Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Upcycling of BPA-PC into trimethylene carbonate by solvent assisted organocatalysed depolymerisation

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Chemical Reagents

1,3-propanediol (98%), butane-1,3-diol (99,5%), Di(trimethylolpropane) (97%) Trimethylolpropane allyl ether, 2,2-dimethylpropane-1,3-diol (99%), 2,2-diethylpropane-1,3-diol (99%) 2-methyl-2-propylpropane-1,3-diol (98%), 2,2-Bis(hydroxymethyl) propionic acid (98%) ethylene diamine (99%) anhydrous ethylene glycol (99,8%), glycerol (99%), ethanedithiol (98%), 1-methylimidazole, imidazole (99%), benzimidazole (98%), benzotriazole (99%) and 1,2,4-triazole (98%) were purchased from Sigma Aldrich. Deuterated solvents such as $CDCl_3$ and DMSO-d_6 were purchased from Eurisotop. Commonly employed solvents such as Tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (DCM), toluene and methanol were purchased in HPLC grade from Sigma Aldrich or Fisher Scientific. All materials were used without further purification. BPA-PC pellets were purchased from Idemitsu Chemical Europe (TARFLON IV1900R).

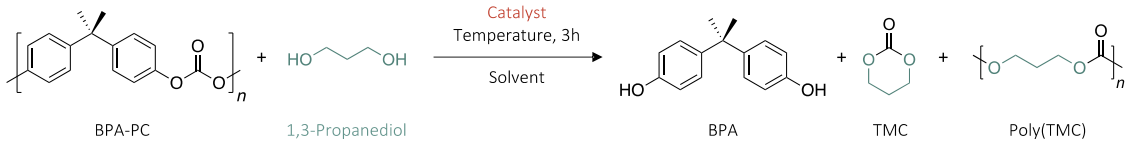
Characterisation techniques

^1H and ^{13}C Nuclear Magnetic Resonance (NMR). NMR spectra were recorded at room temperature with Bruker Avance 400 spectrometer using DMSO-d_6 as solvent. The NMR chemical shifts were reported as δ (in parts per million – ppm) relative to the traces of non-deuterated solvent (*e.g.* δ = 2.50 ppm for DMSO-d_6). Data were reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (J) given in Hertz (Hz), and integration.

F*ourier transformation infrared spectra (FT-IR).* FT-IR spectra were obtained by FT-IR spectrophotometer (Nicolet 6700 FT-IR, Thermo Scientific Inc., USA) using attenuated total reflectance (ATR) technique (Golden Gate, spectra Tech). Spectra were recorded between 4000-525 cm^{-1} with a spectrum resolution of 4 cm^{-1}. All spectra were averaged over 10 scans.

Experimental procedures

General procedure for the depolymerisation reactions



In a typical reaction, BPA-PC pellets (1 g, 3.9 mmol, 1 eq.) 1,3-propanediol (1.05, 1.25, 1.5 or 1.75 eq.), catalyst (0, 0.5, 1 and 2 eq.) and solvent (2.5, 5, 10 or 20 eq.) and were loaded into a 25 ml vial along with an oval magnetic stirrer. The mixture was introduced in an oil bath pre-heated at the desired temperature (40, 50, 60 or 90 °C). To monitor the conversion, DMF was added to the reaction media (0.5 eq.) and aliquots were taken at certain intervals as well as after completion of the reaction to be analysed by means of ^{1}H NMR spectroscopy. The depolymerisation yield was calculated through the integration of the characteristic aromatic signals of BPA, *i.e.* δ (ppm) 6.98 (d, 4H) and 6.67 (d, 4H), compared to DMF standard.

Procedure for the purification of TMC

The depolymerisation of BPA-PC (1 g, 3.9 mmol, 1 eq.) was performed in 10 eq. of 1-Methylimidazole (3.2 g, 39 mmol), with 1.05 eq. of 1,3-propanediol (0.30 g, 3.9 mmol) as nucleophile and 1 eq. of imidazole as catalyst (0.27 g, 3.9 mmol) at 50 °C. After 3 h of reaction and following the isolation method already described by Hedrick and co-workers[1], the crude product is dissolved in a large excess of DCM and passed through an acidic resin (*i.e.* Amberlyst 15) for retaining the catalyst (imidazole) and the solvent (1-methylimidazole) by forming the corresponding acid:base salt. The column was refrigerated below 45 °C to compensate the heat created through the exothermic formation of the salts. The solution is then concentrated by means of rota-evaporation and TMC is precipitated in diisopropyl ether for eliminating BPA before re-crystallisation in DCM. White crystals are obtained (0,13 g, 1,25 mmol, 32% yield) and analysed through ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 4.39 (t, 2H, CH_2), 2,03 (q, 4H, CH_2).

^{13}C NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 152.9 (s, 1C, C=O), 77.6 (s, 2C, CH_2-O), 14.8 (s, 1C, CH_2-CH_2).

Hansen Solubility Parameters Theory

The basis of Hansen solubility parameters (HSP) is the assumption that the total cohesive energy (E) must be the sum of individual contributions from nonpolar (dispersion) interactions (E_d), polar (dipole-dipole and dipole-induced-dipole) interactions (E_p), and hydrogen-bonding or other specific association interactions (including Lewis acid-base interactions) $(E_h)^2$:

$$E = E_d + E_p + E_h$$

Dividing the individual cohesive energy terms by the molar volume (V) gives Equation.

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V}$$

The square of the total solubility parameter (δ_T^2) is the sum of the squares of the Hansen dispersion (δ_D^2), polar (δ_P^2) and hydrogen-bonding (δ_H^2) contributions.

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

The distance between two molecules, a solute *i* and a solvent *j*, in Hansen three-dimensional space defined as "distance", R_a, depends on their respective partial solubility parameter components.

$$R_a = \sqrt{4(\delta_{Di} - \delta_{Dj})^2 + (\delta_{Pi} - \delta_{Pj})^2 + (\delta_{Hi} - \delta_{Hj})^2}$$

By a trial-and-error system, solvents tested are plotted in Hansen three-dimensional space creating the "solubility sphere". Thus, this solubility sphere is defined as the region where solvent–solute combinations occur as a solution and the radius of the sphere is known as "interaction radius" (R_0). Thereby, the Relative Energy Difference (RED) is defined as follows:

$$RED = \frac{R_a}{R_0}$$

The RED value indicates how strong is the interaction of the solvent with the polymer. Good solvents for a given polymer have a RED value inferior to 1, while superior values are synonymous of low affinity.

Table S1. Values obtained for the solute, BPA-PC.

Polymer	δ_d [MPa$^{1/2}$]	δ_P [MPa$^{1/2}$]	δ_H [MPa$^{1/2}$]	R_0
BPA-PC	19,1	10,1	9,3	6,4

Table S2. Values for the different solvents and corresponding RED values for BPA-PC.

Solvent	δ_d [MPa$^{1/2}$]	δ_P [MPa$^{1/2}$]	δ_H [MPa$^{1/2}$]	R_a [MPa$^{1/2}$]	RED*
1-Methyl-1H-imidazole	19,7	15,6	11,2	5,94	0,92834067
Tetrahydrofuran	16,8	5,7	8	6,50	1,01514412
Chloroform	17,8	3,1	5,7	8,29	1,29527386
2-methyltetrahydrofuran	16,9	5	4,3	8,39	1,3107317
Dioxane	19,00	1,80	7,40	8,52	1,33078777
Acetonitrile	15,3	18	6,1	11,42	1,78433122
Toluene	18	1,4	2	11,57	1,80750929
Benzene	18,4	0	2	12,54	1,95942733
Triethylamine	17,8	0,4	1	13,03	2,03569226
1,3-Propanediol	16,8	13,5	23,2	15,03	2,34858876
Formamide	17,2	26,2	19	19,18	2,99633565

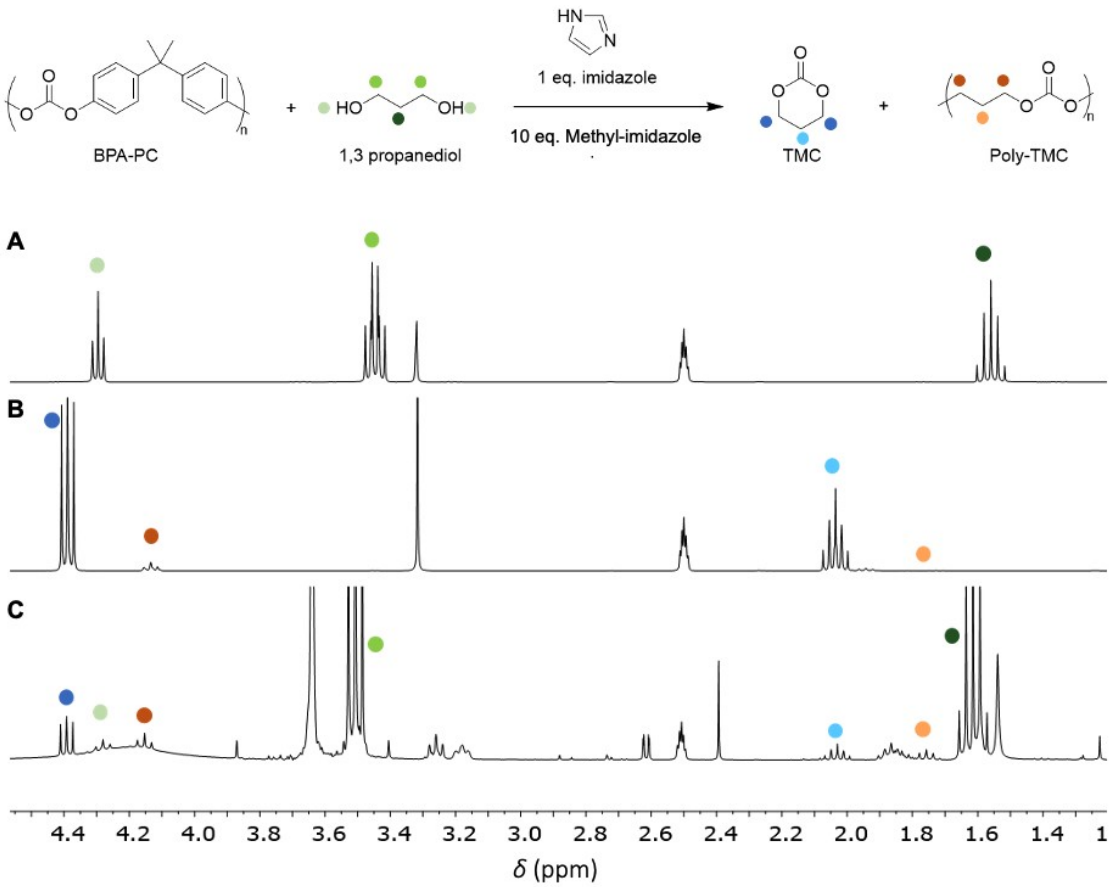


Figure S1. ^{1}H NMR spectra and assignation of **A.** the reactant, 1,3-propnaediol, **B.** the products formed, TMC and PTMC, and **C.** the crude of the depolymerisation reaction.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) TMC δ (ppm): 4.40 (t, J = 11.3 Hz, 4H), 2.04 (m, J = 5.7 Hz, 2H).

