

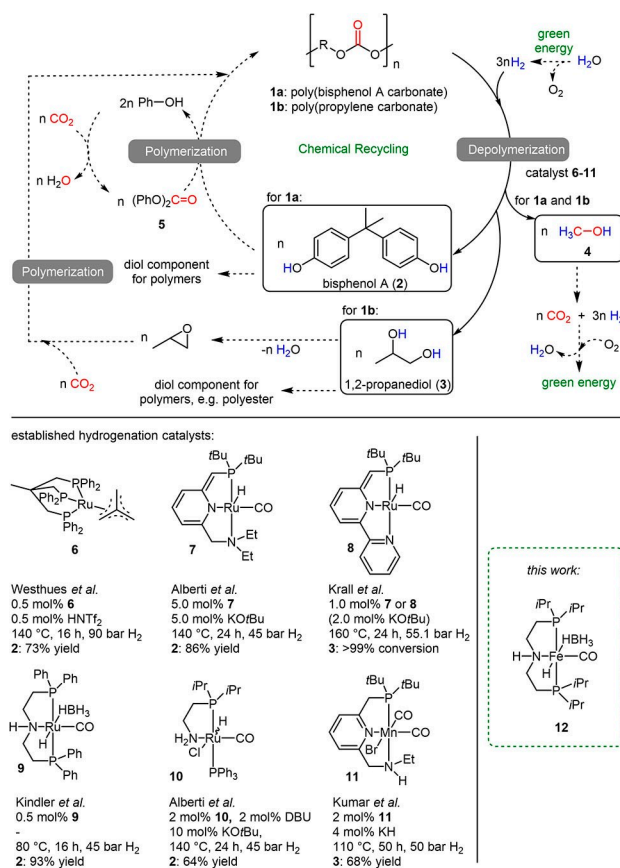
# Hydrogenative Depolymerization of End-of-Life Polycarbonates by an Iron Pincer Complex

Christoph Alberty, Elena Fedorenko, and Stephan Enthaler<sup>\*[a]</sup>

Chemical recycling processes can contribute to a resource-efficient plastic economy. Herein, a procedure for the iron-catalyzed hydrogenation of the carbonate function of end-of-life polycarbonates under simultaneous depolymerization is presented. The use of a straightforward iron pincer complex leads to high rate of depolymerization of poly(bisphenol A carbonate) and poly(propylene carbonate) yielding the monomers bisphenol A and 1,2-propanediol, respectively, as products under mild reaction conditions. Furthermore, the iron complex was able to depolymerize polycarbonates containing goods and mixture of plastics containing polycarbonates.

The high standard of life in modern societies strongly benefits from easily affordable plastic<sup>[1]</sup> goods, which results at the same time in the generation of plastic waste after completing the operational purpose.<sup>[2]</sup> In general, waste management depends on landfill storage and incineration that results in long-term environmental problems and pollutions.<sup>[3]</sup> Moreover, significant amounts of plastic waste are reaching uncontrolled the biosphere generating environmental problems.<sup>[4]</sup> As an alternative, primary recycling is applied which is defined as reusing the good without mechanical or chemical transformations of the latter, which is in contrast to secondary recycling.<sup>[5–6]</sup> Hereby, the material is thermally or mechanically converted to another good of similar or lower quality, because chemical degradation, contaminations or additives of the virgin material hamper the properties of the recycled material.<sup>[7]</sup> Both, primary and secondary recycling are downcycling processes because after several cycles the material has to be submitted to landfill or incineration.<sup>[8]</sup> This lost material has to be replaced by consumption of fossil resources, whereby several synthetic transformations are required. Alternatively, chemical recycling allows the conservation of the monomeric unit, so that the number of transformations is reduced and significant amounts of energy and resources are saved. As a consequence, it has

become a matter of research to enable end-of-life polymers as feedstock for new polymers with adjustable properties.<sup>[9–10]</sup> Therefore, a sequence of depolymerization followed by purification of the monomers and a (re)polymerization are required, which can, under optimal conditions, substitute fossil resources.<sup>[9]</sup> Polycarbonates, especially on the basis of bisphenol A (2) as diol component, are used as materials for data storage (CD/DVD, hard disk drives, Blu-Ray), suit cases and artificial glass.<sup>[11]</sup> Moreover, poly(propylene carbonate) (1b) based plastics have been established for packaging applications.<sup>[12]</sup> A variety of chemical depolymerization approaches for polycarbonates are reported, e.g. pyrolysis, biochemical degradation and chemical recycling, e.g. alcoholysis, glycolysis or aminolysis.<sup>[13–14]</sup> In addition, several procedures were reported for the ruthenium-catalyzed hydrogenative depolymerization (Scheme 1).<sup>[15]</sup> In case of end-of-life 1a bisphenol A (2) and methanol are formed as suitable chemicals during hydro-



