

Valuing CO₂ in the development of polymer materials

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Abstract. Reducing the concentration of carbon dioxide in the atmosphere is a major challenge for humanity as well as for living species on Earth. Not least because of the adverse effects of climate warming caused by the anthropological emissions of the CO₂. We are interested in a complementary approach to capturing and storing CO₂, which is to use CO₂ as a raw material for chemical reactions. Specifically, it is a question of using the CO₂ for the synthesis of certain types of biocompatible polymers. For the time being, these remain restricted to polycarbonates for economic reasons. The use of CO₂ is also motivated by its abundance as a potentially unlimited source of carbon. The challenge of this chemical process is to use appropriate catalysts to synthesize polycarbonates in sufficient quantities and with interesting physical properties. There is also talk of producing biodegradable and biocompatible polycarbonates to ensure a relatively green footprint compared to conventional polycarbonate production processes.

1 Introduction

The increase in emissions of carbon dioxide (CO₂) into the atmosphere, due to the consumption of fossil fuels (coal, gas and oil), is the main cause of climate change. Because CO₂ is a greenhouse gas, it blocks heat from the planet. Its high concentrations in the atmosphere, reaching a level above 415 parts per million in 2019 [1] (historical record) have led to an increase in global temperature with devastating effects on the environment and human well-being (Fig. 1).

Although the CO₂ can be eliminated by natural processes, the current rate of CO₂ emissions exceeds that of natural elimination. This has led to growing public dissatisfaction, putting pressure on governments around the world to take action to reduce emissions from CO₂ and exploit its abundance in the atmosphere.

The top priority is therefore to avoid CO₂ emissions, mainly by developing renewable energies, also reducing energy consumption and improving energy efficiency. At the same time, energy companies are also working on Carbon Capture and Storage (CCS) which is a major strategy that can be used to reduce CO₂ emission. There are three methods for CCS: pre-combustion capture, oxy-fuel process, and post-combustion capture. Among them, post-combustion capture is the most important one because it offers flexibility and it can be easily added to the

operational units [2–4]. Beside the geological storage, the CO₂ mineralization or the algae feeding are two complementary technologies to “sequester” CO₂ [5].

Beyond these interesting approaches that tackle with the stakes with the stakes of reduction CO₂ emissions, there is also another approach, which interestingly sees CO₂ as a new chemical building block. Hence, even if chemistry accounts only for 10% of oil and gas consumption, thus same percentage of CO₂ emission, there is still interest to reduce environmental impacts of chemistry through the use of renewable resources, to follow the principles of Green Chemistry. Hence, considering CO₂ as a raw material, known as Carbon Capture and Use (CCU), notably, as a basic brick in the production of polymers, may have also interest to follow the principles of Green Chemistry. Hence, CO₂ could be a renewable and inexhaustible platform chemical, produced locally from multiple sources and find utility for the synthesis of commodities (methanol, urea, (in)organic carbonates, formic acid), fuel (methane, alkanes) and particularly polymers. The polymers annual production is around 400 million tonnes compared to the global CO₂ emission (nearly 40 Gt/y), the utilization of CO₂ a raw material to fabricate polymers will only show marginal effect on the anthropologic CO₂ emissions and climate change but it could draw the reuse of CO₂ and improves the circularity of polymer economy [6, 7].