^{1}H NMR (400 MHz, DMSO-d_6, 298K) PTMC δ (ppm): 4.16 (m, J = 7.9, 3.9, 2.1 Hz, 4H), 1.80 – 1.72 (m, 2H).

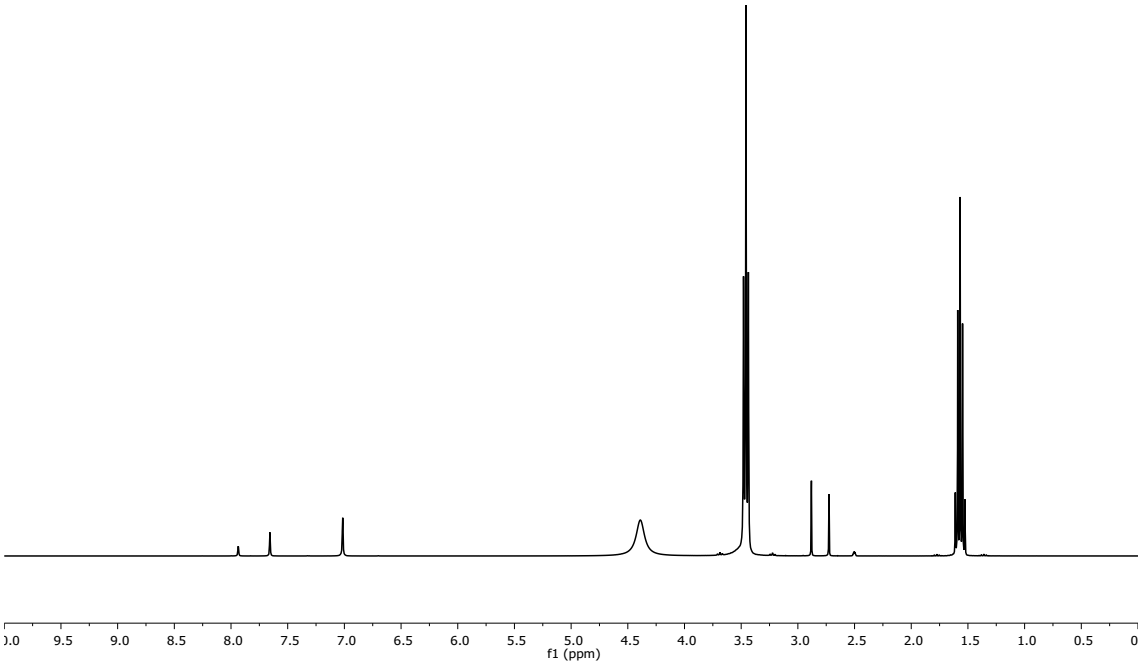


Figure S2. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 10 eq. of 1,3-propanediol as nucleophile, in bulk, after 3 h at 50 °C. No conversion was observed.

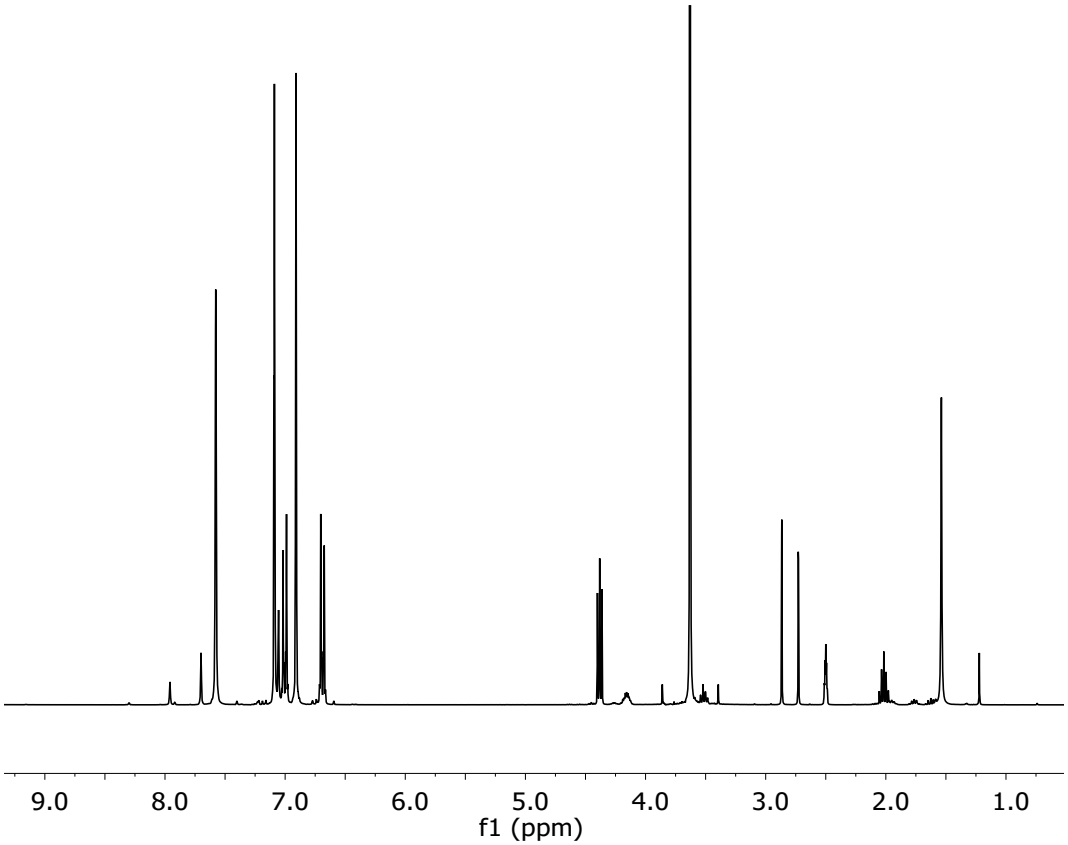


Figure S3. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

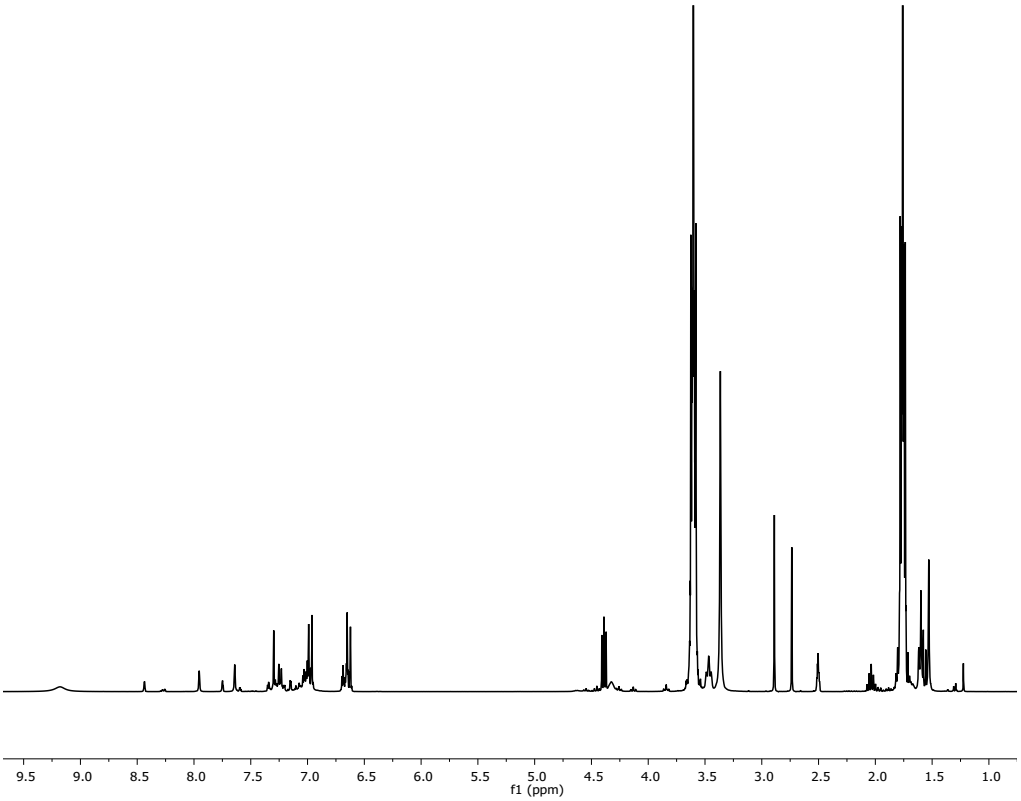


Figure S4. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of THF as solvent, after 3 h at 50 °C.

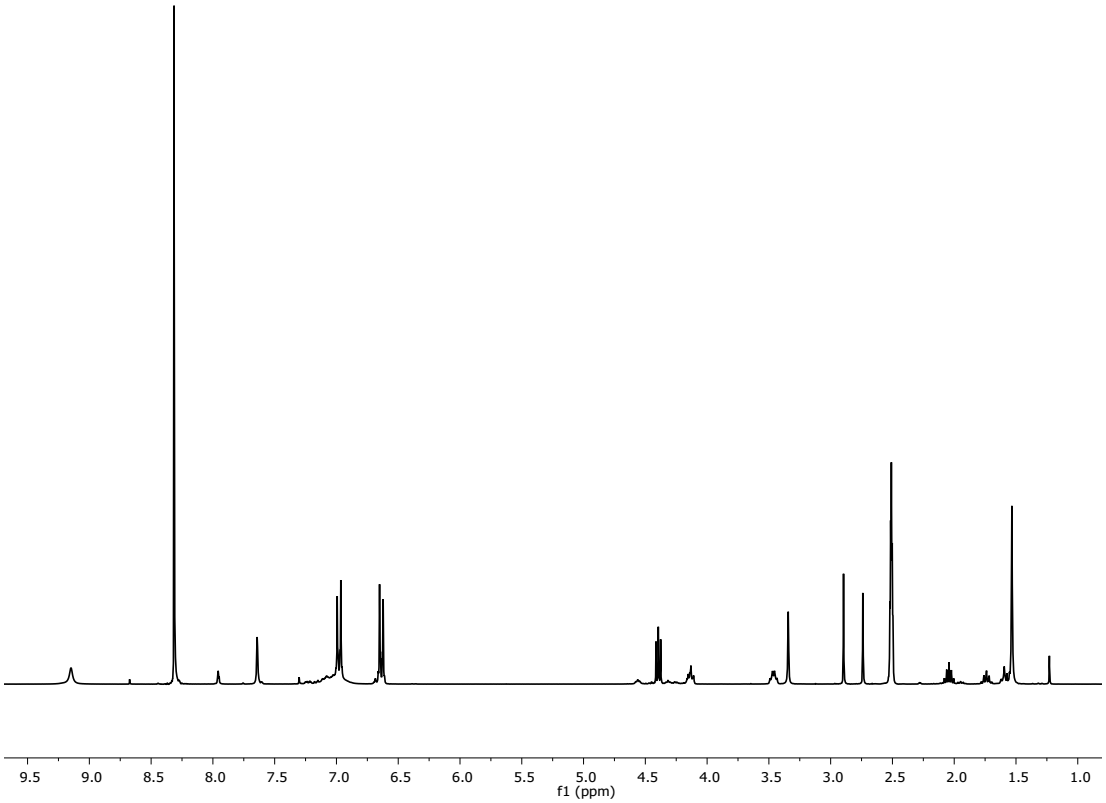


Figure S5. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1 eq. of 1,3-propanediol as nucleophile and 10 eq. of chloroform as solvent, after 3 h at 50 °C.

