Recycling of End-of-Life Poly(bisphenol A carbonate) via Alkali Metal Halide-Catalyzed Phenolysis

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The chemical recycling of end-of-life plastic waste streams can contribute to a resource-conserving and sustainable society. This matter of recycling is composed of a sequence of depolymerization and subsequent polymerization reactions. In this regard, we have studied the chemical recycling of end-of-life poly(bisphenol A carbonate) applying phenol as depolymerization reagent. In the presence of catalytic amounts of alkali metal halides as products bisphenol A and diphenyl carbonate were obtained in excellent turnover frequencies of up to 1392 h⁻¹ and short reaction times. These depolymerization products offer the straightforward possibility to close the cycle by producing new poly(bisphenol A carbonate) and as second product phenol, which can be reused for further depolymerizations.

Every year, a steadily increasing amount of end-of-life plastics[1] is generated, which is originated from non-renewable resources.[2] The established management for collected end-of-life plastic streams is composed of energy recovery, mechanical recycling, downcycling and (landfill storage).[3,4] Disadvantageously, all these methods finally transform the carbon-based chemical functionalities of the polymers into greenhouse gases (e.g. carbon dioxide), therefore a negative impact on the ecosphere/anthroposphere results and for new plastics fossil resources are needed.[5] A potentially more resource-conserving and environmental-benign methodology is the chemical recycling.[6] Initially, the end-of-life polymer is converted via depolymerization processes to low-molecular weight chemicals, which can be used as feedstock in subsequent polymerization processes to produce new polymers/plastics. Notably, linking the depolymerization and the polymerization makes a recycling of polymers/plastics feasible. Moreover, chemical recycling allow a decoupling of the quality/abilities of the new polymer from the quality/abilities of the end-of-life polymer as noticed in the case of mechanical recycling and/or downcycling. Nevertheless, some issues hamper the implementation of chemical recycling, e.g. high energy demand, copolymers, additives, selectivity, and the current low price for fossil resources.[7] Consequently, the development of new chemical recycling methodologies is of significance for reaching the goal of a sustainable society.[10,11]

For instance poly(carbonates), e.g. based on bisphenol A, are widely applied components in plastics, e.g. used in optical storage (CD, DVD, Blu-ray) or as artificial glass.[8] Until now for the recycling of poly(bisphenol A carbonate) (1) (PBPAC) a number of methodologies have been described including mechanical recycling, blending with other materials, pyrolysis (feedstock recycling), biochemical degradation and chemical recycling (e.g. hydrolysis, (hydro)glycolysis, alcoholysis and aminolysis).[13–19] Especially, the methanolysis (transesterification with methanol) has been extensively studied. In more detail mixtures of polymer 1 and an excess of methanol are converted to bisphenol A and dimethyl carbonate in presence of catalysts.[15,16] The bisphenol A can be easily isolated and potentially reused for the synthesis of new poly(bisphenol A carbonate) (1). Conversely, the second product dimethyl carbonate and methanol forms an azeotrope, which requires some efforts for separation.[20] A potentially more attractive approach is the use of phenol as depolymerization reagents, while forming bisphenol A and diphenyl carbonate as products, which are the components for one of the major industrial synthesis of poly(bisphenol A carbonate) (1) (Scheme 1).

However, only a few numbers of reactions following this path have been accounted so far, requiring long reaction times and/or “complicated” catalysts.[14] For instance ionic liquids/ionic compounds have been proven as active catalysts in depolymerization reactions.[14,16,18] It was assumed that the anion activates the alcohol and the cation activates the carbonyl function of the polycarbonate. In this regard, we wonder if simple and abundant alkali metal halides can mimic the behavior of the ionic liquids.[21] Moreover, straightforward alkali metal salts have some advantages with respect to “Green Chemistry” considerations.[22] Based on that, we report herein our investigations on a concept for the chemical recycling of end-of-life 1 applying simple alkali metal halide as catalyst (Scheme 1).

Initially, the depolymerization of commercially available poly(bisphenol A carbonate) pellets 1a (dimension: ~3 mm) was investigated (Table 1). In this regard, 1a (1.35 mmol based
on the monomeric unit) was reacted with an excess of phenol (technical grade) as depolymerization reagent (47.3 equiv. based on the monomeric unit of 1a) in the presence of catalytic amounts of potassium fluoride (5 mol% based on the monomeric unit of 1a) and THF as solvent. The reaction mixture was placed in a sealed glass vial in a microwave (MW) and was heated under microwave conditions at 180 °C for 15 minutes, while stirring (Table 1, entry 2). Afterwards, the mixture was cooled to room temperature and an aliquot was dissolved in chloroform-d1 for 1H NMR analysis. Noteworthy, a clear homogenous solution was obtained. In the aliphatic range of the 1H NMR spectrum a signal with a chemical shift of 1.58 ppm (C(CH3)3) was detected, which are assigned to the depolymerization product bisphenol A. Moreover, some minor signals of left-over polymers or oligomers were observed in the aliphatic area, which allow an integral relation to the integrals of bisphenol A and therefore a determination of the rate of depolymerization. A yield of 2 of 85% was calculated. Furthermore, in the aromatic region two sets of signals were observed, which can be assigned to the two sets (2 × 4H) of aromatics C−H in bisphenol A. Besides, the signals for diphenyl carbonate at 7.36-7.40 ppm (4x o−C−H) were found in the aromatic region, which were related to the signals of 2 to calculate the yield of 3.