**Scheme 1.** Chemical recycling concept for poly(bisphenol A carbonate) and poly(propylene carbonate).

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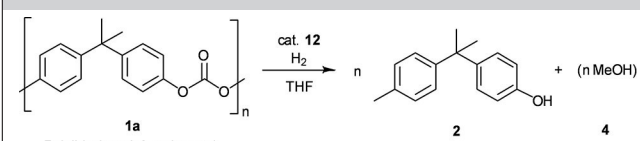
genative depolymerization. The monomer bisphenol A (**2**) can be used to regenerate the polymer **1a**, while methanol can be used as hydrogen or energy carrier.<sup>[16]</sup>

After releasing the in methanol stored energy carbon dioxide is formed, which can be converted with phenol to diphenylcarbonate (**5**), which can be applied with **2** for synthesizing **1a**.<sup>[17]</sup> On the other hand, poly(propylene carbonate) (**1b**) is converted to 1,2-propanediol (**3**) and methanol by hydrogenative depolymerization. Chemical **3** can be transformed to propylene oxide, which can react with carbon dioxide to polymer **1b**.<sup>[12,18]</sup> In both cases a cycling of monomeric units of the polycarbonates is feasible. A number of ruthenium-based catalyst (**6-10**) have been found suitable for the hydrogenative depolymerization of **1a** (Scheme 1).<sup>[15]</sup> However, the use of ruthenium as catalyst compartment causes some economic and sustainability problems.<sup>[19]</sup> In this regard, the use of systems with non-noble, cheap and abundant metals can be an alternative.<sup>[20]</sup> For instance the group of Milstein reported the application of a manganese complex (**11**) modified with a pincer type ligand in the hydrogenative depolymerization of **1b**. After 50 h **1b** was converted to 1,2-propanediol in 68% yield and propylene carbonate in 30% yield.<sup>[21]</sup>

In this regard, we studied the hydrogenative depolymerization of **1a** and **1b** in the presence of catalytic amounts of an iron complex modified with a pincer type ligand (**12**), which has been established for the hydrogenation of low-molecular weight organic esters.<sup>[22]</sup>

At first, the influence of reaction parameters on the hydrogenative depolymerization of commercially available **1a** (pellets, diameter ~3 mm) was investigated. Therefore, a mixture of **1a** and catalytic amounts of complex **12** (1.0 mol%) in THF was placed in an autoclave and pressurized with 45 bar of hydrogen and kept at 120 °C for 24 hours (Table 1, entry 2). After cooling to ambient temperature, quantification of the product was performed by <sup>1</sup>H NMR spectroscopy using the ratios of the Ar-H of the polymer/oligomers **1a** (7.06–7.07 ppm) and of the Ar-H signal of **2** (6.70–6.71 ppm). Based on that, a NMR yield of 90% of **2** was calculated. Increasing the amount of catalyst revealed an increase of the yield of **2**, while decreasing the catalyst loading showed a diminished yield (Table 1, entries 3–5). Importantly, in the absence of the catalyst no product formation was observed (Table 1, entry 1). Lowering the catalyst loading to 0.5 mol% reveals high yields for **2**, while at 0.1 mol% no significant product formation is observed. Next, the influence of the reaction temperature was evaluated. The yield of **2** decreases significantly when the temperature is reduced below 80 °C when the temperature is reduced to 100 °C still excellent yields are observed. At 80 °C, a notable decrease was observed while almost no catalytic activity is observed at 60 °C (Table 1, entries 6–8). When the reaction is stopped after 6 h at 140 °C a yield of 31% was observed (Table 1, entry 9). Moreover, the influence of the hydrogen pressure was evaluated, revealing, that at 20 bar or 5 bar pressure, the yield was significantly diminished (Table 1, entries 10 and 11). Replacement of THF by anisole or 1,4-dioxane as solvent had a negative influence on the reaction outcome (Table 1, entries 12 and 13).

