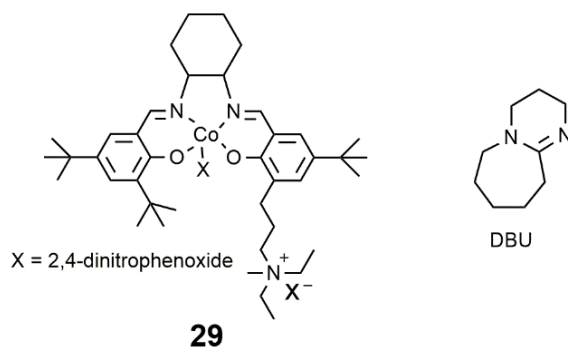


Figure 11. Complex **29** and organocatalyst DBU [55].

Indeed, the cobalt complex **29** produced with high activity poly(styrene carbonate) (PSC) from CO₂ and SO, after the complete consumption of SO, a given amount of H₂O,

which was added to the reaction mixture, resulting in the production of hydroxy-terminated PSC. Consequently, the polycarbonate formed, having the hydroxy chain-end, can act as a macroinitiator for the ROP of LA catalyzed by DBU. As a matter of fact, after adding two equivalent of H₂O with respect to the cobalt catalyst and the removal of CO₂, the addition of LA and DBU results in the production of the AB copolymer PSC-*b*-PLA with molecular weight M_n up to 17.2 kg mol⁻¹ and narrow dispersity ($D = 1.04$ – 1.12). The copolymers obtained from *rac*-LA display a single T_g at lower values with respect to PSC (60–72 °C), and by polymerizing *D*-LA, the resulting diblock copolymers also display a $T_m = 133$ – 137 °C depending on the length of the PLA block.

The same authors also used this strategy to synthesize ABA block copolymers from CO₂/PO/LA. They used the system composed of the salen Co(III) complex **29** activated by PPNY ($Y = CF_3COO^-$) and DBU [56]. In this case, the obtaining of PLA-*b*-PPC-*b*-PLA was possible because of the addition of an excess of H₂O (5–20 equiv. with respect to CO) to stop the CO₂/PO copolymerization of a PPC with two α,ω hydroxy groups. Indeed, the presence of a hydroxy group on both chain-ends allows the growth of two PLA blocks, giving the desired PLA-*b*-PPC-*b*-PLA triblock copolymers. The molecular weight was rather low, M_n up to 20.1 kg mol⁻¹, with narrow dispersity ($D = 1.02$ – 1.04). Additionally, in this case, on one hand the copolymers obtained from *rac*-LA displayed a single T_g at higher values with respect to PPC (43–44 °C), and on the other hand, by polymerizing *D*-LA, the resulting ABA copolymers also displayed a $T_m = 110$ – 128 °C depending on the length of the PLA blocks.

Later on, Pang and coworkers developed a ternary system composed by the dinuclear Co(II) and the Co(III) complexes with salen ligands (Figure 12) and PPNCl [57].