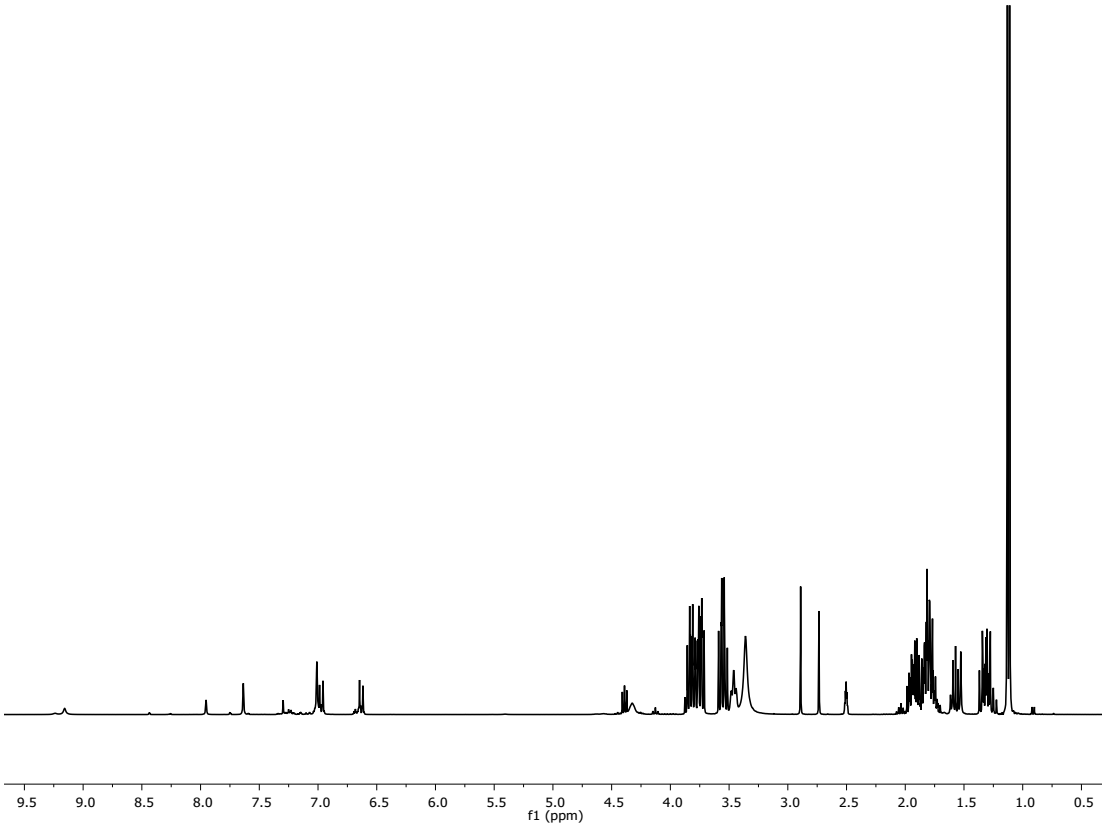


Figure S6. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 2-Methyl-THF as solvent, after 3 h at 50 °C.

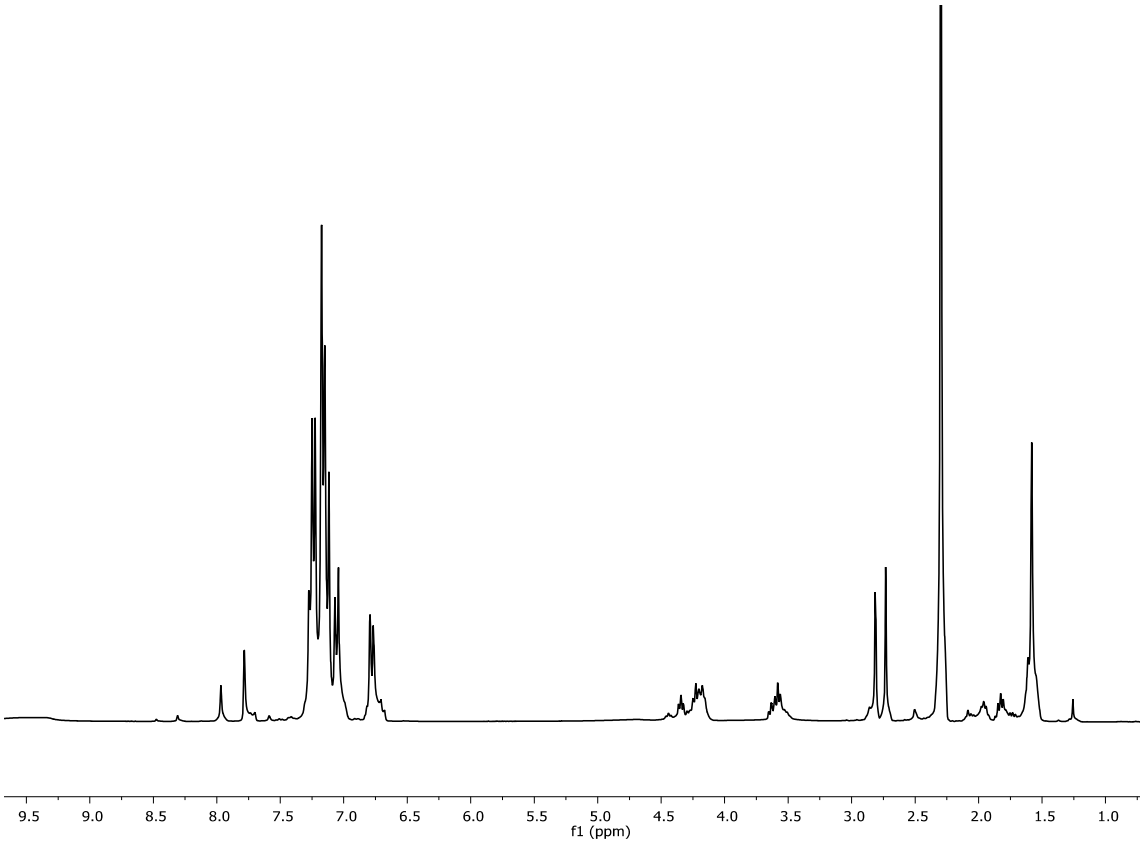


Figure S7. ^{1}H NMR spectra of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of toluene as solvent, after 3 h at 50 °C.

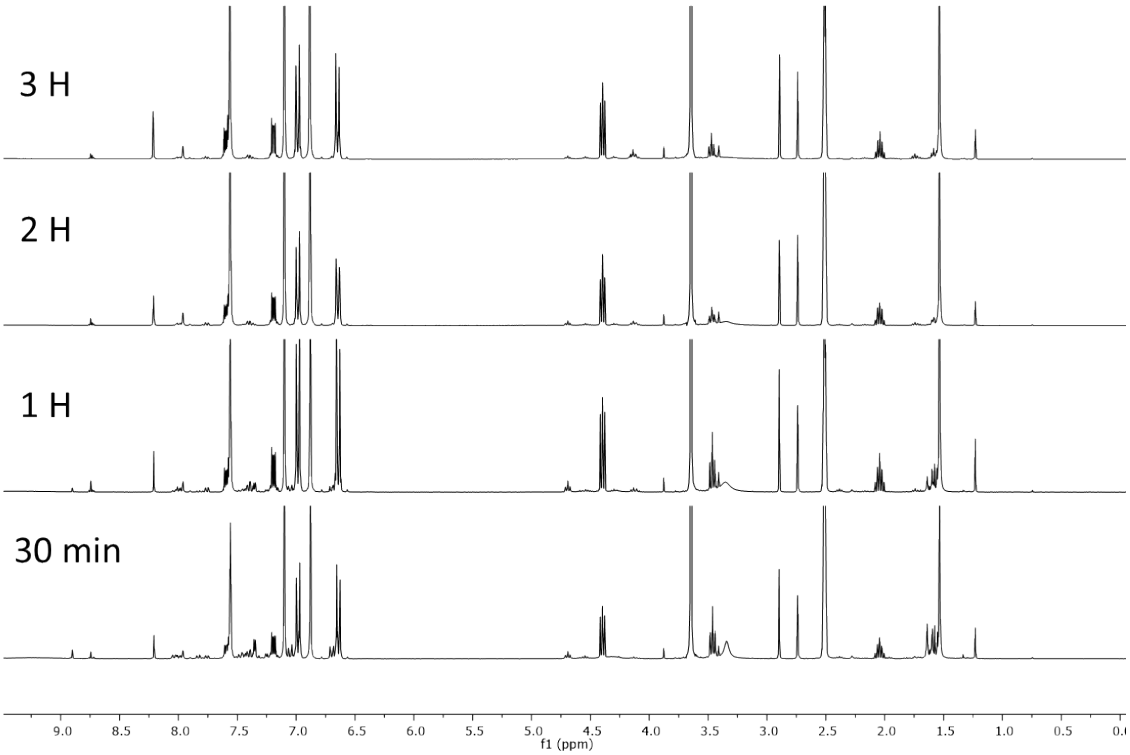


Figure S8. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of benzimidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

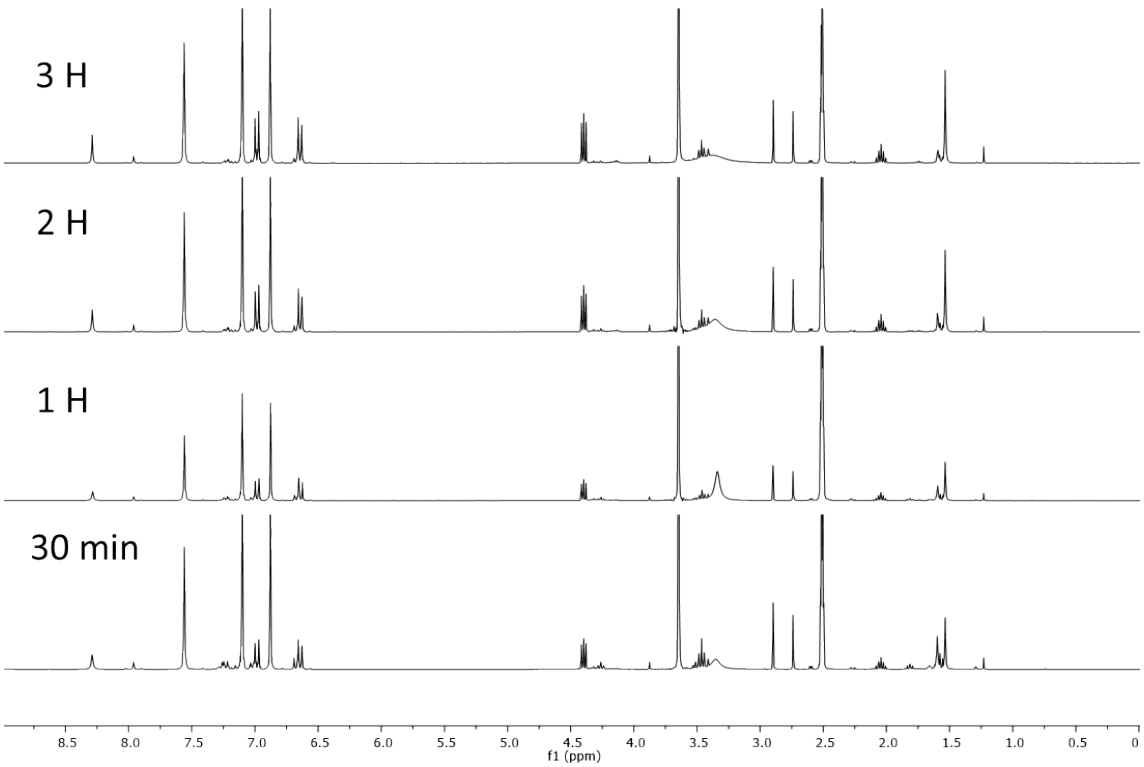


Figure S9. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of triazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

