

# Hydrogenative Depolymerization of End-of-Life Poly-(Bisphenol A Carbonate) Catalyzed by a Ruthenium-MACHO-Complex

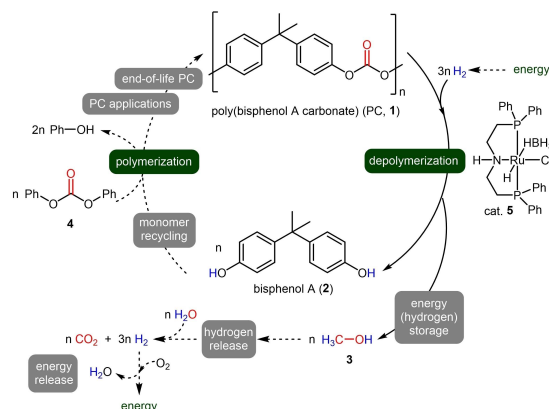
Tim-Oliver Kindler, Christoph Alberti, Jannis Sundermeier, and Stephan Enthaler<sup>\*[a]</sup>

The valorization of waste to valuable chemicals can contribute to a more resource-efficient and circular chemistry. In this regard, the selective degradation of end-of-life polymers/plastics to produce useful chemical building blocks can be a promising target. We have investigated the hydrogenative depolymerization of end-of-life poly(bisphenol A carbonate). Applying catalytic amounts of the commercial available Ruthenium-MACHO-BH complex the end-of-life polycarbonate was converted to bisphenol A and methanol. Importantly, bisphenol A can be reprocessed for the manufacture of new poly-(bisphenol A carbonate) and methanol can be utilized as energy storage material.

The state-of-the-art waste treatment for collected end-of-life plastic<sup>[1]</sup> streams is based on energy recovery, mechanical recycling, downcycling and landfill storage and the share of each methods strongly depends on regional conditions.<sup>[2,3,4]</sup> Disadvantageously, the energy recovery as one of the major treatment protocol, changes the chemical functionalities of the polymers into inappropriate chemicals (e.g. carbon dioxide), therefore for new polymers/plastics the depleting fossil resources are required.<sup>[5,6]</sup> In contrast, the chemical recycling presents a more resource-conserving and environmental-benign methodology.<sup>[7]</sup> A key component of the chemical recycling is the selective depolymerization of the polymer chain to generate low-molecular weight substances, which will be converted in the second process (polymerization) to new polymers. The connection of both processes allows the recycling of polymers/plastics. Nevertheless, currently implementation of chemical recycling suffers from high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources for the production of new polymers etc.<sup>[8]</sup> Consequently, the design and development of new methodologies is of significance for reaching the goal of a more

circular economy.<sup>[9,10]</sup> Polycarbonates, e.g. bisphenol A based polycarbonates are a widely utilized kind of polymers with applications in the area of constructions, automobile industry, electronics, artificial glass, or for optical storage (CD, DVD, Blu-ray).<sup>[11]</sup> For the recycling of poly(bisphenol A carbonate) (1) numerous procedures have been described so far including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).<sup>[12]</sup> Recently, Westhues *et al.* described the selective hydrogenative depolymerization of 1.<sup>[13,14,15]</sup> A ruthenium(II) complex was applied to hydrogenate the carbonate functionality of 1 to obtain bisphenol A (2) and methanol (3) in excellent yields and selectivities (Scheme 1). Importantly, 2 can be applied in the industrial synthesis as monomer in combination with diphenyl carbonate (4) to obtain new 1.<sup>[16]</sup> In contrast, the formed methanol can be used as hydrogen (energy) carrier/storage and may be used in fuel cells for electric energy generation.<sup>[17,18]</sup> Therefore a connection of depolymerization/recycling of end-of-life plastics with energy storage is achievable.

More recently, we have studied the application of the well-established Milstein catalyst in the depolymerization of 1 via hydrogenation to produce 2 (Scheme 1).<sup>[19]</sup> However, high catalyst loadings (5 mol%), catalytic amounts of a base (5 mol%), high temperatures (140 °C) and long reaction times (24 h) are required to obtain 2 in significant amounts. In this ongoing study we tried to solve the limitations of the Milstein catalyst system by application of another Ruthenium complex 5 containing a tridentate PNP-ligand (Ruthenium-MACHO-BH).

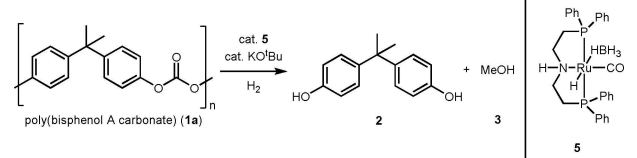


Scheme 1. Concept for the chemical recycling of 1 via hydrogenation.

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**Table 1.** Ruthenium-MACHO-BH-catalyzed depolymerization of poly(bisphenol A carbonate) (**1a**) – optimization of the reaction conditions.