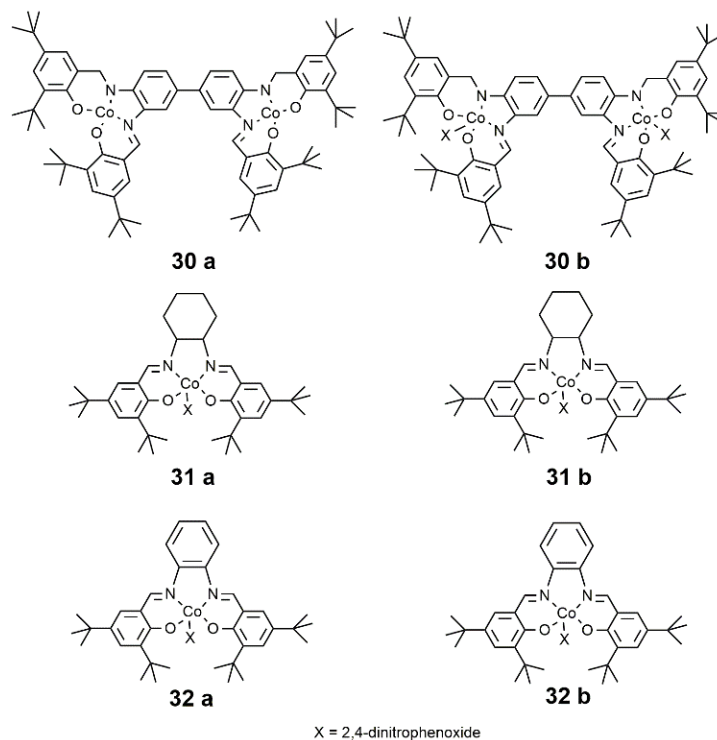
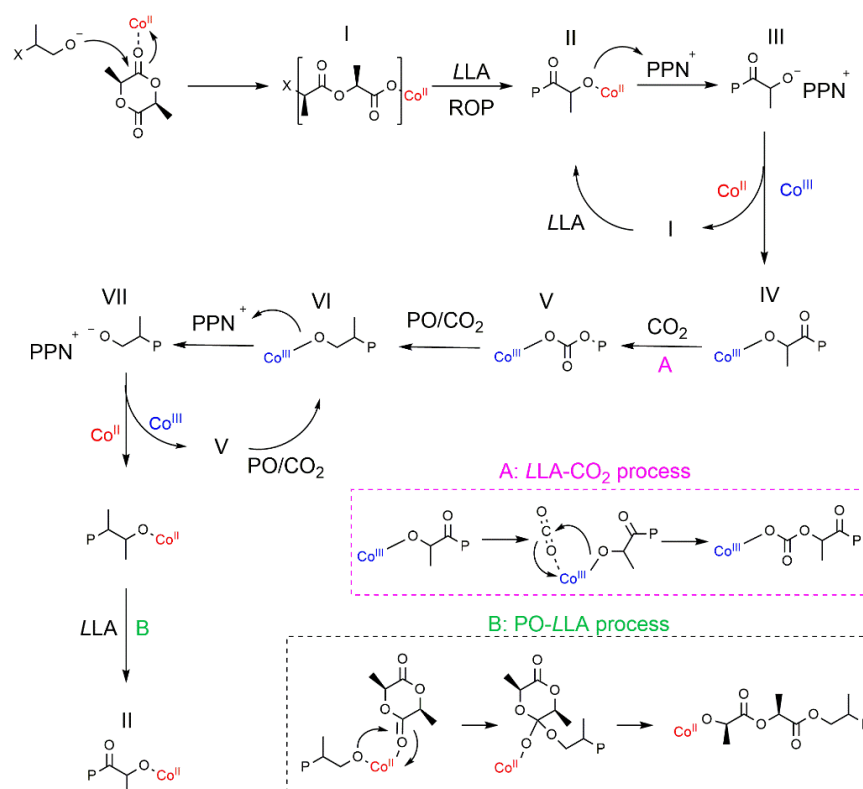


Figure 12. Structures of salenCo^{II} complexes (**30a**–**32a**) and salenCo^{III} complexes (**30b**–**32b**) [57].

Indeed, the Co(II) complexes (**30a**–**32a**) are active in the ROP of LA, and the Co(III) complexes (**30b**–**32b**), in combination with PPNCl, are active in the ROCOP of CO₂ with various epoxides (PO, CHO, SO). The terpolymerization was possible for the chain transfer between the two metal centers (Scheme 8).



Scheme 8. Copolymerization of LLA (*L*-Lactide), PO and CO₂: the proposed cycle. Reproduced with modification and permission from ref [57]. Copyright (2018) Royal Society of Chemistry.

By using **30a** and **30b** and PPNCl in an equimolar amount, the terpolymerization of CO₂/LA/PO gives terpolymers, as revealed by ¹H and ¹³C NMR analysis, possessing a multiblock microstructure with *M_n* up to 13.6 kg mol⁻¹ and narrow dispersity (*D* = 1.19–1.47). Notably, the dispersity broadens in the absence of PPNCl (*D* = 3.15) and with two equivalents of PPNCl (*D* = 2.28), confirming the crucial role of the onium salt in the chain-transfer between the metal centers.

More recently, the same authors further developed this ternary system by changing the Co(II) and Co(III) complexes (**30a** and **30b**), obtaining a more active system or combining a salen Co(III) complex with ZnGA and PPNCl [58].

Finally, in the presence of an enantiopure chiral salenCo(III) complex **33** (Figure 13) in combination with PPN-DNP (PPN = bis(triphenylphosphine)iminium, DNP = 2,4-dinitrophenoxide), Lu and coworkers also succeeded in producing CO₂/CHO/BBL terpolymers with isotactic -PCHC blocks [59].

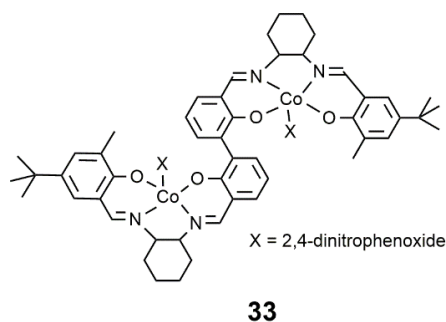


Figure 13. Enantiopure chiral dinuclear (*S,S,S,S*)-**33** complex [59].

More in detail, when an equimolar amount of CHO and BBL is present in the feed, the terpolymerization proceeds smoothly with the good conversion of both monomers

($p\text{CO}_2 = 2 \text{ MPa}$, $T = 40 \text{ }^\circ\text{C}$, $t = 2\text{--}4 \text{ h}$). The resulting copolymers display, in the $^1\text{H NMR}$ spectra, the signals relative to the carbonate-ester linkages, indicating a multiblock structure. Molecular weights are rather low, $M_n = 3.3\text{--}14.6 \text{ kg mol}^{-1}$, with narrow dispersity ($D = 1.19\text{--}1.44$), and display thermal behavior with a $T_m = 204\text{--}220 \text{ }^\circ\text{C}$, evidencing the presence of stereoregular crystalline blocks along the polymer chain.