Importantly, for the other signals of 3 an overlap with the signals of the phenol was observed. The occurrence of 2 and 3 was also confirmed by GC-MS analysis. Next, the loading of potassium fluoride was studied, revealing still good performance at 0.5 mol% with a yield of 58% for 2, while in the absence of KF no reactivity was observed (Table 1, entries 1, 6–11). Furthermore, in the absence of THF a decrease of the yield was observed, demonstrating the need for THF (Table 1, entry 5). Then the effect of the reaction temperature was investigated (Table 1, entries 11–13). A moderate yield of 31% of 2 was detected at a temperature of 140 °C (Table 1, entry 13). Furthermore, the influence of the phenol:1a ratio was examined (Table 1, entries 15–18). Reducing the amount of phenol to 3.9 equiv. revealed still a good yield of 2 (80%). Decreasing the amount of phenol to 3.9 equiv. resulted in the formation of 2 in a decreased yield of 31% (Table 1, entries 19). In addition the activity of a selection of alkali metal halides was tested in the depolymerization of 1a (Table 1, entries 20–25). Comparative yields to KF were detected for KI and NaI, while other salts resulted in the formation of 2 in moderate yields. However, best performance was realized with potassium fluoride.

Afterwards, the reaction was performed with conventional heating at 180 °C (oil bath temperature, internal temperature 125–130 °C) following the conditions in Table 1, entry 3 (Table 1, entry 4). Products 2 and 3 were detected in 86% NMR yield and were furthermore separated by column chromatography and isolated in 69% (2) and 71% (3) yield. Conversely, removal of the excess phenol by vacuum distillation revealed the formation of new poly(bisphenol A carbonate) by the reaction of depolymerization products 2 and 3 observed by 1H NMR.

Moreover, the depolymerization was monitored over the course of reaction using 0.5 mol% KF under conventional heating (Figure 1). Noteworthy, the NMR yield of 58% after 5 min corresponds to a turnover frequency (TOF) of ca. 1392 h⁻¹.

After having verified the operability of the depolymerization we transferred the procedure to commodities containing poly(bisphenol A carbonate) 1. In this regard, end-of-life digital versatile discs (DVDs) containing 1b as major component were studied (Scheme 2). Noteworthy, alongside with poly(bisphenol A carbonate) 1b CDs/DVDs containing additives e.g. metal foils, plastic foils and dyes, which can potentially influence/inhibit the rate of depolymerization. Two different pathways of DVD depolymerizations were investigated. Pathway A: The DVDs were crushed into small pieces and THF was added. The polymer 1b dissolved within 30 min under refluxing conditions,
Depolymerization of poly(bisphenol A carbonate) 1a originated from DVDs with phenol-time vs. yield of 2 (Reaction conditions: conventional heating: 1a (1.35 mmol, based on the monomeric unit), phenol (47.3 equiv.), KF (0.5 mol%), based on the monomeric unit), 180 °C, yield determined by 1H NMR.}

The residue was washed with acetone and dried in vacuum to yield a (colorless) solid. To the purified polymer 1b, phenol and THF was added. The reaction mixture was heated to 180 °C. Afterwards catalytic amounts of potassium fluoride (2 mol%) were added. The mixture was kept for 30 min at 180 °C. Subsequently, the mixture was cooled to room temperature and an aliquot was taken for 1H NMR investigations. A NMR yield of 90% (2) and 90% (3) was detected. The excess of phenol was carefully removed in vacuum (1.1 mbar) at 50–55 °C. Noteworthy, the phenol can be reused for next depolymerizations. At a level of ca. 3 equiv. of phenol with respect to bisphenol A the yield of 2 drops to 85%, while the polymerization started and new poly(bisphenol A carbonate) 1 is formed. After an increase of the temperature to 200 °C (1.1 mbar) a solid residue was obtained. After washing and drying, compound 1ba was obtained in 54% yield as colorless powder. The powder was characterized by 1H NMR revealing the occurrence of polymer 1ba. Moreover, with GPC analysis a number average molar mass of Mn~4162 g/mol, a mass average molar mass Mw~6412 g/mol and a polydispersity of 1.54 was found. In addition, pathway A was performed on a 19.7 mmol scale of 1b. According to 1H NMR yield of 84% (2) and 84% (3) was measured in the presence of 0.5 mol% KF and the products were separated by successive crystallization after partial removal of phenol by distillation.

