Electronic Supplementary Information

Depolymerization of poly-(bisphenol A carbonate) under mild conditions by solvent-free alcoholysis catalyzed by 1,8-diazabicyclo[5.4.0]undec-7ene as a recyclable organocatalyst: a route to chemical recycling of waste polycarbonate

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ATR-FT-IR spectrum of unreacted polycarbonate

Fig. S1. ATR-FT-IR spectrum: (red) unreacted PC recovered at the end of the catalytic run; (bleu) commercial polycarbonate. $v_{C=0}$: 1770 cm⁻¹.

Work-up of the reaction mixture: extraction with diethyl ether/H₂O

After the complete conversion of the polymer, the reaction mixture was distilled at room temperature in vacuum. The residue of distillation was purified from DBU by extraction with diethyl ether/H₂O. The organic phase was dried on MgSO₄, filtered and evaporated in vacuum to give a DBU-free residue containing BPA and 4-cumylphenol (Fig. S2). The aqueous phase was evaporated in vacuum under gentle warming to afford a colorless oil. The GCMS analysis of the oily residue is shown in Fig. S3.



Fig. S2. ¹H NMR (500 MHz, CD₃OD) spectrum of the BPA/4-CP mixture isolated after removal of DBU by extraction with diethyl ether/H₂O. The signals due to BPA are found at 1.56 (s, Me), 6.65 (dm, H3) e 7.01 ppm (dm, H2), while resonances assigned to 4-CP can be located at 1.60 (s, Me) and in the range 7.08-7.22 ppm (Ph). <u>The spectrum does not contain signals due to DBU</u>.



Fig. S3. GC-MS analysis of the oily residue obtained from the aqueous layer after evaporation in vacuum of H₂O. (a) DBU; (b) 1-(3-aminopropyl)azepan-2-one (m/z = 170; hydrolysis product of DBU); (c) BPA.

Work-up of the reaction mixture: washing with diethyl ether

After the complete conversion of the polymer, the reaction mixture was distilled at room temperature in vacuum. The residue of distillation was purified from DBU by washing it with diethyl ether (20 mL). The resulting suspension was filtered and the ethereal phase was evaporated in vacuum to give a DBU-free residue (Fig. S4 and S5) containing BPA and 4-CP. The solid insoluble in ether was dried in vacuum and characterized spectroscopically as a BPA-DBU adduct (Fig. S6-S10).



Fig. S5. ¹H NMR (500 MHz, DMSO-d₆) spectrum of the BPA/4-CP mixture. The resonances of BPA are found at 1.51 (s, Me), 6.62 (dm, H3) e 6.96 ppm (dm, H2), while signals assigned to 4-CP can be located at 1.57 (s, Me) and in the range 7.09-7.26 ppm (Ph). The triplet at 1.1 ppm and the partially masked quartet at 3. 4 ppm are due to residual amounts of diethyl ether. The spectrum does not contain signals due to DBU.



Fig. S6. FT-IR (nujol) spectrum of the adduct BPA-DBU: 3267 (v br), 1643 (ms), 1610 (m), 1593 (m), 1506, 1323, 1247, 1228, 1175, 1101, 1080, 1012, 831, 761, 723 cm⁻¹.



Fig. S7. ¹H NMR (400 MHz, DMSO-d₆) spectrum of the adduct BPA-DBU: the resonances of BPA are located at δ 1.51(Me), 6.60 (dm, 8.6 Hz, H3) and 6.95 (dm, 8.5 Hz, H2) ppm, while the signals of DBU are found at δ 1.6-1.4 (H3, H4, H5), 1.70 (quint, 6 Hz, H10), 2.34 (m, H6), 3.10 (t, H9), 3.19-3.23 ppm (H2 e H11). The OH protons of BPA give a very broad poorly evident signal at around 8 ppm. The signals near 1.1 and 3.4 ppm are due to residual amounts of diethyl ether.

Fig. S8. ¹³C NMR (100 MHz, DMSO-d₆) spectrum of the adduct BPA-DBU: the resonances of BPA are located at δ 30.87 (Me), 40.83 (*C*Me₂), 114.60 (C3), 127.18 (C2), 140.60 (C1), 155.36 ppm (C4), while the signals of DBU are found at δ 21.55 (C10), 25.24, 27.59, 28.84 (C3, C4, C5), 34.98 (C6), 41.99 (C9), 47.53, 52.06 (C2 and C11), 161.27 ppm (C7).

Fig. S9. ¹H NMR (500 MHz, CD₃OD) spectrum of the adduct BPA-DBU: the resonances of BPA are located at δ 1.55 (Me), 6.62 (dm, 8.8 Hz, H3) e 6.98 (dm, 8.3 Hz, H2) ppm, while the signals of DBU fall at δ 1.68-1.80 (H3, H4, H5), 2.00 (quint, 5.9 Hz, H10), 2.63 (m, H6), 3.31 (H9), 3.50 (t, 6 Hz, H11), 3.56 ppm (m, H2).

Fig. S10. ¹³C NMR (500 MHz, CD₃OD) spectrum of the adduct BPA-DBU: the resonances of BPA are located at δ 31.73 (Me), 42.38 (CMe₂), 115.99 (C3), 128.64 (C2), 142.69 (C1), 157.29 ppm (C4), while the signals of DBU are observed at δ 20.57 (C10), 25.03, 27.57, 29.99 (C3-C5), 33.89 (C6), 39.64 (C9), 49.45, 55.25 (C2 and C11), 167.20 ppm (C7).