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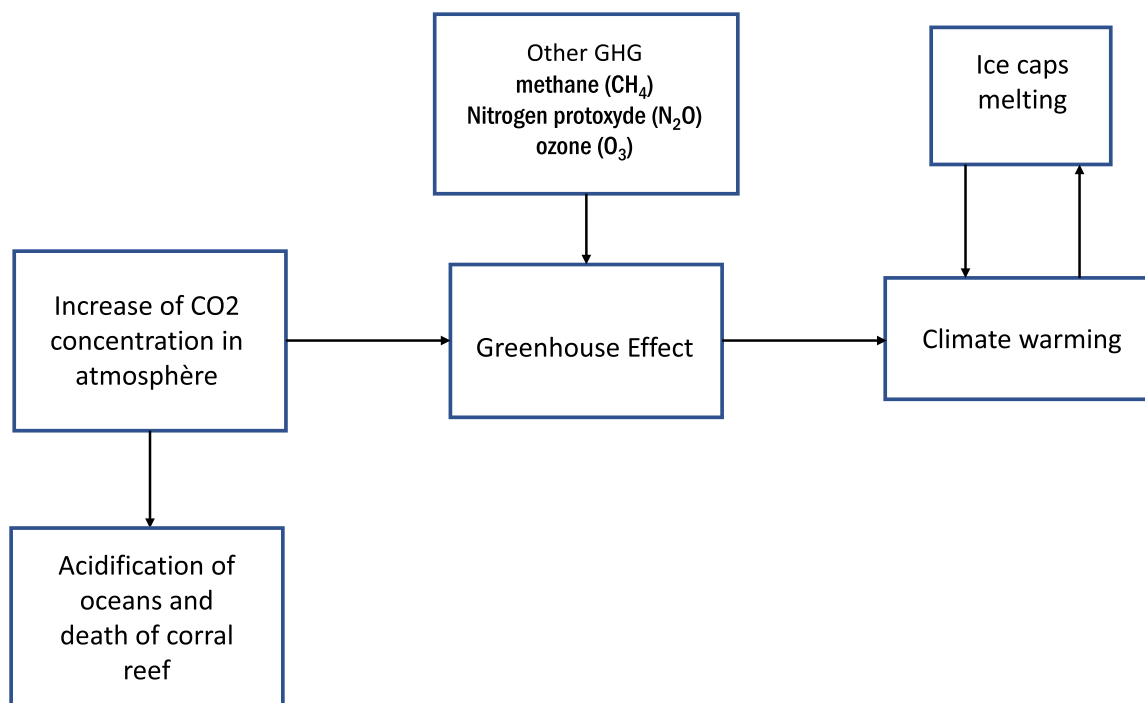


Fig. 1. Main effects of CO₂ emissions.

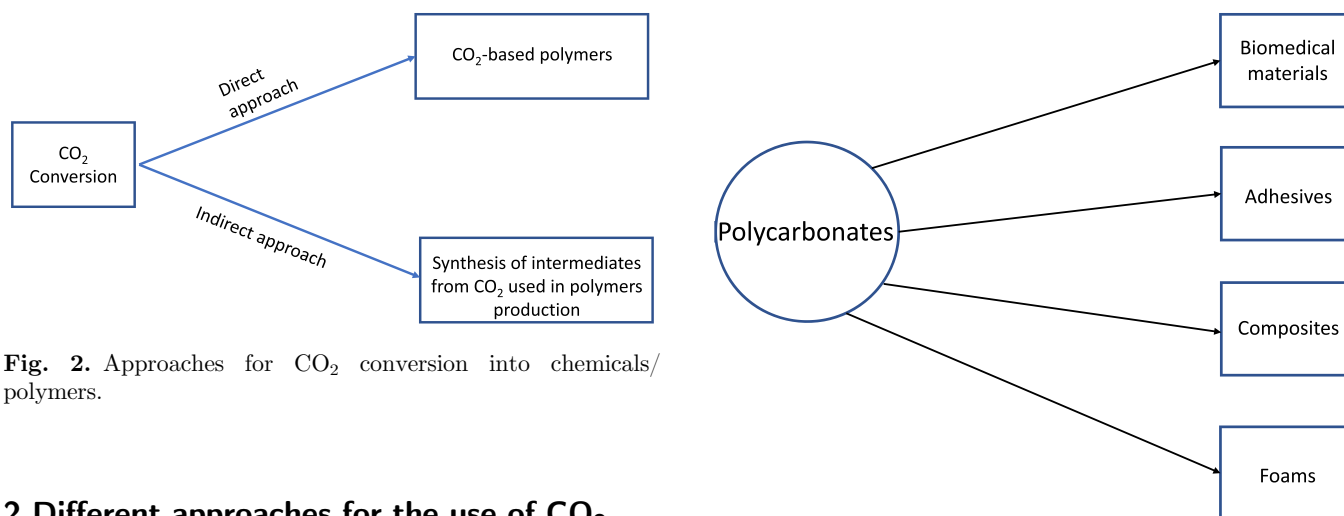


Fig. 2. Approaches for CO₂ conversion into chemicals/polymers.

2 Different approaches for the use of CO₂

Until now, the production of polymers has been mainly based on petrochemical raw materials, *i.e.* mainly oil. However, we dispose of finite fossil resources while CO₂ is inexhaustible. In addition, converting oil into precursor chemicals also consumes energy, resulting in further CO₂ emissions, even if industries has developed improved energy efficacy for last decades. Moreover, the chemical industry has already made a lot of progress in implementing CO₂ as a new raw material [8–17].

The use of CO₂ for the manufacture of plastic is beneficial to the environment in two ways: First, the CO₂ is directly incorporated into the polymers and partially replaces oil as a raw material. In order to compare efficacy

Fig. 3. Examples of applications of polycarbonates.

of the whole process from cradle to gate (raw material), a Life Cycle Assessment would be required. Recently, some companies have studied such analyses to improve their processes either conventional or new [18].