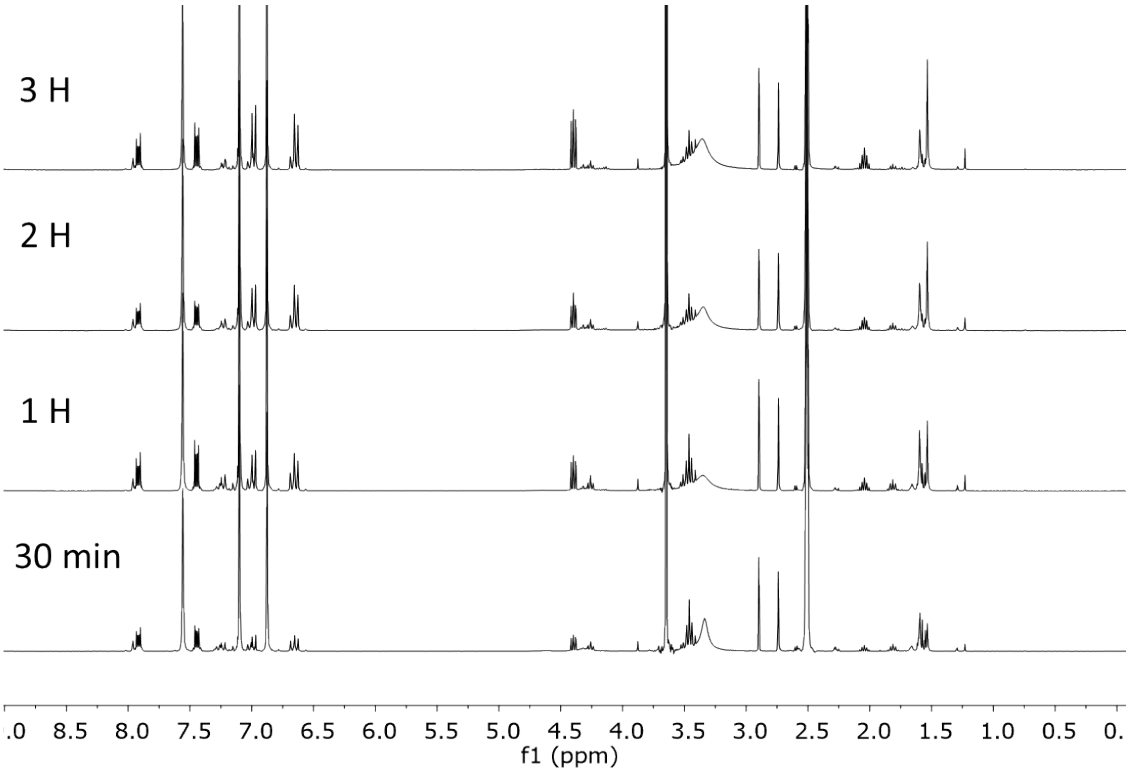


Figure S10. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of benzotriazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

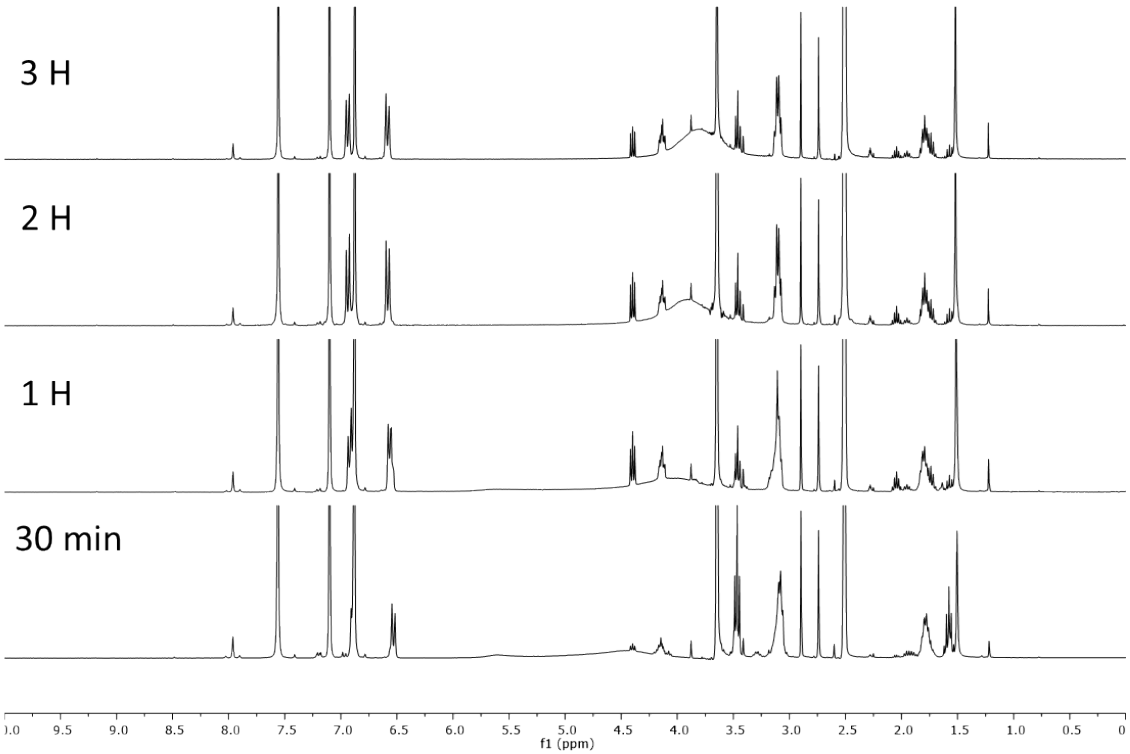


Figure S11. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of TBD as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

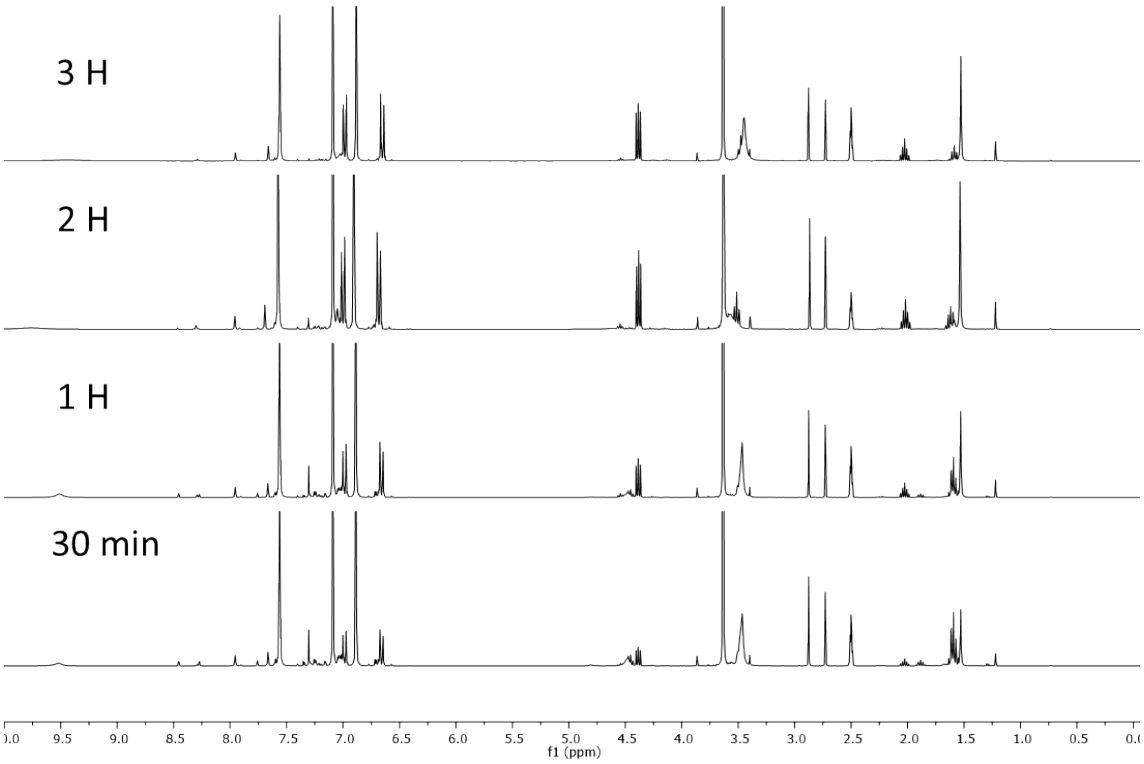


Figure S12. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 40 °C.

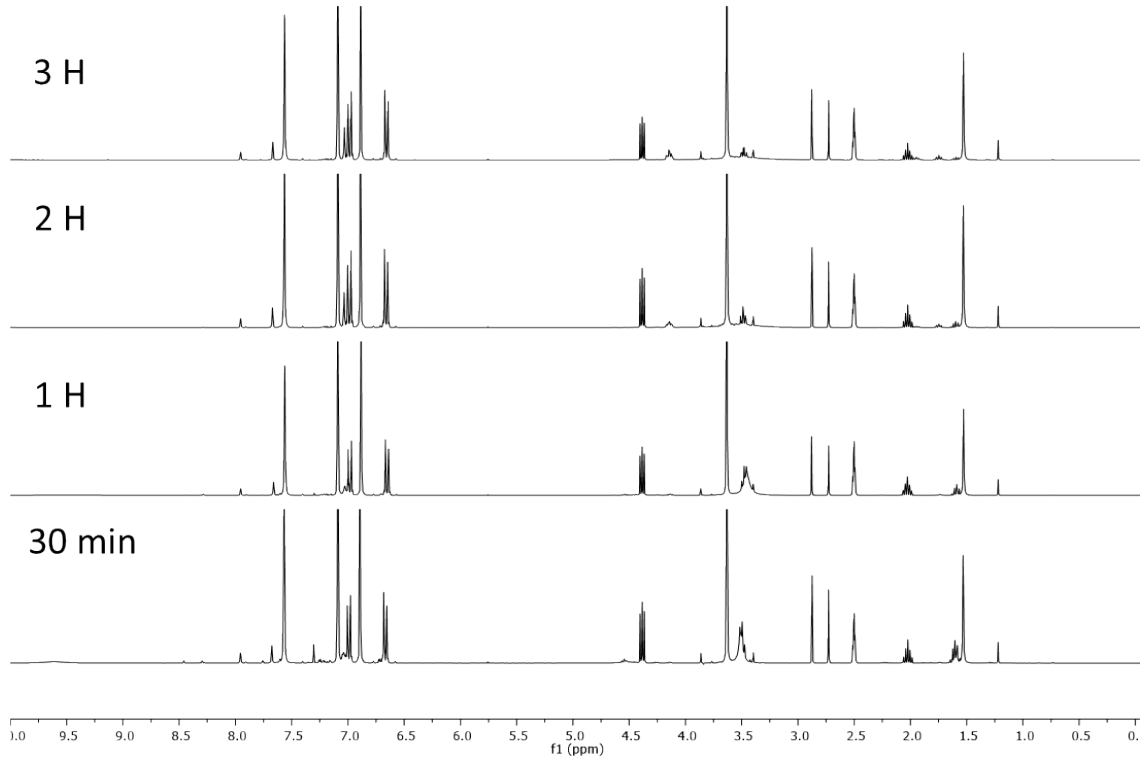


Figure S13. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 60 °C.