Work-up of the reaction mixture: isolation of pure BPA and 4-CP

BPA (Fig. S11 and S12) and 4-CP (Fig. S13 and S14) can be isolated as a pure compounds by fractionating the residue of distillation on a silica gel column, using, as eluent, petroleum ether/ethyl acetate 6:1 (v/v) until elution of 4-cumylphenol and, afterwords, petroleum ether/ethyl acetate 2:1 (v/v).

Fig. S11. ¹H NMR (400 MHz, DMSO-d₆) spectrum of BPA isolated by chromatography. $\delta = 1.51$ (Me), 6.62 (dm, 8.8 Hz, H3), 6.96 (dm, 8.8 Hz, H2), 9.11 ppm (s, OH).

Fig. S12. ¹³C NMR (100 MHz, DMSO-d₆) spectrum of BPA isolated by chromatography. $\delta = 30.84$ (Me), 40.87 (*C*Me₂), 114.49 (C3), 127.23 (C2), 140.99 (C1), 154.82 ppm (C4).

Fig. S13. ¹H NMR (500 MHz, CDCl₃) spectrum of 4-CP isolated by chromatography: δ 1.66 (s, Me), 5.30 (s, OH), 6.73 (dm, H3), 7.10 (dm, H2), 7.17 (m, H4'), 7.22-7.28 ppm (m, H2' and H3').

Fig. S14. ¹³C NMR (100 MHz, DMSO-d₆) spectrum of 4-CP isolated by chromatography: $\delta = 30.57$ (Me), 41.63 (*C*Me₂), 114.60 (C2), 125.28 (C4'), 126.32 (C2'), 127.32 and 127.83 (C3 and C3'), 140.41 (C4), 150.76 (C1'), 154.98 ppm (C1).

Fig. S15. Mass spectrum of 1a.

Comparison of ¹H and ¹³C NMR spectra of DBU, DBU HCl, and the BPA-DBU adduct in CD₃OD and DMSO-d₆

Fig. S17. ¹H NMR (DMSO-d₆) of (a) DBU: δ 1.58-1.44 (m, H3, H4, H5), 1.63 (quint, H10), 2.23 (m, H6), 3.05 (t), 3.11-3.14 (m) ppm; (b) BPA-DBU adduct: the resonances of BPA are located at δ 1.51(Me), 6.60 (dm, 8.6 Hz, H3) and 6.95 (dm, 8.5 Hz, H2) ppm, while the signals of DBU are found at δ 1.6-1.4 (H3, H4, H5), 1.70 (quint, 6 Hz, H10), 2.34 (m, H6), 3.10 (t, H9), 3.19-3.23 ppm (H2 e H11). The signals near 1.1 and 3.4 ppm are due to residual amounts of diethyl ether; (c) DBU-HCI: δ 1.58 and 1.64 (H3, H4, H5), 1.88 (quint, 5.9 Hz, H10), 2.74 (m, H6), 3.20 (t, 5.9 Hz, H9), 3.45 (t, 5.9 Hz, H11), 3.53 ppm (m, H2).

Fig. S18. ¹³C NMR (DMSO-d₆) of (a) DBU: δ 22.36 (C10), 25.79, 28.11, 29.07, 36.40 (C6), 43.51 (C9), 47.46 (C2), 51.76 (C11), 159.47 (C7) ppm; (b) BPA-DBU adduct: the resonances of BPA are located at δ 30.87 (Me), 40.83 (CMe₂), 114.60 (C3), 127.18 (C2), 140.60 (C1), 155.36 ppm (C4), while the signals of DBU are found at δ 21.55 (C10), 25.24, 27.59, 28.84 (C3, C4, C5), 34.98 (C6), 41.99 (C9), 47.53, 52.06 (C2 and C11), 161.27 ppm (C7); (c) DBU HCl δ 18.89 (C10), 23.40, 25.97, 28.27, 31.12, 37.34, 47.82, 53.23 (C11), 165.30 ppm (C7).

Fig. S19. ¹H NMR (CD₃OD) of (a) DBU: δ 1.58-172 (m, H3, H4, H5), 1.81 (quint, 5.9 Hz, H10), 2.39 (m, H6), 3.19 (t), 3.28-3.32 (m); (b) BPA-DBU adduct: the resonances of BPA are located at δ 1.55 (Me), 6.62 (dm, 8.8 Hz, H3) e 6.98 (dm, 8.3 Hz, H2) ppm, while the signals of DBU fall at δ 1.68-1.80 (H3, H4, H5), 2.00 (quint, 5.9 Hz, H10), 2.63 (m, H6), 3.31 (H9), 3.50 (t, 6 Hz, H11), 3.56 ppm (m, H2); (c) DBU HCI: δ 1.69-1.82 (m, H3, H4, H5), 2.05 (quint, 6 Hz, H10), 2.71 (m, H6), 3.36 (t, 5.9 Hz, H9), 3.57 (t, 5.9 Hz, H11), 3.63 ppm (m, H2).

Fig. S20. ¹³C NMR (CD₃OD) of: (a) DBU: δ 22.91 (C10), 26.74, 29.14, 30.58, 36.44 (C6), 43.63 (C9), 49.28 (C2), 53.90 (C11), 164.66 ppm (C7); (b) BPA-DBU adduct: the resonances of BPA are located at δ 31.73 (Me), 42.38 (CMe₂), 115.99 (C3), 128.64 (C2), 142.69 (C1), 157.29 ppm (C4), while the signals of DBU are observed at δ 20.57 (C10), 25.03, 27.57, 29.99 (C3-C5), 33.89 (C6), 39.64 (C9), 49.45, 55.25 (C2 and C11), 167.20 ppm (C7); (c) DBU HCI: δ 20.41 (C10), 24.91, 27.47, 29.95, 33.69, 39.29, 49.59, 55.37 (C11), 167.44 ppm (C7).