**Table 1.** Iron-catalyzed depolymerization of poly(bisphenol A carbonate) **1a**.

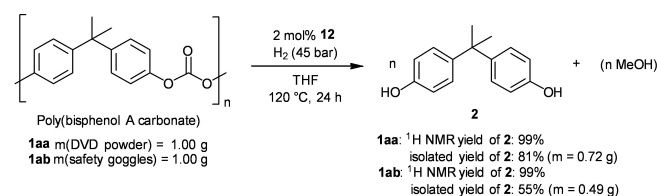


Entry <sup>[a]</sup>	Catalyst loading [mol%]	T [°C]	t [h]	p (H <sub>2</sub> ) [bar]	Yield [%] <sup>[b]</sup>
1	0	120	24	45	< 1
2	1.0	120	24	45	90
3	2.0	120	24	45	> 99
4	0.5	120	24	45	91
5	0.1	120	24	45	4
6	2.0	100	24	45	93
7	2.0	80	24	45	70
8	2.0	60	24	45	2
9	2.0	140	6	45	31
10	2.0	120	24	20	70
11	2.0	120	24	5	26
12 <sup>[c]</sup>	2.0	120	24	45	42
13 <sup>[d]</sup>	2.0	120	24	45	58

[a] Reaction conditions: **1a** (0.135 mmol, based on repeating unit of **1a**), **12** (0–2 mol%, 0–2.7 μmol based on the repeating unit of **1a**), THF (1.0 mL), 60–140 °C, 6–24 h, 5–45 bar H<sub>2</sub>. [b] The yield was determined by <sup>1</sup>H NMR. [c] 1,4-dioxane (1.0 mL) as solvent. [d] PhOMe (1.0 mL) as solvent.

With the optimized conditions (2.0 mol% **12**, 120 °C, 45 bar H<sub>2</sub>, 24 h) two kinds of plastics containing **1a** were studied in the hydrogenative depolymerization (Scheme 2). For instance, a digital versatile disc (DVD) a composite of **1a**, aluminum, plastic foils and dyes was tested. The DVD was ball-milled to get a powder (**1aa**), which was subjected to depolymerization without further pretreatments. Interestingly, after 24 hours a NMR yield of 99% of **2** was observed, revealing that the depolymerization was successful and the additional compounds had no negative impact on the catalytic activity. A similar result was obtained for a sample of safety goggles (**1ab**) containing **1a**.

For purification/isolation of **2** filtration over silica gel and subsequent crystallization was carried out. Chemical **2** was attained in 81% (**1aa**) and 55% (**1ab**) isolated yield or 93% (**1aa**) under the assumption that the DVD contains 87 wt% of **1a**.<sup>[15b–d]</sup> The isolated yields obtained for this catalyst systems are comparable to those reported for other catalysts.<sup>[15]</sup> Importantly, additives for catalyst activation are not required



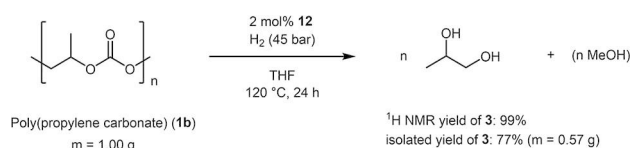
**Scheme 2.** Hydrogenative depolymerization of poly(bisphenol A carbonate) products (Reaction conditions: **1aa** or **1ab** (3.95 mmol, based on repeating unit of **1a**), **12** (2 mol%, 79.0 μmol based on the repeating unit of **1a**), THF (20 mL), 120 °C, 24 h, 45 bar H<sub>2</sub>).

and reaction temperature and pressure are sufficiently lower than for other system.<sup>[15]</sup>

Nevertheless, with regards to reaction temperature and time, pressure and catalyst loading, the Fe-catalyst was outperformed by Ru-catalyst **9** (Scheme 1).<sup>[15]</sup>

Next, the iron-catalyzed procedure was applied in the hydrogenative depolymerization of poly(propylene carbonate) (**1b**) (Scheme 3). In accordance to the optimized conditions (2.0 mol% **11**, 120 °C, 45 bar H<sub>2</sub>, 24 h) a sample of **1b** was tested. 1,2-propanediol (**3**) was observed in 99% NMR yield. Purification by distillation gave selectively **3** in 77% yield. In comparison to the Mn-based catalyst established Kumar *et al.*<sup>[21]</sup> the system does not require the usage of additional base and reveals higher yields for diol formation within shorter reaction times. Moreover, the Fe-based system demonstrated some benefits regarding temperature and pressure compared to the work of Krall *et al.*<sup>[15e]</sup>

Moreover, the hydrogenative depolymerization of polycarbonate **1a** was studied in the presence of different types of polymers, which can add some benefits to separation technologies (Table 2). Therefore, best conditions for **1a** were applied



**Scheme 3.** Hydrogenative depolymerization of poly(propylene carbonate) (Reaction conditions: **1b** (9.84 mmol, based on repeating unit of **1b**), **12** (2 mol%, 197 μmol based on the repeating unit of **1b**), THF (40 mL), 120 °C, 24 h, 45 bar H<sub>2</sub>).