There are two chemical approaches to incorporating CO₂ into the development of polymer materials (Fig. 2): either directly using it as a polymer construction block, or indirectly through the involvement of CO₂-based monomers to form other polymers. Both approaches are proven possible and feasible to a certain extent [19–27].

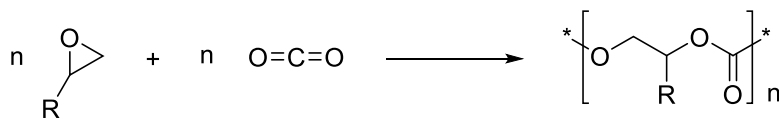


Fig. 4. Catalyzed copolymerization of CO₂ and epoxides yielding polycarbonates.

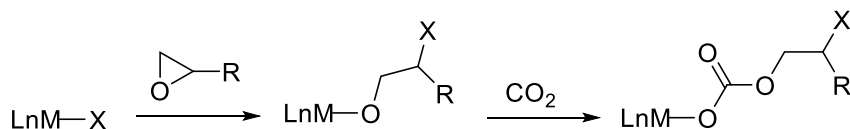


Fig. 5. Initiation of General coordination–insertion mechanism for the synthesis of PCs by ROCOP of CO₂ and epoxides.

2.1 The direct approach

Chemical fixation of CO₂ is very interesting from a carbon use perspective, as CO₂ is a low-cost, non-toxic, carbon-rich resource that can be used to produce value-added chemicals and materials. The most promising area of use of CO₂ is the co-polymerization of CO₂ and epoxide monomers to obtain Polycarbonates (PCs), which has been pioneered by Inoue *et al.* in 1969 [28]. These polymers not only have excellent barrier properties to oxygen and water, but they also have excellent biocompatibility and biodegradability. Given their exceptional properties, PCs can be used as non-polluting materials for the production of disposable medical products, in addition to food packaging, adhesives and composite materials, etc. (Fig. 3)

However, it is necessary to mention that the thermodynamic stability of the CO₂, limits its use as a reagent. Hence the value of using energy-rich reagents such as epoxides in the presence of suitable catalysts (Fig. 4) [29–38].

Indeed, since the pioneering work of Inoue *et al.* who prepared Polypropylene Carbonate (PPC) from the CO₂ and Propylene Oxide (PO), using a heterogeneous catalytic water/diethylzinc system, the copolymerization of epoxides and CO₂ has been widely developed. In general, the catalysts used for copolymerization of CO₂ and epoxides are components based on transition metals or metals from the main group of elements that are abundant on earth, such as Zn, Co, Cr, Mg, Al, which are either insoluble or soluble in the reaction system during copolymerization.

The most accomplished CO₂/epoxide copolymerization systems are based on the Transition Metal Complexes Cr (III), Co (III) or Zn (II) with Schiff base ligands. In the case of CO₂ copolymerization and Propylene Oxide (PO), Polypropylene Carbonate (PPC) with a molar mass of up to 300,000 g mol⁻¹ can be prepared using a recyclable catalyst ((salen)Co(III)) [39].

2.1.1 Catalysts

Depending on the type of catalyst, the reaction can be directed to produce a specific type of polymer. A wide range of metal complexes (Zn, Cr, Co, Al, Fe) with the general formula “LnMX” (Ln is a suitable, often multidentate ligand; X is typically a halide or other suitable initiating

group; M is typically a di- or trivalent metal cation) have been designed to promote the ROCOP of CO₂ with epoxides (Fig. 5) [40, 41].

These catalysts can be roughly divided into two categories:

- The homogeneous catalysts, represented by cobalt and chromium with salen ligands.
- The heterogeneous catalysts represented by zinc glutarate and Double Metal Cyanides (DMCs).

Homogeneous catalysts are more active and selective compared to heterogeneous ones, and are more suitable for research because their chemical structures are well defined. However, these first ones require a multi-step synthesis due to the complexity of the ligands (Fig. 6). However, regardless of the catalysts used in copolymerization, the polycarbonates produced are contaminated with metals, making them toxic and coloring during degradation. A disposal step after polymerization is therefore necessary to ensure a wide applicability, especially when it comes to products dedicated to electronic processing or in packaging.

Recently, great importance has been placed on processes that are environmentally friendly. This has resulted in the use of catalysts based on metal complexes of the main group.