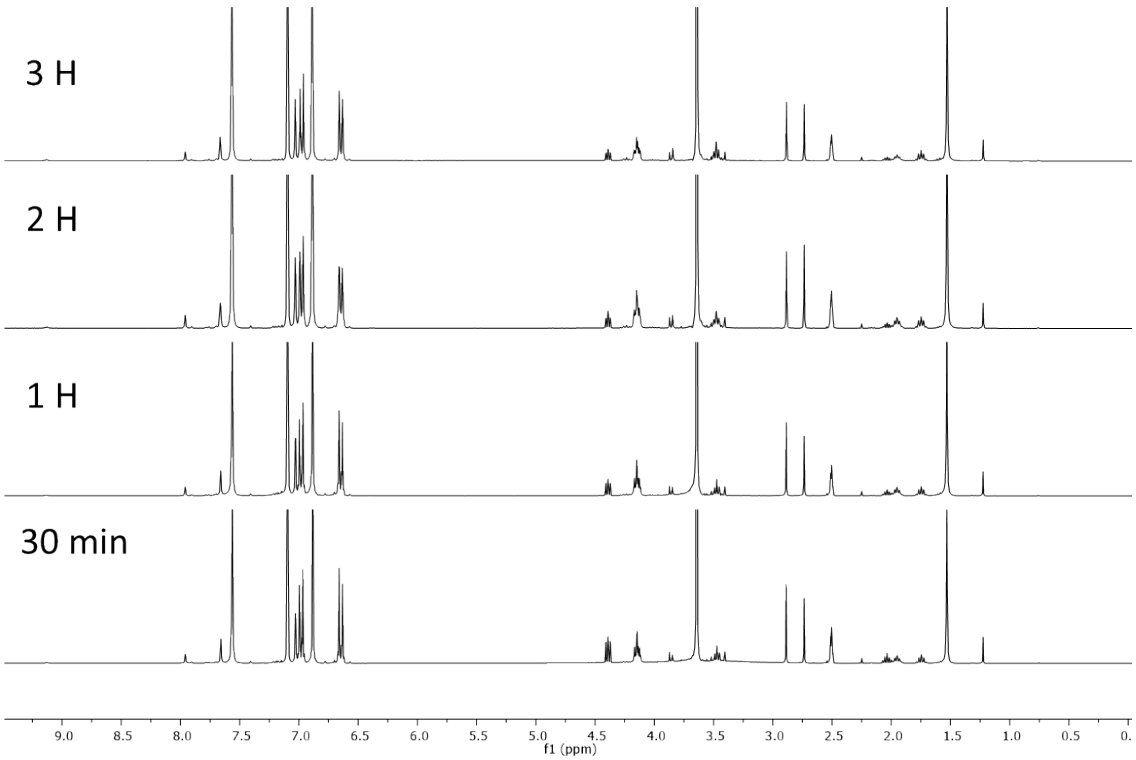


Figure S14. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 90 °C.

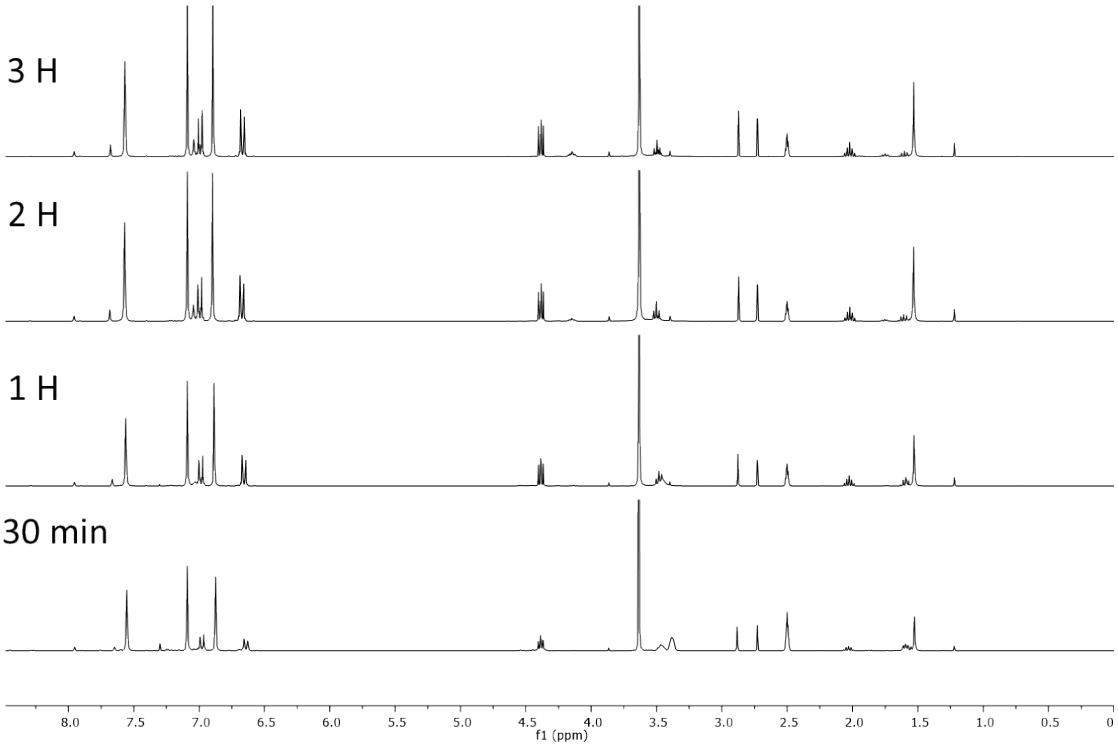


Figure S15. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.25 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

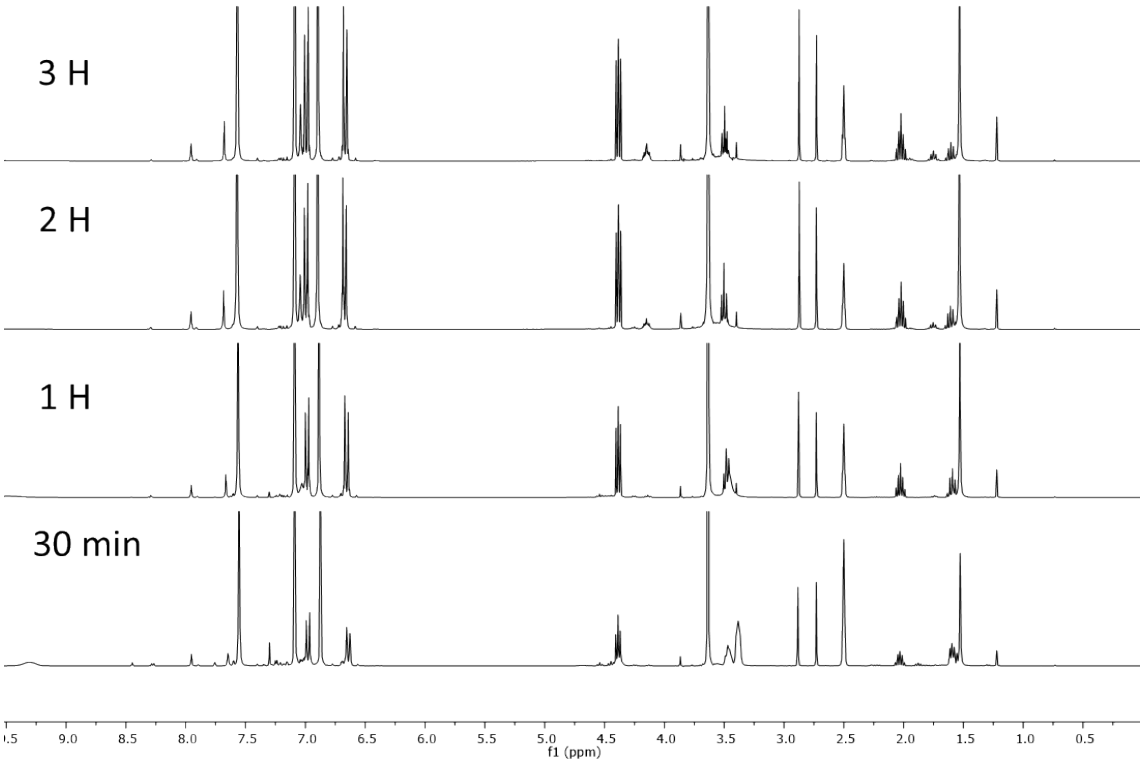


Figure S16. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.5 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

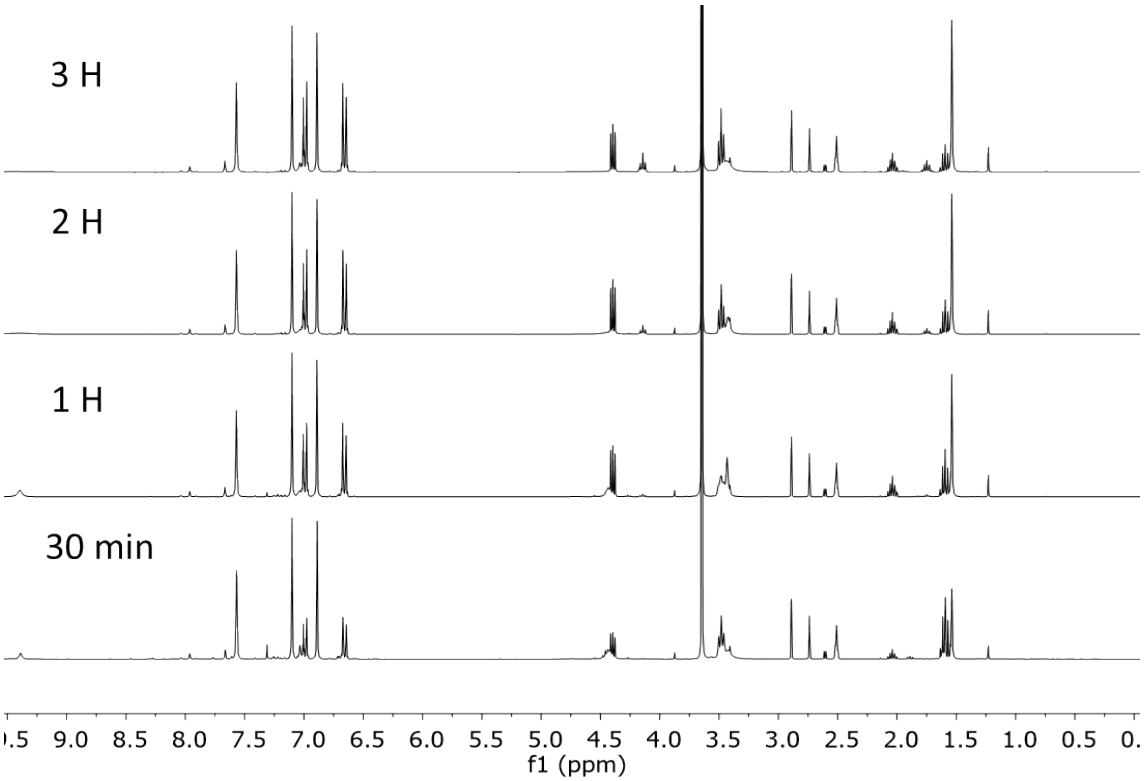


Figure S17. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.75 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