**Table 2.** Influence of additional polymers on the hydrogenative depolymerization of **1a**.

Entry <sup>[a]</sup>	Additional polymer <sup>[b]</sup>	Yield <b>2</b> [%] <sup>[c]</sup>	Yield [%] <sup>[c]</sup>
1	<b>1b</b>	91	89 ( <b>3</b> )
2	Poly(lactide) (PLA)	> 99	< 1
3	Poly(ethylene terephthalate) (PET)	> 99	< 1
4	Poly(ε-caprolactone) (PCL)	72	46 <sup>[d]</sup>
5	Nylon 6	89	< 1
6	Poly(formaldehyde) (POM)	> 99	–
7	Poly(phenylene sulfide) (PPS)	> 99	< 1
8	Poly(ethylene) (PE)	87	< 1
9	Epoxy resin	99	< 1
11	Poly(styrene) (PS) <sup>[e]</sup>	observed	–
10	Poly(vinyl chloride) (PVC)	11	< 1
12	Poly(ethylene glycol) (PEG)	52	< 1
13	Silicone (PDMS)	50	< 1

[a] Reaction conditions: **1a** (0.135 mmol, based on repeating unit of **1a**), **12** (2 mol%, 0–2.7 μmol based on the repeating unit of **1a**), THF (1.0 mL), 120 °C, 24 h, 45 bar H<sub>2</sub>. [b] 0.135 mmol, based on repeating unit. [c] The yield was determined by <sup>1</sup>H NMR for **2** and the hydrogenation product of the additional polymer. [d] 1,6-hexanediol. [e] Determination of yield was impossible due to signal overlap. However, the bisphenol A was qualitatively detected.

(2.0 mol% **12**, 120 °C, 45 bar H<sub>2</sub>, 24 h). In more detail, polymer **1a** was mixed with an equimolar amount of another polymer (based on its repeating unit) and the mixture was subjected to the hydrogenation. First, a mixture of **1a** and **1b** was investigated, revealing the formation of **2** in 91% and **3** in 89% NMR yield, which is comparable to earlier experiments (Table 2, entry 1). Moreover, polymers containing ester functionalities like poly(lactide) (PLA), poly(ethylene terephthalate) (PET) and poly(ε-caprolactone) (PCL) were tested as additives (Table 2, entries 2–4). Excellent NMR yields of **2** of > 99% were detected in the presence of PLA and PET. In case of the experiment with PLA the formation of 1,2-propanediol (**3**) was not observed. However, a reduction of the molecular weight of the initial PLA was observed by DOSY NMR. For PET no formation of 1,4-benzenedimethanol and ethylene glycol was detected maybe due to solubility issues. Conversely, using poly(ε-caprolactone) (PCL) as second polymer the iron catalyst produces 46% (NMR yield) of 1,6-hexanediol and 72% (NMR yield) of **2** as depolymerization products (Table 2, entry 4). Other polymers containing functional groups, which can be potentially hydrogenated by **12**, revealed no hydrogenation of the second polymer (Table 2, entries 5–6). Polymers “inert” to hydrogenation with **12** revealed good to excellent bisphenol A formation (Table 2, entries 6–10). Diminished yields of **2** were observed when poly(vinyl chloride) (PVC), poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) (PEG) were added (Table 2, entries 11–13).

In summary, we have set up a protocol for the hydrogenation of end-of-life polycarbonates enabled by iron catalysis. High yields of the corresponding diols were obtained under mild conditions. At 120 °C and 45 bar H<sub>2</sub> pressure, bisphenol A was isolated in 93% yield when a DVD was submitted to depolymerization. Moreover, poly(propylene carbonate) was successfully converted to 1,2-propanediol, which was isolated in 77% yield. Furthermore, the catalytic hydrogenation of poly(bisphenol A carbonate) was carried out in the presence of other industrially relevant polymers, demonstrating the robustness of the applied iron catalyst.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** green chemistry · catalysis · polymers · recycling · depolymerization

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