In Table 2, the main data relating to the terpolymerizations of CO_2 with epoxides and cyclic esters discussed in this second part are summarized.

Table 2. Summary of terpolymerization of CO_2 with epoxides and cyclic esters.

Catalyst	Monomers	Polymerization Conditions $p\text{CO}_2, T, t$	M_n * (D) kg mol^{-1}	Polymer Microstructure	Ref.
1	$\text{CO}_2, \text{PO}, \text{CL}$	4.0 MPa, 50–90 °C, 16 h	-	random	[44]
4	$\text{CO}_2, \text{PO}, \text{CL}$	2.8 MPa, 60 °C, 40 h	27.5 (1.50–2.97)	block	[41]
4	$\text{CO}_2, \text{PO}, \text{CL}$	1.0 MPa, 60 °C, 6 h	10.8 (1.3–1.6)	grafted	[42]
15–22	$\text{CO}_2, \text{CHO}, \text{LA}$	4.0 MPa, 90 °C, 16 h	41.6 (1.09–1.96)	alternated/random	[43]
23	$\text{CO}_2, \text{PO}, L\text{-LA}$	4.0 MPa, 70 °C, 10 h	15.4 (4.2–9.9)	tapered/random	[45]
24	$\text{CO}_2, \text{CHO}, \text{CL}$	0.1 MPa, 80 °C, 2–21 h	4.8 (1.38–1.49)	block	[46]
24	$\text{CO}_2, \text{CHO}, \text{CL}$	0.1 MPa, 80 °C, 16–25 h	13.8 (1.29–1.49)	block	[48]
24	$\text{CO}_2, \text{CHO}, \text{VCHO}, \text{PA/NA}, \text{CL}$	0.1 MPa, 100 °C	16 (1.06–1.16)	block	[49]
25–26	$\text{CO}_2, \text{CHD}, \text{DL}$	2 MPa, 40–100 °C, 2–24 h	114 (1.38–1.49)	block	[50]
27	$\text{CO}_2, \text{CHO}, \text{DL}$	2 MPa, 80 °C, 21 h	71.9 (1.07–1.16)	block	[52]
28	$\text{CO}_2, \text{BBL}, \text{CHO/CPO}$	0.3–4 MPa, 60 °C, 0.1–7 h	166 (1.2–1.8)	random/block	[53]
28	$\text{CO}_2, \text{BBL}, \text{LO}$	0.9–4 MPa, 40–60 °C, 8–22 h	233 (1.23–1.39)	random/block	[54]
29	$\text{CO}_2, \text{SO}, \text{LA}$	1.5 MPa, 25 °C, 2–6 h	17.2 (1.04–1.12)	block	[55]
29	$\text{CO}_2, \text{PO}, \text{LA}$	1.5 MPa, 25 °C, 1–4 h	20.1 (1.02–1.04)	block	[56]
30–32	$\text{CO}_2, \text{PO/CHO/SO}, \text{LA}$	2 MPa, 60 °C, 4–48 h	13.6 (1.19–3.15)	block	[57]
33	$\text{CO}_2, \text{CHO}, \text{BBL}$	2.0 MPa, 40 °C, 2–4 h	14.6 (1.19–1.44)	block	[58]

* The highest reported value.

4. Conclusions

The possibility to terpolymerize CO_2 with epoxides and other cyclic monomers (cyclic esters, organic anhydrides) offers not only a simple way to obtain a wide range of materials with unprecedented properties, but also the possibility to have such material in a completely sustainable way, combining CO_2 with monomers originating from biomasses. The last decade has witnessed tremendous efforts in the development of efficient catalytic systems able to combine the ROP of cyclic esters and the ROCOP of CO_2 or cyclic organic anhydrides with epoxides, allowing us to obtain polymers with various microstructural features spanning from statistical, to AB, ABA, and even more complex architectures. Notwithstanding these endeavors, however, fine control of the microstructure and the molecular weight is still a major challenge in the field. Furthermore, the number of metal centers active in the terpolymerization of CO_2 with epoxides and cyclic esters of anhydrides is still limited, offering active catalysts only in the case of Zn, Cr and Co, and, only in the case of the terpolymerization with cyclic anhydrides, in the presence of metal-free borane-based catalysts.

Therefore, this review is not only an overview on the progress in the field, but also shows that there is a large space for further developments. More precisely, higher control over the polymer microstructure, an extension to a wider range of monomers and the development of new catalytic systems based on other metal centers to improve the activity and the control of the polymerization process will be highly desirable targets in future developments.

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