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**Citation for published version:**

Garden, JA 2017, 'Exploiting multimetallic catalysts to access polymer materials from CO<sub>2</sub>', *Green Materials*, pp. 1-6. <https://doi.org/10.1680/jgrma.16.00022>

**Digital Object Identifier (DOI):**

[10.1680/jgrma.16.00022](https://doi.org/10.1680/jgrma.16.00022)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

Green Materials

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# Exploiting Multimetallic Catalysts to Access Polymer Materials from CO<sub>2</sub>

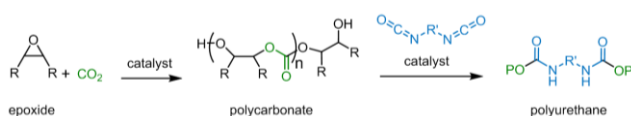
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**Polycarbonates and polyurethanes derived from CO<sub>2</sub> have the potential to consume a greenhouse gas and convert it into value added polymer products. To be commercially viable, these processes are dependent on the development of highly efficient polymerization catalysts, which are often multimetallic. One emerging method to improve catalyst efficiency is through the design of co-operative, mixed-metal catalysts. Such heterometallic, homogenous catalysts have shown significantly improved performance metrics for CO<sub>2</sub>/epoxide ring-opening copolymerization, in comparison to their homometallic analogues. This perspective highlights the recently realized reactivity enhancements achieved using multimetallic catalysts, along with the material properties and scope of CO<sub>2</sub>-derived polymers.**

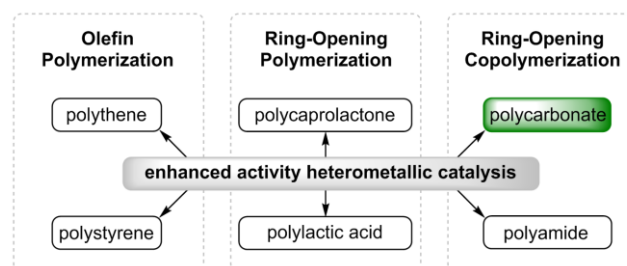
## 1. Introduction

Reforming the current plastics industry to incorporate renewable resources, reduce our reliance on petrochemical feedstocks and diminish our impact on the environment presents a major challenge for the immediate future. Although this is a significant task, progress has already been achieved with some commercial polymer materials now produced either partially or wholly from renewable sources.<sup>1</sup> One of the best-established commercial examples is bio-degradable polylactic acid, produced through the ring-opening polymerization (ROP) of bioderived lactide. Another particularly promising strategy is the ring-opening copolymerization (ROCOP) of CO<sub>2</sub> and epoxides, to form polycarbonates (Scheme 1). In today's climate, the use of CO<sub>2</sub> as an alternative C1 feedstock is rapidly gathering attention, as CO<sub>2</sub> is abundant, cheap, non-toxic and a waste product from many industrial processes. The CO<sub>2</sub>/epoxide ROCOP process is currently on the brink of commercialization, and the resultant telechelic polycarbonates can subsequently be used to synthesize polyurethanes, through reaction with a diisocyanate (Scheme 1). Polyurethane materials have many applications, including construction materials, high performance coatings and furniture.<sup>2</sup> Assessment of the life cycle analysis of polyurethane materials shows that incorporating 20% of CO<sub>2</sub> content can reduce the overall greenhouse gas emissions of the polymer synthesis by up to 19%.<sup>3</sup>



**Scheme 1.** Synthesis of polycarbonates and polyurethanes from CO<sub>2</sub>/epoxide ring-opening copolymerization.

The commercial success of producing sustainable polymer materials is crucially dependent on a suitable and efficient catalyst system; some of the most active are multimetallic complexes. The emerging theme of mixed-metal (heterometallic) cooperativity is an attractive means to improve catalyst activity and selectivity.<sup>4</sup> This concept is particularly appealing, from both an economic and environmental perspective, when the metals involved are abundant, low-toxicity main-group and first-row transition metals. When two different metals are held in close proximity within a molecular environment, cooperative effects are often observed, which can give unusual and sometimes unexpected reactivities that cannot be accessed using either homometallic component in isolation.<sup>4-10</sup> Elegant homogeneous heterometallic catalysts have been designed for a range of polymerizations, which outperform their homometallic analogues in terms of activity and selectivity (Figure 1).<sup>11-21</sup> However, until recently, heterometallic ROCOP catalyst development was lagging behind that of olefin polymerization and the ROP of lactones.