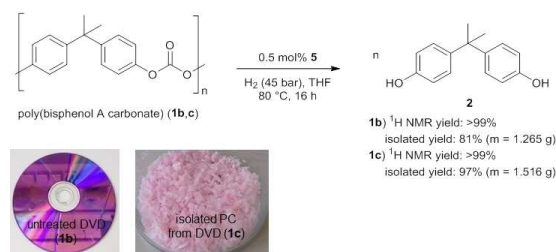
Entry <sup>[a]</sup>	Catalyst loading [mol %]	KO <sup>t</sup> Bu [mol %]	T [°C]	t [h]	p [bar]	Yield <b>2</b> [%] <sup>[b]</sup>
1	0	0	140	24	45	< 1
2	0	5	140	24	45	< 1
3	5	5	140	24	45	99
4 <sup>[c]</sup>	5	5	140	24	45	80
5	2.5	5	140	24	45	98
6	1	5	140	24	45	96
7	0.5	5	140	24	45	92
8	5	0	140	24	45	99
9	0.1	0	140	6	45	85
10	0.5	0	120	6	45	82
11	0.5	0	100	6	45	76
12	0.5	0	80	6	45	69
13	0.5	0	140	6	20	87
14	0.5	0	140	6	10	91
15	0.5	0	140	6	5	96
16	0.5	0	140	6	2	23

[a] Reaction conditions: poly(bisphenol A carbonate) (**1a**) (0.068 mmol), **5** (0–5 mol%, 0–0.0034 mmol based on the repeating unit of **1a**), KO<sup>t</sup>Bu (0–5 mol%, 0–0.0034 mmol), THF (1.0 mL), 80–140 °C, 6–24 h, 10–45 bar H<sub>2</sub>. [b] The yield was determined by <sup>1</sup>H NMR. [c] Solvent: 1,4-dioxane.

Initially, the depolymerization of commercially available pure poly(bisphenol A carbonate) **1a** (pellet dimension: ~3 mm) was examined (Table 1). First control experiment have been carried out in the absence of any catalysts and/or base (Table 1, entries 1 and 2). Importantly, no depolymerization processes were observed and the polymer was recovered. Next catalytic amounts of complex **5** (5 mol% based on the monomeric unit of **1a**) and the base potassium *tert*-butoxide (5 mol%) were tested in THF in accordance to the best conditions found for the Milstein system (yield of **2**: 95%). After heating the mixture for 24 hours at 140 °C under a hydrogen pressure of 45 bar, an excellent yield for **2** of 99% was detected by <sup>1</sup>H NMR analysis using the methyl functionalities as probe (Table 1, entry 3).<sup>[20]</sup> Changing the solvent from THF to 1,4-dioxane revealed a decrease of yield to 80% (Table 1, entry 4).

Moreover, the catalyst loading was reduced to 0.5 mol% and still an excellent yield of 92% was detected (Table 1, entries 5–7). Interestingly, the catalyst works also in the absence of base with comparable activity (Table 1, entry 8). Next the reaction time was shortened to 6 hours (Table 1, entry 9). Excellent yields were found with a catalyst loading of 5.0 mol%, while a reduction to 0.1 mol% resulted in 85% yield of **2**. This result corresponds to a turnover frequency (TOF) of ~142 h<sup>-1</sup>, which is significantly higher as observed for the Milstein catalyst (~4.7 h<sup>-1</sup>).<sup>[19]</sup> In addition the influence of the reaction temperature was investigated (Table 1, entries 10–12). Here still product formation was observed at a low temperature of 80 °C with a yield of 69%, while the Milstein catalyst is limited to 120 °C. Moreover, it was possible to reduce the hydrogen pressure to 5 bar and obtaining yields of 96% for **2**, while at lower pressure the yield decreased (Table 1, entries 13–16).

After successful confirmation of the operability of the depolymerization catalyst a digital versatile disc (DVD) mainly composed of **1** was attempted to degradate (Scheme 2). Alongside to **1** the DVD can contain additives like metal as well as plastic foil and dyes. In this regard, the DVD was crushed by ball-milling to get a powder (**1b**). With respect to the reaction conditions, the conditions stated in Table 1, entry 14 (0.5 mol% **5**, 80 °C, 45 bar, THF), but the reaction time was elongated to 16 hours to allow full conversion. Moreover, the scale was increased to 6.82 mmol (1.74 g) (based on the monomeric unit, presumption that the powder contains 100% of **1**). After heating to 80 °C for 16 hours the mixture was cooled to room temperature and filtered to remove insoluble compounds. An aliquot was dissolved in chloroform-*d* for analysis by <sup>1</sup>H NMR revealing a NMR yield of **2** of >99%. Additionally, the generation of methanol during depolymerization process was proven. For purification/isolation of **2** column chromatography and subsequent crystallization was used. In consequence **2** was



**Scheme 2.** Depolymerization of poly(bisphenol A carbonate) **1** originated from a DVD [Reaction conditions: **1b/1c** (6.82 mmol, based on the monomeric unit), **5** (0.5 mol%, 0.0341 mmol based on the repeating unit of **1a**), THF (50.0 mL), 80 °C, 16 h, 45 bar H<sub>2</sub>].

obtained in 81 % isolated yield or 93 % taking into account that the DVD contains 87 wt % of 1.

In a second attempt polymer 1 was separated from the DVD before hydrogenative depolymerization.<sup>[21]</sup> In this regard, the DVD was dissolved in THF at refluxing conditions within 30 min. The hot mixture was filtered to remove the insoluble components of the DVD. Subsequently, the solvent was removed and the solid was washed with acetone and dried in vacuum to give 1b. In agreement to the depolymerization conditions for 1b the isolated 1c was degraded (Scheme 2). 2 was detected in > 99% NMR yield and was isolated in 97 % yield.

In conclusion, an efficient hydrogenation process for the depolymerization of end-of-life 1 to generate 2 and methanol as products was set-up. Both compounds can be beneficial for on the one hand the reproduction of poly(bisphenol A carbonate) (bisphenol A) or on the other hand for the hydrogen economy (methanol). In detail, the commercially available complex Ruthenium-MACHO-BH was able to perform the depolymerization at low reaction temperatures, low pressure and within short time. Noteworthy, compared to established catalysts the Ruthenium-MACHO-BH catalyst showed excellent performance. Lastly, the protocol can add some value to the UN's Sustainable Development Goals (SDGs) e.g. SDGs 9,11 (clean/green technologies, waste management/urban mining) and SDG 12 (supply chain, more efficient and less consumptive technologies, recycling, waste streams).

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

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