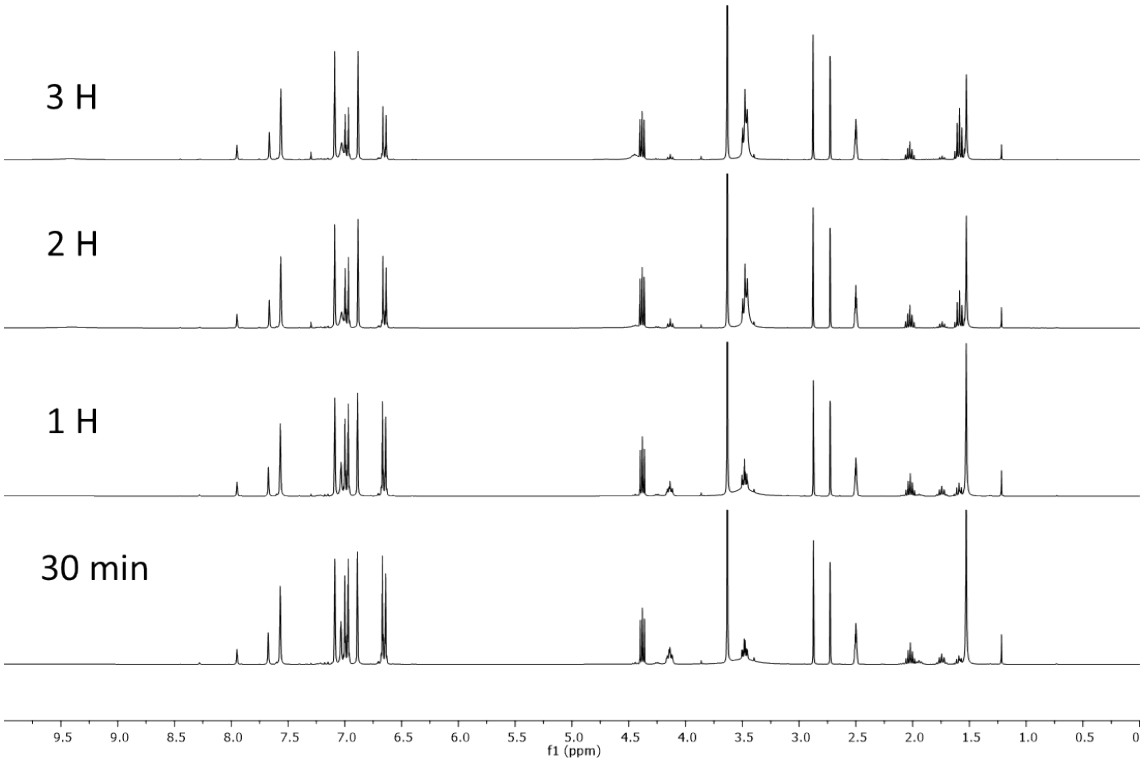


Figure S18. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 2.5 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

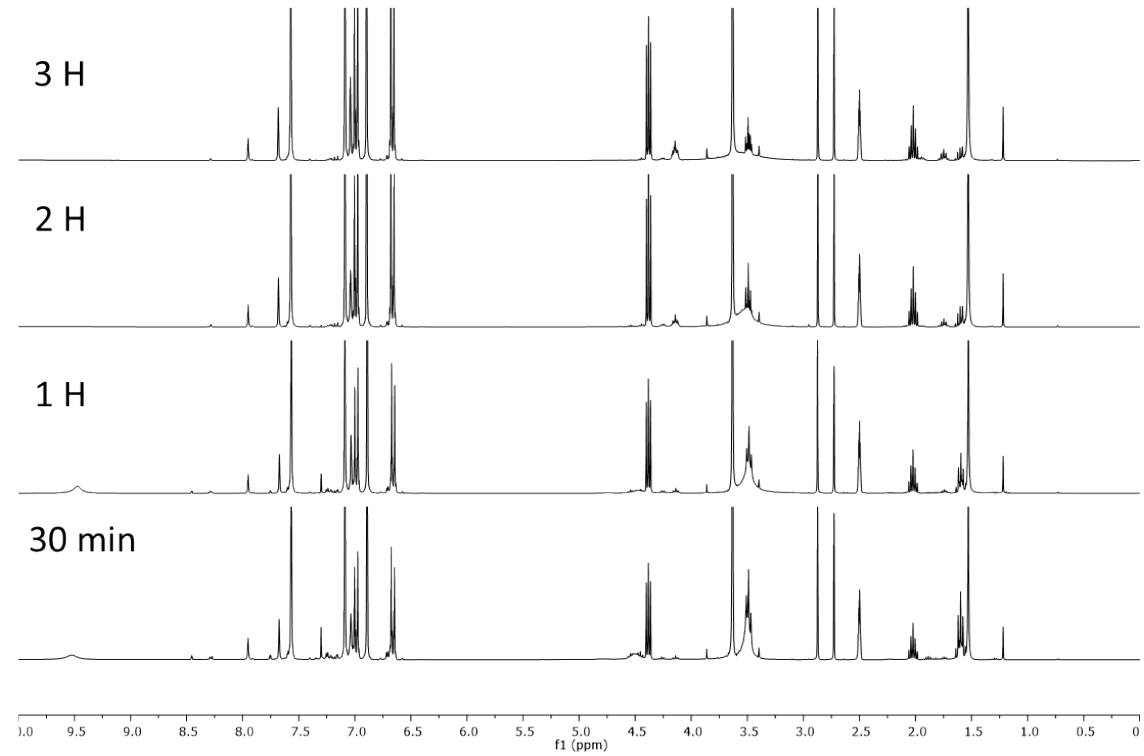


Figure S19. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 5 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

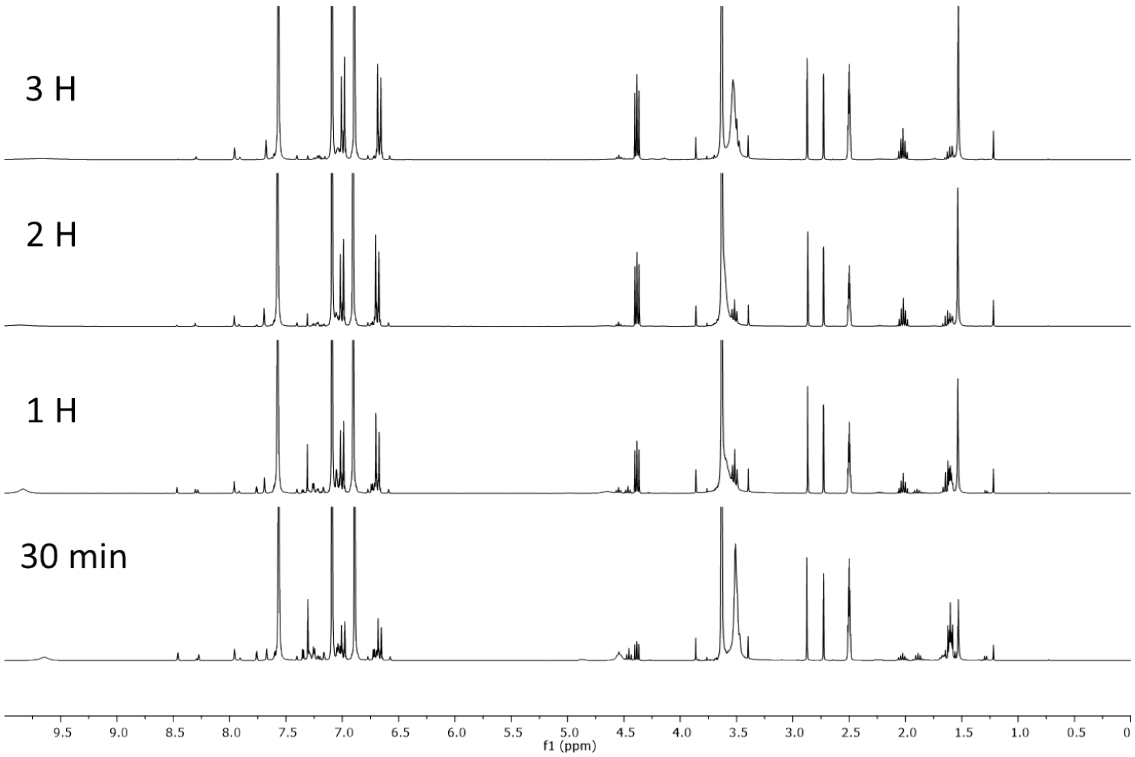


Figure S20. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 20 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

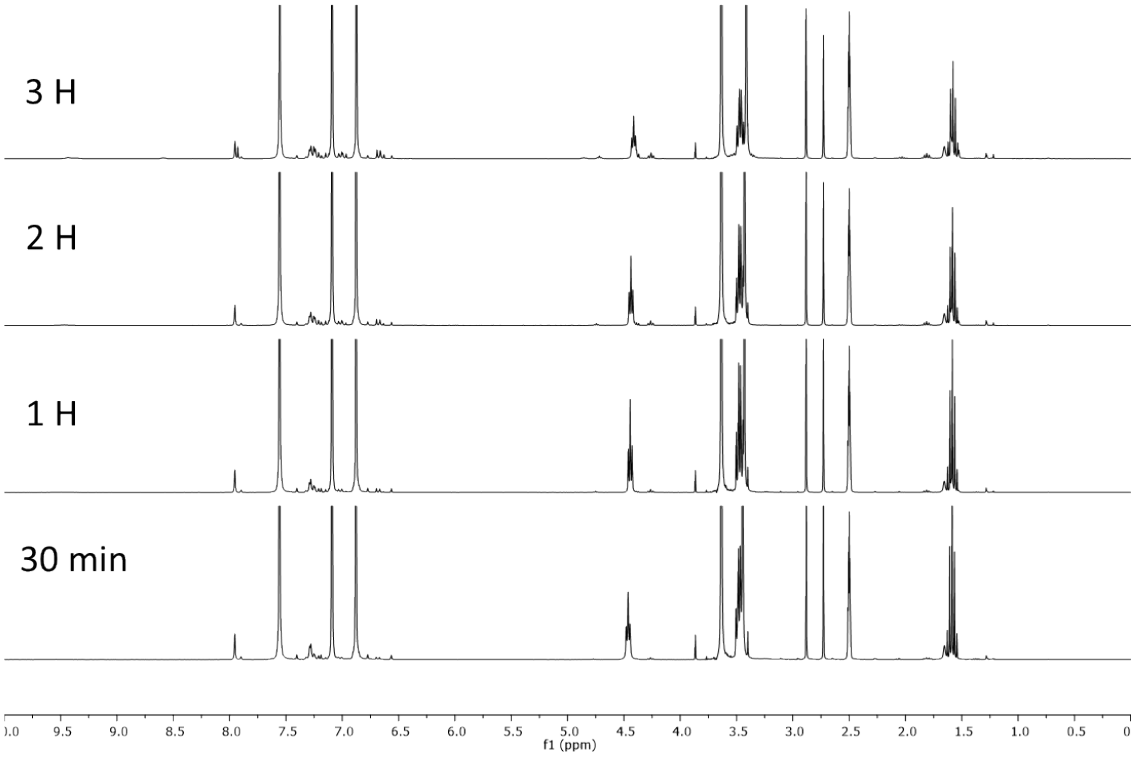


Figure S21. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out without catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