**Figure 1.** Polymer materials accessed using high efficiency heterometallic catalysts.

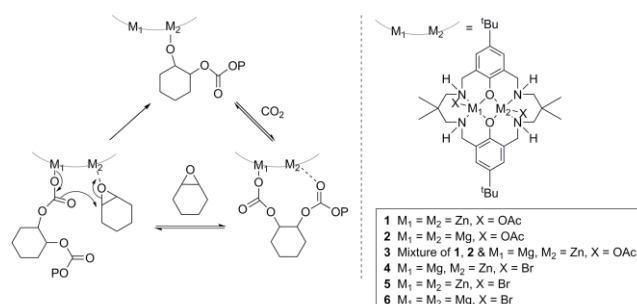
## 2. Advances in Multimetallic Catalyst Development for CO<sub>2</sub>/epoxide ROCOP

The presence of a catalyst underpins the successful synthesis of polycarbonates from CO<sub>2</sub>/epoxide ROCOP, where some of the most active are homogeneous homometallic metal complexes based on salen,<sup>22</sup> porphyrin,<sup>23</sup>  $\beta$ -diiminato<sup>24</sup> or di-phenolate<sup>25</sup> ligand scaffolds.<sup>26-29</sup> Careful homogeneous catalyst design has led to improved activities and selectivities, along with high CO<sub>2</sub> uptake (>99%) to form nearly perfect polycarbonate linkages. A breakthrough in the mechanistic understanding came from the realization that epoxide opening and enchainment could occur through a bimetallic mechanism, as discerned using dimeric  $\beta$ -diiminato zinc acetate catalysts bearing two zinc centres in close proximity.<sup>30</sup> This finding inspired the development of multimetallic catalysts comprising two metals in a dinucleating ligand scaffold,<sup>31-34</sup> which have shown exceptional activities<sup>24, 35</sup> and some of which are active at just 1 bar of CO<sub>2</sub> pressure.<sup>36-39</sup> However, until recently, the development of homogeneous heterometallic catalysts has been neglected, despite reports that ternary mixed-metal systems display cooperative heterometallic effects, and have demonstrated good activities for CO<sub>2</sub>/epoxide ROCOP.<sup>40-48</sup> A major contributor to this lack of investigation is the synthetic challenge associated with the synthesis and characterization of heterometallic catalysts, which often includes the synthesis, purification and manipulation of highly air- and moisture-sensitive starting materials.

Detailed kinetic and mechanistic studies based on a multimetallic catalyst, supported by a macrocyclic ligand scaffold (Scheme 2, RHS, **1**), have indicated that the polymerization occurs through a “chain shuttling” mechanism, where the growing polymer chain switches between two metal centres (Scheme 2, LHS).<sup>49</sup> These insights suggested that the two metal centres play different roles in the propagation. Whilst one metal binds the epoxide, to position it in close proximity and activate it towards nucleophilic attack, it is the second metal carbonate bond which ring opens the epoxide to propagate the polymerization. These studies hinted that a heterometallic catalyst could exhibit even greater activity than the homometallic systems. This hypothesis was further supported by preliminary experimental studies, where a mixed catalyst system comprising di-Mg, di-Zn and MgZn acetate complexes (Scheme 2, **3**), gave double the activity of a 1:1 mixture of the di-Zn (Scheme 2, **1**) and di-Mg (Scheme 2, **2**) acetate catalyst systems.<sup>50</sup>

In 2015, a pure, homogeneous, heterometallic MgZn catalyst was reported (Scheme 2, **4**).<sup>18</sup> The preparation of this complex presents a significant synthetic challenge: to incorporate two labile metals of similar properties within a symmetrical ligand scaffold, whilst avoiding redistribution of the two metal centres to form the homometallic analogues (**5** and **6**). This heterometallic catalyst gave efficient, well-controlled polymerizations, with TOF

values of 624 h<sup>-1</sup> achieved at 120 °C and 50 bar of CO<sub>2</sub> pressure. Heterometallic **4** showed significantly improved performance metrics for CO<sub>2</sub>/cyclohexene oxide (CHO) ROCOP, in comparison to the homometallic analogues, either alone or in combination. Notably, **4** is active at atmospheric pressure, and the productivities (turnover numbers, TON = 344) and activities (turnover frequencies, TOF = 34 h<sup>-1</sup>) are five times higher than a 1:1 mixture of the homometallic di-Mg and di-Zn analogues.



