Supporting Information

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

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General: All chemicals were used as received without further manipulations. $^1$H and $^{13}$C($^1$H) NMR spectra were recorded on a Fourier 300 MHz ($^1$H: 300 MHz, $^{13}$C: 75 MHz) or Avance I-400 ($^1$H: 400 MHz, $^{13}$C: 101 MHz) by Bruker, using the proton signals of the deuterated solvents as reference or external standards. Mass spectrometry was performed using a Thermo ISQ LT EI by Thermo Fisher Scientific. TLC was performed on ALUGRAM XTRA SIL G/UV$_{254}$ cards from Macherey-Nagel GmbH & Co. KG with a thickness of 0.20 mm. Detection succeeded with UV-light (254 nm). For preparative column chromatography silica gel 60 (particle size 40 – 63 µm) from Fluka was used. All catalytic set-ups were prepared in a glovebox under argon. Ru-MACHO®-BH: Carbonylhydrido(tetrahydroborato)[bis(2-diphenylphosphinoethyl)amino]ruthenium(II) (CAS Number: 1295649-41-0) was received from TCI Deutschland GmbH. THF was dried over sodium-benzophenone, was distilled off and stored over molecular sieves 4 Å under a nitrogen atmosphere. The hydrogenations were performed in a Parr autoclave (model: 4774) (Parr Instrument Company).

General procedure for the hydrogenation of poly(bisphenol A carbonate) 1a (optimization of reaction conditions): A mixture of commercially available poly(bisphenol A carbonate) (1a) (17.3 mg, 0.0682 mmol based on the repeating unit, obtained from Sigma Aldrich), potassium tert-butoxide (0-0.38 mg, 0-0.0034 mmol, 0-5 mol% based on the repeating unit of 1a) and catalytic amounts of complex 5 (0-2.0 mg, 0-0.034 mmol, 0-5 mol%, based on the repeating unit of 1a) were placed with a stir bar in a vial. THF (1.0 mL) was added. The vial was placed in an autoclave, which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted (10-45 bar) and the autoclave was heated to the desired temperature. The temperature was hold for 6-24 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. An aliquot of the solution was transferred to a NMR tube and was dissolved in CDCl$_3$ (0.6 mL). The sample was subjected to $^1$H NMR to determine the yield of bisphenol A (2). The yield of 2 was calculated on the basis of the Ar-H or C(CH$_3$)$_2$ and the Ar-H or C(CH$_3$)$_2$ leftover signals of the polymer/oligomer. Note: Methanol was not detected. The screening of reaction conditions were performed in a Parr autoclave (model: 4774) containing sites for six glass-vials (~4 mL). Importantly, the vials were not sealed; hence during reaction the methanol may evaporate from the vials.
Bisphenol A (2): $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.05-7.10 (m, 4H, Ar-H), 6.69-6.75 (m, 4H, Ar-H), 1.60 (s, 6H, (CH$_3$)$_2$. (The signal for 2xOH was not observed).

Figure S1. $^1$H NMR spectrum of a reaction mixture (0.5 mol% Ru-MACHOBH, THF, 140 °C, 45 bar H$_2$, 6 h) (300 MHz, CDCl$_3$, 25 °C).

Bisphenol A (2): $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.04–7.07 (m, 4H, Ar-H), 6.71–6.74 (m, 4H, Ar-H), 1.59 (s, 6H, -CH$_3$, 7 ppm).

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C): $\delta$ = 156.0 (C$_q$-OH, 2), 142.9 (C$_q$(C-CH$_3$)$_2$, 5), 128.5 (C$_{Ar}$, 4), 115.5 (C$_{Ar}$, 3), 42.1 (C$_q$(CH$_3$)$_2$, 6), 31.6 (CH$_3$, 7) ppm.

EI-MS m/z: 228 [M$^+$], 213 [M$^+$ -(CH$_3$)].

IR (ATR): $\tilde{\nu}$ [cm$^{-1}$]: 3307 (w), 2969 (m), 1508 (s), 1216 (s), 824 (vs), 562 (vs).
Figure S2. $^1$H NMR spectrum of 2 obtained from depolymerization of DVD powder (400 MHz, acetone-$D_6$, 25 °C).
Figure S3. $^{13}$C($^1$H) NMR spectrum of 2 obtained from depolymerization of DVD powder (125 MHz, acetone-$D_6$, 25 °C)).
Figure S4. H,H COSY spectrum of 2 obtained from depolymerization of DVD powder.
Figure S5. $^1$H,$^{13}$C($^1$H) HSQC spectrum of 2 obtained from depolymerization of DVD powder.
Figure S6. $^1$H, $^{13}$C{$^1$H} HMBC spectrum of 2 obtained from depolymerization of DVD powder.

Figure S7. GC-MS-EI spectrum of 2 obtained from depolymerization of DVD powder.
Figure S8. $^1$H NMR spectrum of the reaction mixture obtained from depolymerization of DVD powder with detection of methanol.

Procedure for the depolymerization of poly(bisphenol A carbonate) starting from DVD:

a) Depolymerization of poly(bisphenol A carbonate) 1b (DVD)

A mixture of the DVD powder 1c (obtained by ball milling of DVD pieces) (1.74 g, 6.85 mmol based on the repeating unit, catalytic amounts of complex 5 (19.9 mg, 0.0341 mmol, 0.5 mol%, based on the repeating unit of 1c) and THF (2.0 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was held for 16 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 4:1, $R_t = 0.18$). Bisphenol A was obtained as colorless crystals in 81 % yield (1.2 g, 5.54 mmol). The content of 1 in the DVD is ~87 %; therefore the yield of 2 can be corrected to approximately 92 %. The NMR spectra are in
accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) 1a (vide supra).

b) Poly(bisphenol A carbonate) 1c isolation from DVDs

To pieces of a DVD (16.7 g, cut in small pieces) and a stir bar in a 250 mL-flask was added THF (100 mL). A reflux condenser was added and the flask was placed in an oil bath. The mixture was heated under reflux for 30 min. The polycarbonate part of the DVD dissolved, while the aluminum foil and another plastic foil didn’t dissolve. The hot mixture was filtered through a filter paper into a 250 mL flask. The solvent was removed on a rotary evaporator (Note: the collected solvent can be reused for further poly(bisphenol A carbonate) dissolving). The solid residue was added to a frit and was washed with acetone. Afterwards the solid was dried in an oven at 80 °C for 6 hours yielding poly(bisphenol A carbonate) 1b (13.7 g, 82 wt% based on the starting DVD) (Note: the color of the poly(bisphenol A carbonate) varies depending on the applied starting DVD).

A mixture of the isolated poly(bisphenol A carbonate) (1c) (1.74 g, 6.85 mmol based on the repeating unit, catalytic amounts of complex 5 (20.2 mg, 34.4 µmol, 0.5 mol%, based on the repeating unit of 1c) and THF (2.0 mL) was added with a stir bar in an autoclave (Parr Instrument Company), which was sealed and purged with hydrogen (5 times). Afterwards the desired hydrogen pressure was adjusted and the autoclave was heated to the desired temperature. The temperature was hold for 16 hours, while stirring the reaction mixture. Afterwards the autoclave was cooled to room temperature and the hydrogen pressure was carefully released. Purification was performed by silica gel column chromatography (petroleum ether: acetone, 8:2, Rf = 0.18). Bisphenol A was obtained as colorless crystals in 97 % yield (1.516 g, 6.641 mmol). The NMR spectra are in accordance to the spectra presented for depolymerization of commercially available poly(bisphenol A carbonate) 1a (vide supra).

References

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