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

| Entry[ia] | Catalyst [mol %] | PhOH [equiv.] | T [°C] | t [min] | Yield 2 [%b] | Yield 3 [%b] |
|-----------|------------------|---------------|--------|---------|-------------|-------------|
| 1[a]      | –                | 47.3          | 180    | 15      | < 1         | < 1         |
| 2         | KF (5)           | 47.3          | 180    | 15      | 85          | n.d.        |
| 3         | KF (5)           | 47.3          | 180    | 30      | 86          | 88          |
| 4         | KF (5)           | 47.3          | 180    | 15      | 86(91)%     | 86(71)%     |
| 5[b]      | KF (5)           | 47.3          | 180    | 15      | 77          | n.d.        |
| 6[b]      | KF (5)           | 47.3          | 180    | 15      | 85          | n.d.        |
| 7[b]      | KF (5)           | 47.3          | 180    | 15      | 85          | n.d.        |
| 8         | KF (10)          | 47.3          | 180    | 15      | 85          | 87          |
| 9         | KF (2)           | 47.3          | 180    | 15      | 85          | n.d.        |
| 10        | KF (2)           | 47.3          | 180    | 5       | 85          | n.d.        |
| 11        | KF (0.5)         | 47.3          | 180    | 5       | 58          | n.d.        |
| 12        | KF (2)           | 47.3          | 200    | 15      | 84          | 85          |
| 13        | KF (2)           | 47.3          | 160    | 15      | 83          | n.d.        |
| 14[b]     | KF (2)           | 47.3          | 140    | 15      | 31          | n.d.        |
| 15[b]     | KF (5)           | 31.5          | 180    | 15      | 80          | n.d.        |
| 16        | KF (5)           | 19.7          | 180    | 15      | 80          | 82          |
| 17        | KF (5)           | 19.7          | 180    | 15      | 74          | 74          |
| 18        | KF (5)           | 7.9           | 180    | 15      | 52          | n.d.        |
| 19        | KF (5)           | 3.9           | 180    | 15      | 31          | n.d.        |
| 20        | LiCl (5)         | 47.3          | 180    | 15      | 13          | n.d.        |
| 21        | NaCl (5)         | 47.3          | 180    | 15      | 12          | n.d.        |
| 22        | NaF (5)          | 47.3          | 180    | 30      | < 1         | n.d.        |
| 23        | KBr (5)          | 47.3          | 180    | 15      | < 1         | n.d.        |
| 24        | KI (5)           | 47.3          | 180    | 15      | 87          | 88          |
| 25        | NaI (5)          | 47.3          | 180    | 15      | 85          | n.d.        |

[a] Reaction conditions: poly(bisphenol A carbonate) 1a (1.35 mmol based on the repeating unit of 1a), MX (0.5 mol %, 0–0.135 mmol based on the repeating unit of 1a), phenol (3.93–47.3 equiv. based on the repeating unit of 1a), THF (20.6 equiv.), microwave heating, 140–200 °C, 5–30 min. [b] The yield was determined by 1H NMR. [c] 99% of the starting polymer was recovered. [d] Not determined, due to signal overlap. [e] In parenthesis the isolated yield is stated. [f] Without THF. [g] THF (41.2 equiv.). [h] THF (61.6 equiv.).

Figure 1. Depolymerization of poly(bisphenol A carbonate) 1a originated from DVDs with phenol-time vs. yield of 2 (Reaction conditions: conventional heating: 1a (1.35 mmol, based on the monomeric unit), phenol (47.3 equiv.), KF (0.5 mol %, based on the monomeric unit), 180 °C, yield determined by 1H NMR).
Pathway B: Initially, the DVD was ball-milled to obtain a DVD-powder, which was used without further pretreatments. The DVD-powder was mixed with phenol and THF. After 5 min at 180°C catalytic amounts of KF (0.5 wt %) were added. After 30 min at 180°C a sample was taken and investigated by $^1$H NMR. A NMR yield of 76% ($^2$) and 76% ($^3$) was obtained. The solution was filtered to remove insoluble components e.g. aluminum foil.

The clear solution was subjected to vacuum distillation to remove the excess of phenol (~3 equiv. leftover) a yield of 64% of 2 was obtained. After increasing the temperature to 200°C (1.1 mbar), washing, filtration and drying 1ca was attained in 40% yield. Moreover, with GPC analysis a number average molar mass of Mn~8304 g/mol, a mass average molar mass Mw~24606 g/mol and a polydispersity of 2.96 was found. Also pathway B was performed on a 19.7 mmol scale. A $^1$H NMR yield of 73% (2) and 71% (3) was measured in the presence of 0.5 mol% KF and the products were separated by successive crystallization after partial removal of phenol by distillation.

In summary, we have set up a straightforward chemical recycling method for end-of-life poly(bisphenol A carbonate) based on depolymerization and polymerization. On the one hand, depolymerization was carried out with phenol as depolymerization reagent to attain as well-defined products bisphenol A and diphenyl carbonate. In the presence of catalytic amounts of potassium fluoride yields up to 90% and turnover frequencies up to 1392 h$^{-1}$ were achieved. Moreover, the mixture of bisphenol A, diphenyl carbonate and phenol can be used as starting point for polymerization chemistry to produce new poly(bisphenol A carbonate) and therefore closing the cycle. Future studies will focus on the improvement of the depolymerization process.
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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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[31] ~10 wt % of the DVD has been recovered (e.g. Al, foil).