**Scheme 2.** “Chain shuttling” mechanism proposed for CO<sub>2</sub>/epoxide copolymerization by a multimetallic catalyst.<sup>49,50</sup>

The concept of heterometallic reactivity enhancement has since been extended to homogeneous rare-earth metal complexes. Rare-earth metal catalysts are attractive for CO<sub>2</sub>/epoxide ROCOP, as the oxyphilic and Lewis acidic nature of rare-earth metals can facilitate epoxide activation and CO<sub>2</sub> insertion. Yao *et al.* recently reported the synthesis of two novel heterometallic catalysts for CO<sub>2</sub>/CHO ROCOP, based on Nd<sub>2</sub>Zn and Y<sub>2</sub>Zn complexes supported by di-phenolate ligands.<sup>51</sup> These novel complexes display high catalyst activities with TOF values up to 267 h<sup>-1</sup> at 70 °C and 0.7 MPa. Furthermore, these systems give impressive, albeit lowered, catalyst activities at ambient temperature (TOF = 82 h<sup>-1</sup>, 25 °C, 7 bar of CO<sub>2</sub> pressure). These heterometallic catalysts were successfully applied to synthesize high molecular weight poly(cyclohexene carbonate) (M<sub>n</sub> = 296 kg mol<sup>-1</sup>). In contrast, the homometallic analogues are completely inactive towards CO<sub>2</sub>/CHO ROCOP. These recent studies highlight how heterometallic systems can offer new potential within ROCOP, and provide an interesting direction for future catalyst exploration.

## 3. CO<sub>2</sub>-derived Polycarbonates and their Material Properties

The ROCOP of CO<sub>2</sub>/epoxides is an attractive route to synthesize polycarbonates which can contain up to 50% CO<sub>2</sub> by mass. The synthesis of CO<sub>2</sub>-derived polycarbonates is considered to be safer than that of conventional polycarbonate materials, which are often produced through the condensation polymerization of bisphenol-A (BPA) with phosgene, which is a highly toxic nerve gas.<sup>52</sup> It is worth noting that an alternative route, based on a melt process using BPA and diphenyl carbonate, is also applied industrially.<sup>53</sup> However, it is important to note that the material properties of

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CO<sub>2</sub>-derived polycarbonates differ from conventional polycarbonates. The amorphous polymers derived from BPA/phosgene copolymerization display high impact strength, heat resistance, toughness and transparency, and are used in a range of applications including medical, optical and electronic devices.<sup>54</sup> CO<sub>2</sub>-derived polycarbonates give markedly different material properties, which vary according to the molecular weight and the epoxide co-monomer selected.

Within academic research, CHO is often selected as the benchmark epoxide for catalyst development, on account of its lower toxicity and ease of handling compared to other epoxides. Characterization studies of high molecular weight poly(cyclohexene carbonate) (PCHC) with a broad distribution ( $M_w = 252 \text{ kg mol}^{-1}$ ,  $\bar{D} = 6$ ) have revealed it to be a brittle material, which displayed an elongation at break of just 1-2% and a  $T_g$  value of 115 °C.<sup>55</sup> Industrial interest has largely focused on CO<sub>2</sub>/propylene oxide ROCOP, where the poly(propylene carbonate) products have environmental benefits, including biodegradability and benign decomposition emissions. Poly(propylene carbonate) materials are of high commercial relevance, thanks to their suitability for many applications including adhesives, coatings and binders.<sup>22, 56</sup> However, the range of applications is limited by the low softening temperature of this material ( $T_g = 40 \text{ °C}$ ). Studies of a homologous series of CO<sub>2</sub>-derived polycarbonates have shown that poly(propylene carbonate), poly(pentene carbonate), poly(hexene carbonate), poly(octene carbonate) and poly(cyclohexene carbonate) are all amorphous materials, and display initial decomposition temperatures ( $T_d$ ) under 300 °C, as determined using TGA and DSC analysis.<sup>57</sup> The  $T_d$  values increase in line with increasing hydrocarbon content of the polymer, with the exception of PCHC, which displays the highest initial decomposition temperature ( $T_d = 290 \text{ °C}$ ) on account of the stiff cyclohexyl rings incorporated into the polymer chain.