Indeed, with catalysts such as Co(III) and Cr(III) that are effective, traces of metal residues are obtained inside the resin that can lead to problems of toxic and coloured degradation, which limits their fields of applicability. These affect their performance and therefore limit their applications. However, this is not the case for aluminum, one of the first metals studied as a catalyst since the discovery of CO₂ copolymerization and epoxides. Aluminum is becoming abundant on land, cheap and biocompatible. Aluminum complexes are also known to catalyze a wide range of other polymerization reactions, which would allow the development of CO₂-based sequential copolymers other than epoxides. However, due to the competitive homopolymerization of aluminum-catalyzed epoxides, more work will be needed to improve its catalytic effects [42].

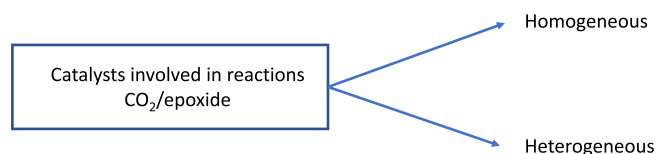


Fig. 6. Different kinds of catalysts.

2.2 The indirect approach

The CO₂ can also be used to produce chemical components for polymer synthesis, particularly urea. Urea is widely used in the fertilizer industries as a rich source of nitrogen. Urea is non-toxic and is a raw material for the production of many important chemical compounds such as various plastics, resins and adhesives. Nowadays, approximately 200 Mt/y of urea is produced in the world. To produce this amount of urea, 150 Mt/y of CO₂ is required. The most common method for production of urea is reforming natural gas, producing both carbon dioxide and ammonia. Carbon dioxide can also be produced from combustion. Hence, considering, CO₂, nitrogen, and water as the main products of the combustion process, capturing of CO₂ and removing water from the combustion gas can lead to a high purity N₂. This N₂ could react with hydrogen to yield ammonia. Therefore, the production of urea by reaction of ammonia with CO₂, captured from combustion flue gases, would increase the economic justification of CO₂ capture unit [43].

This opens up the possibility of obtaining a range of thermosetting polymers, such as Urea-Formaldehyde (UF) resins and Melamine-Formaldehyde (MF), as well as industrial plastics, such as Polyoxymethylene (POM) or Polymethylmethacrylate (PMMA). In the first case, UF resin can be obtained from urea, which is directly produced by the CO₂'s reaction with Ammoniac, and Formaldehyde, which is obtained from methanol derived from the CO₂; similarly, the ingredients of MF resins are Melamine, obtained from urea, and Formaldehyde. For the examples provided last, the POM can be produced from the CO₂ via formic acid, and PMMA from methyl Acrylate obtained from methanol derived from CO₂ [44].

3 Properties of polycarbonates synthesized from CO₂

Despite interesting properties, polycarbonates from catalyzed CO₂ reactions and epoxides exhibit a non-variable structure, linked to alternation of CO₂ and epoxide units, which limits their properties. Moreover, the absence of aromatic ring, compare to conventional polycarbonates, reduces their thermo-mechanical properties.

Hence, the limited properties of these PCs can be extended by combining them with biopolymers, such as starch, or synthetic polymers, such as PMMA, where CO₂-based PCs confer biodegradability or act as an important additive. In addition, these polycarbonates can also be treated using traditional processing techniques, such as

injection molding or molten extrusion. This makes it possible to produce on an industrial scale. PCs from Bisphenol A-based CO₂ can also be synthesized to produce superior traditional polycarbonates, via greener pathways without toxic phosgene. Additionally, high Tg CO₂-based polycarbonates have been reported by Kindermann *et al.* who succeeded in the copolymerization of CO₂ and limonene oxide to obtain polycarbonates with unprecedented high glass transition of up to 180 °C [45]. However, currently, PCs produced by conversion of CO₂ are mainly end functionalized with hydroxyl groups and used as poly (carbonate-ether) polyols, for the synthesis of Polyurethane (PU) with diisocyanates [46].

4 Conclusion

In conclusion, it is important to note that while this area of research is hardly new, the use of CO₂ as a raw material remains one of the most interesting and visionary technologies. With limited fossil resources, the use of CO₂ as a chemical raw material is a promising approach to global carbon management. In this sense, the use of CO₂ to produce polymers has an obvious ecological advantage over conventional polymers. It is even possible to improve this situation by following the different approaches of direct and indirect use. The present review was focused on CO₂-based materials that could be manufactured from precursors already produced in large scale (such as urea) or that are reaching the industrial scale (PC). Pioneering examples already show that the chemical use of CO₂ for the production of polymers on an industrial scale is possible. Hence, the use of CO₂ as an alternative raw material in the chemical industry is still in its infancy. Future efforts will aim to demonstrate the potential of this gas and initiate a possible change of image, from a greenhouse gas harmful to the environment to a new useful and sustainable raw material.

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