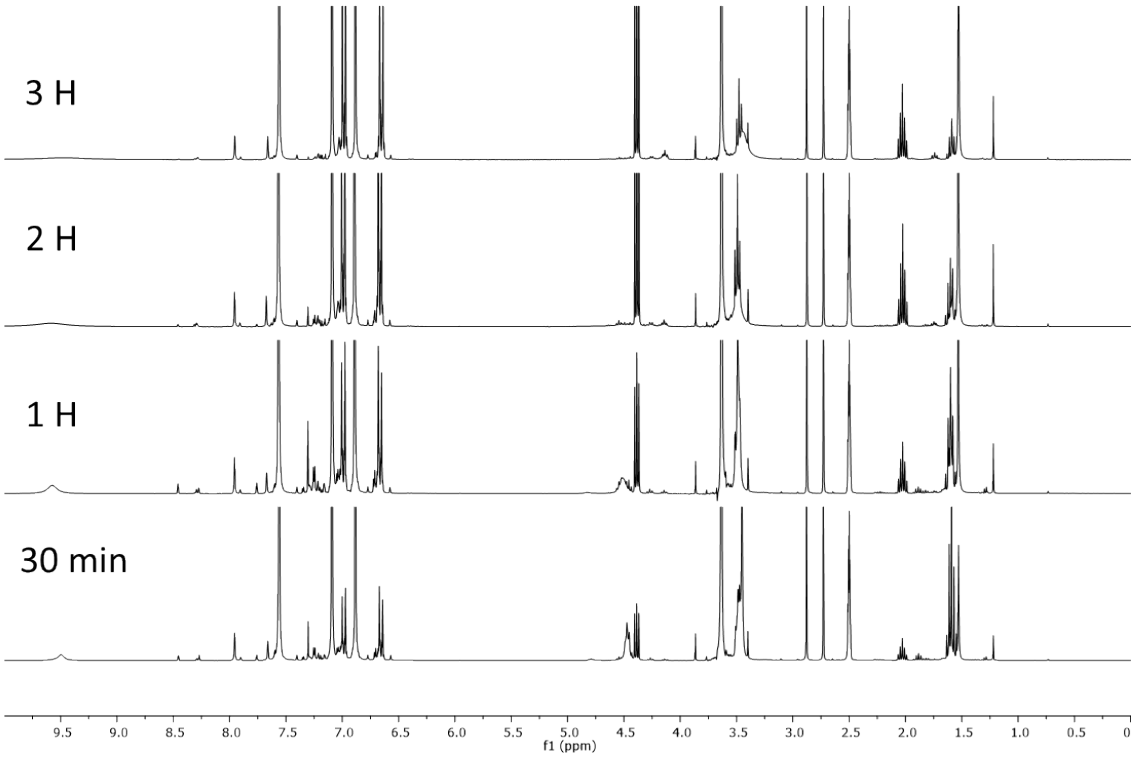


Figure S22. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 0.5 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

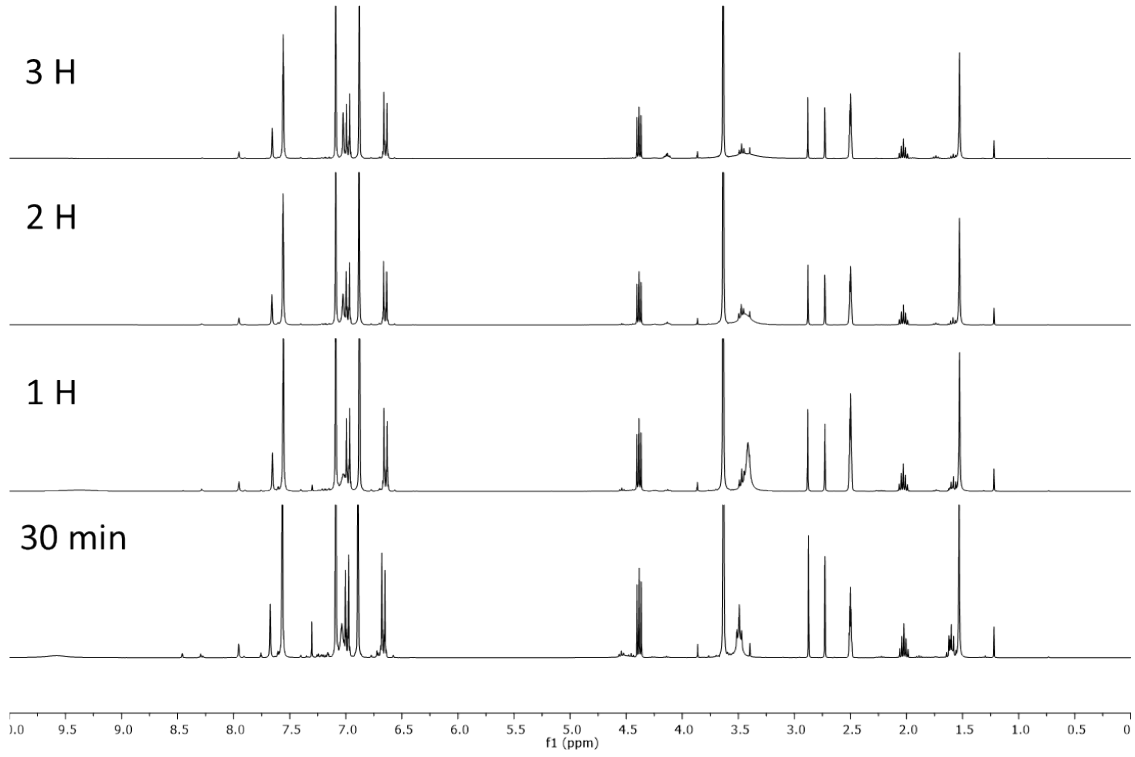


Figure S23. Kinetics of the depolymerisation of BPA-PC monitored through ^{1}H NMR spectroscopy carried out with 2 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 °C.

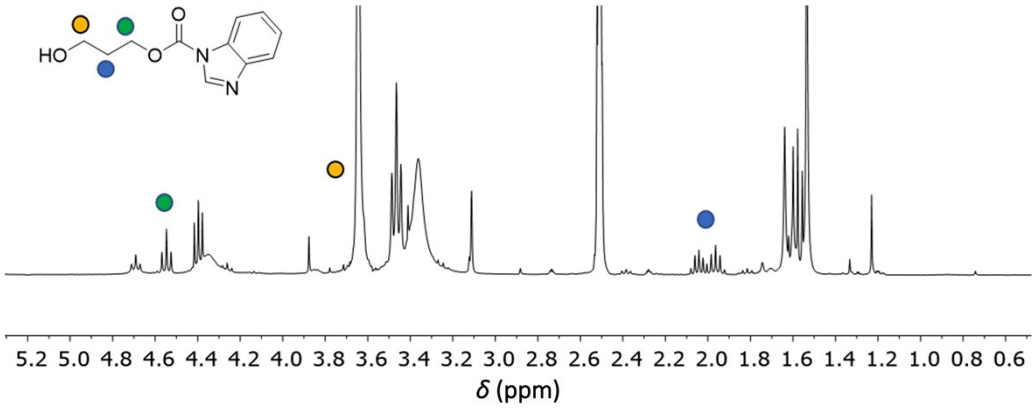


Figure S24. ^{1}H NMR spectrum of the crude product of model reaction 2, 20 min after the addition of 1,3-propnediol. *Reaction conditions: 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 ℃.*

^{1}H NMR (400 MHz, DMSO-d_6, 298K) TMC δ (ppm): δ 4.55 (t, 2H, J = 6.4 Hz), 3.65 (t, 2H) 1.96 (m, 2H, J = 6.2 Hz).

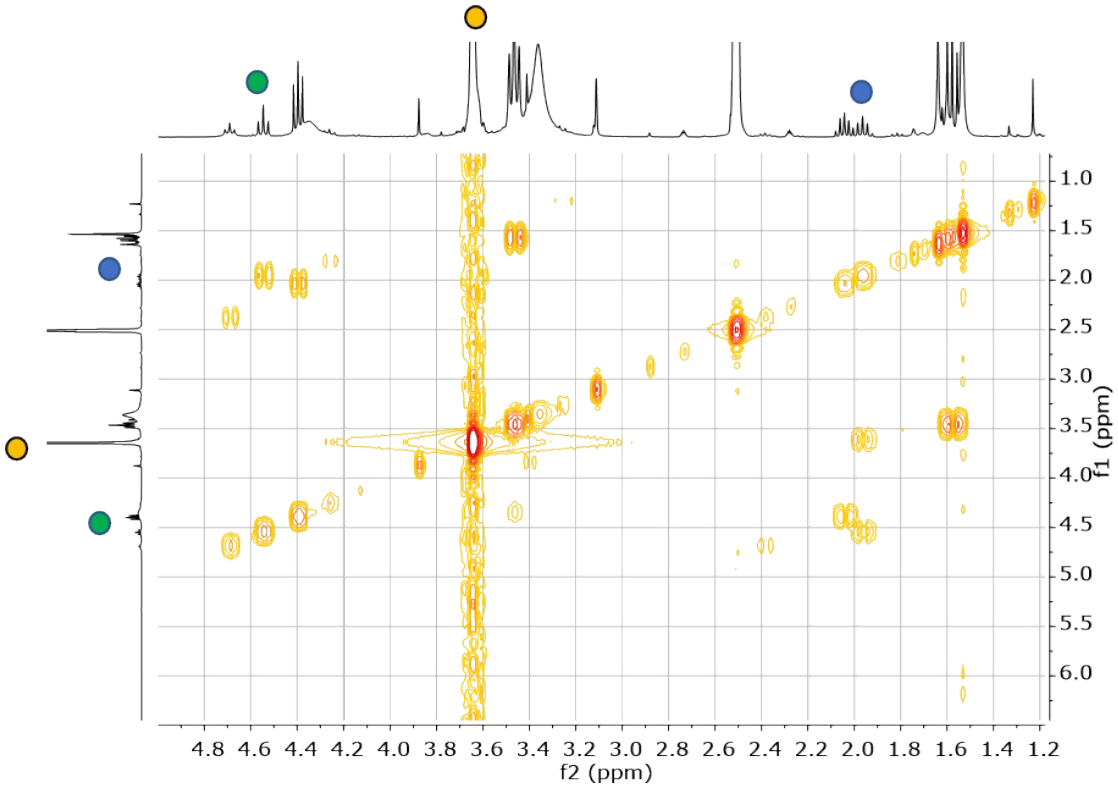


Figure S25. ^{1}H-^{1}H COSY NMR spectrum of the model reaction 2 after addition of 1,3-propnediol after 20 min of reaction. *Reaction conditions: 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-propanediol as nucleophile and 10 eq. of 1-Methylimidazole as solvent, after 3 h at 50 ℃.*