To access completely bio-based poly(carbonates) from CO<sub>2</sub>/epoxide ROCOP, additional research has focused on the use of renewable epoxides, such as limonene oxide<sup>58</sup> and 1,4-cyclohexadiene oxide.<sup>59</sup> Limonene oxide is derived from limonene, an alicyclic terpene which is annually produced on a scale exceeding 70, 000 tons from waste orange peel.<sup>60</sup> High molecular weight (>100 kg mol<sup>-1</sup>) poly(limonene carbonate) has successfully been synthesized through CO<sub>2</sub>/limonene oxide ROCOP, using a  $\beta$ -diiminate zinc acetate catalyst.<sup>52</sup> This bio-based polycarbonate displayed attractive material properties, including excellent thermal resistance ( $T_g = 130 \text{ °C}$ ), thermal stability (up to 240 °C), hardness and optical transparency. Indeed, recent advances have shown that post-polymerization modification of poly(limonene carbonate) can offer rigid polymers, with tunable  $T_g$  values up to 180 °C, as a potential

alternative to BPA-based polycarbonates.<sup>61, 62</sup> An alternative renewable epoxide, 1,4-cyclohexadiene oxide, has been derived from the mono-epoxidation of cyclohexa-1,4-diene from fatty acid methyl esters found in plant oils.<sup>59</sup> Subsequent ROCOP with CO<sub>2</sub> produced renewable, unsaturated polycarbonates, with the same  $T_g$  value as the saturated analogue, PCHC ( $T_g = 115 \text{ °C}$ ).

Through rapid recent advances in CO<sub>2</sub>/epoxide ROCOP, a range of polycarbonate materials have been synthesized, with different material properties. To make these processes truly sustainable, the CO<sub>2</sub> source must be carefully considered. High energy compressions of CO<sub>2</sub> gas should be avoided, and the reaction system must be tolerant towards impurities found in industrial waste CO<sub>2</sub>. Promising advances have recently been made in this area. The application of metal-organic frameworks (MOFs), to capture, store and release CO<sub>2</sub> into CO<sub>2</sub>/epoxide ROCOPs, has been reported by Darensbourg *et al.* The commercially available MOF, HKUST-1 ([Cu<sub>3</sub>(btc)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>], where btc = benzene-1,3,5-tricarboxylate), was used to capture CO<sub>2</sub> under aerobic conditions at atmospheric pressure.<sup>63</sup> The captured CO<sub>2</sub> was thermally released and directly copolymerized with propylene oxide or *cis*-2-butylene oxide, in the presence of a Co(III) salen catalyst, to form poly(propylene carbonate) or poly(butylene carbonate), respectively. Importantly, the polymer yields obtained and the material properties observed were near-equivalent, when the CO<sub>2</sub> source was the MOF filled under aerobic conditions, or a pressurized CO<sub>2</sub> cylinder in the absence of HKUST-1. Studies using CO<sub>2</sub> captured from a CCS demonstrator plant attached to a UK power station showed that a homogeneous di-Mg catalyst (Scheme 2, 2) could successfully catalyze CO<sub>2</sub>/CHO ROCOP.<sup>36</sup> The catalyst performance was almost equivalent using this “impure” CO<sub>2</sub> source in comparison to “pure”, research grade CO<sub>2</sub>. Further studies revealed that this catalyst system demonstrated a high level of tolerance towards added impurities which are often present in captured CO<sub>2</sub>, including air, water, CO, N<sub>2</sub> and amines. These findings indicate that CO<sub>2</sub>/epoxide ROCOP has real world potential to convert waste CO<sub>2</sub> to useful polymer materials. There is much scope to derivatize such polycarbonate materials, through reaction with diisocyanates to form polyurethanes,<sup>64</sup> “switch chemistry” to form block copolymers,<sup>65, 66</sup> or post-polymerization derivatization of functional groups on the epoxide, such as olefins<sup>59</sup> or trimethoxysilane.<sup>67</sup>

#### 4. Conclusion

Whilst homogeneous heterometallic catalyst design for CO<sub>2</sub>/epoxide ROCOP is still in its infancy, recent findings suggest that it has the potential to grow into a fruitful area of high activity catalyst development. Not only have enhanced activities been reported using cooperative heterometallic catalysts but good

activities have been achieved under atmospheric pressure and ambient temperature reaction conditions. Thanks to efforts across a range of fields, including catalyst design, engineering and materials, CO<sub>2</sub>-derived polymers synthesized through CO<sub>2</sub>/epoxide ROCOP are now on the edge of commercialization.

This process provides an exciting opportunity to expand and exploit multimetallic catalyst development for a range of CO<sub>2</sub>-derived materials in the immediate future, to contribute to a more sustainable world.

**Acknowledgements** J. A. Garden gratefully acknowledges the University of Edinburgh for funding (Christina Miller Research Fellowship).

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