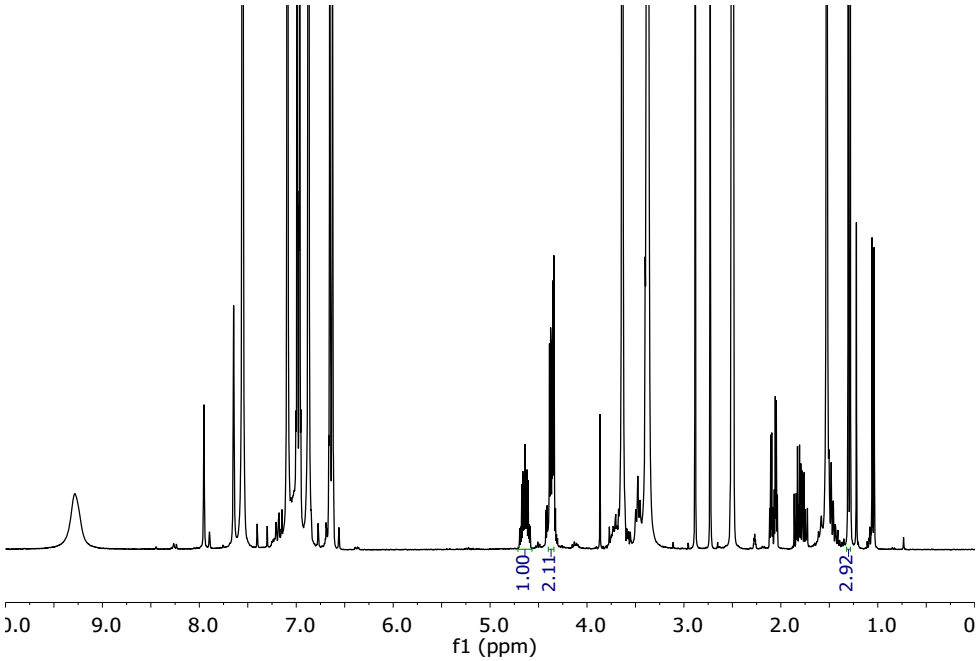


Figure S26. ^{1}H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 1,3-butanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^{1}H NMR (400 MHz, DMSO-d6, 298K) δ (ppm) 4.65 (m, 1H, CH, J = 6.2, 4.0, 3.3 Hz), 4.37 (m, 2H, CH2, J = 4.4 Hz), 1.79 (m, 2H, CH2), 1.29 (d, 6H, CH3, J = 6.3 Hz).

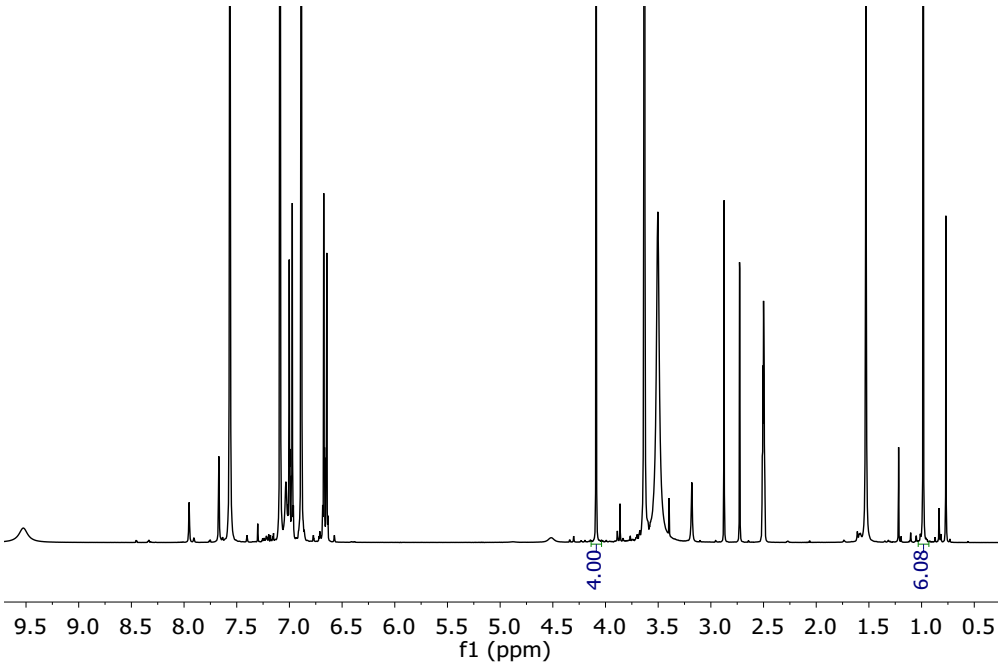


Figure S27. ^{1}H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of 2,2-dimethyl propanediol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 4.09 (s, 4H, CH_2), 0.99 (s, 6H, CH_3).

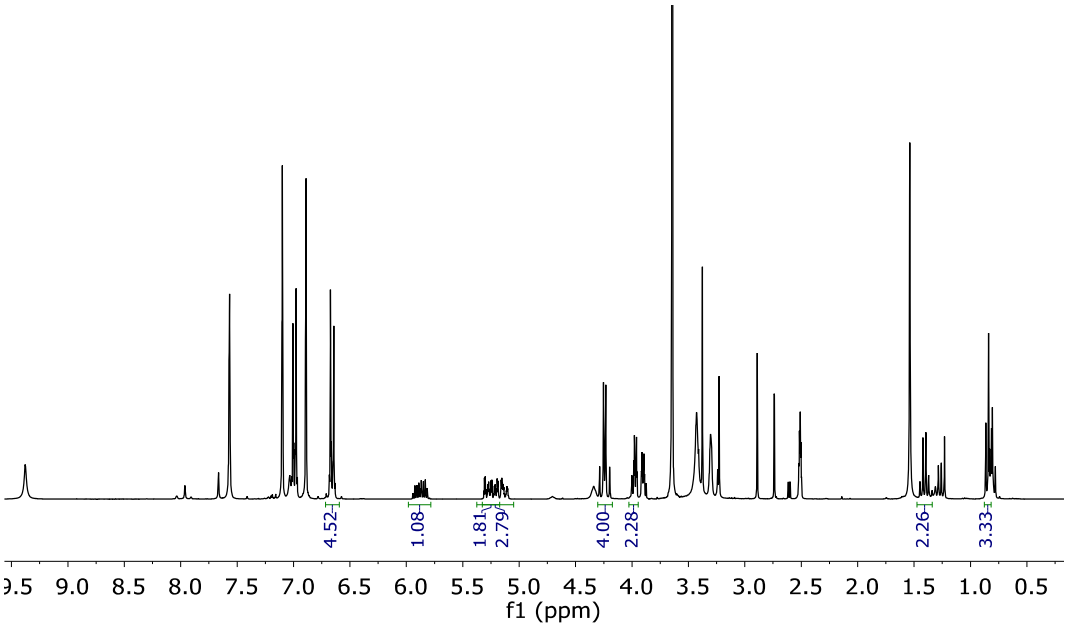


Figure S28. ^{1}H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of trimethylolpropane allyl ether as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 5.94 – 5.79 (m, 1H, J = 17.3, 10.5, 5.3 Hz, CH=CH_2), 5.27 – 5.11 (m, 2H, CH=CH_2, J = 33.3, 15.7, 10.4, 1.7 Hz), 4.23 (q, 2H, O-CH_2-C-CH_2-O), 4.00 (m, 2H, O-CH_2-C-CH_2-O, J = 5.4, 1.5 Hz), 3.98 (s, 2H, O-CH_2-CH), 1.39 (m, 2H, CH_2-CH_3, J = 7.6 Hz), 0.84 (m, 6H, CH_2-CH_3, J = 7.1, 2.3 Hz).

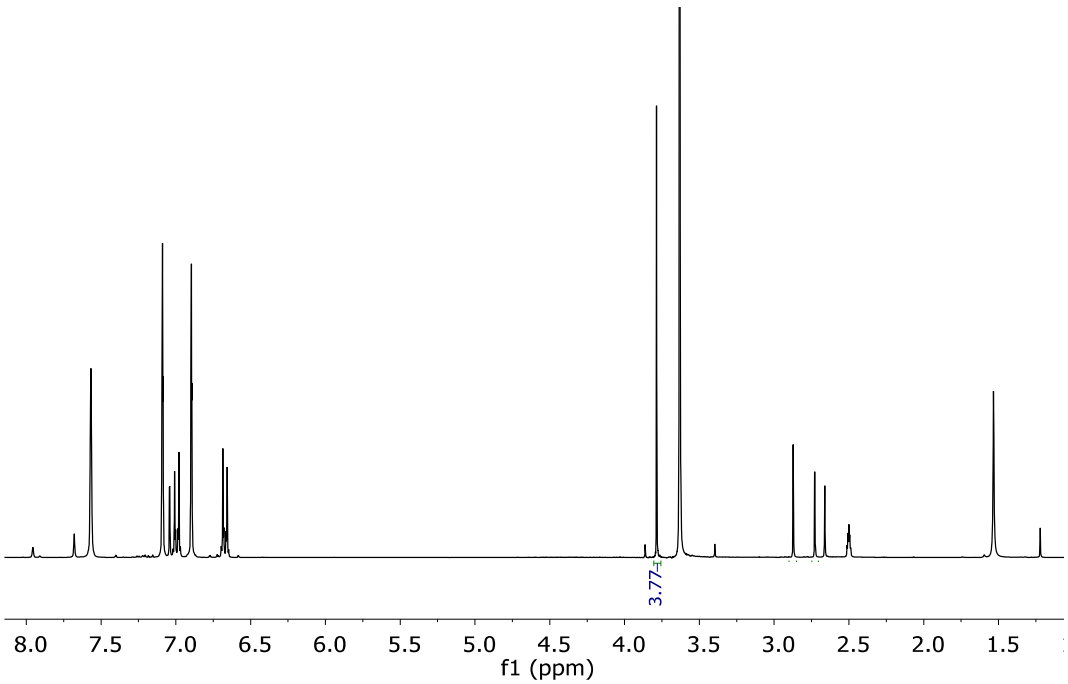


Figure S29. ^{1}H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of ethanedithiol as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 3.77 (s, 4H, J = 6.8 Hz, CH_2).

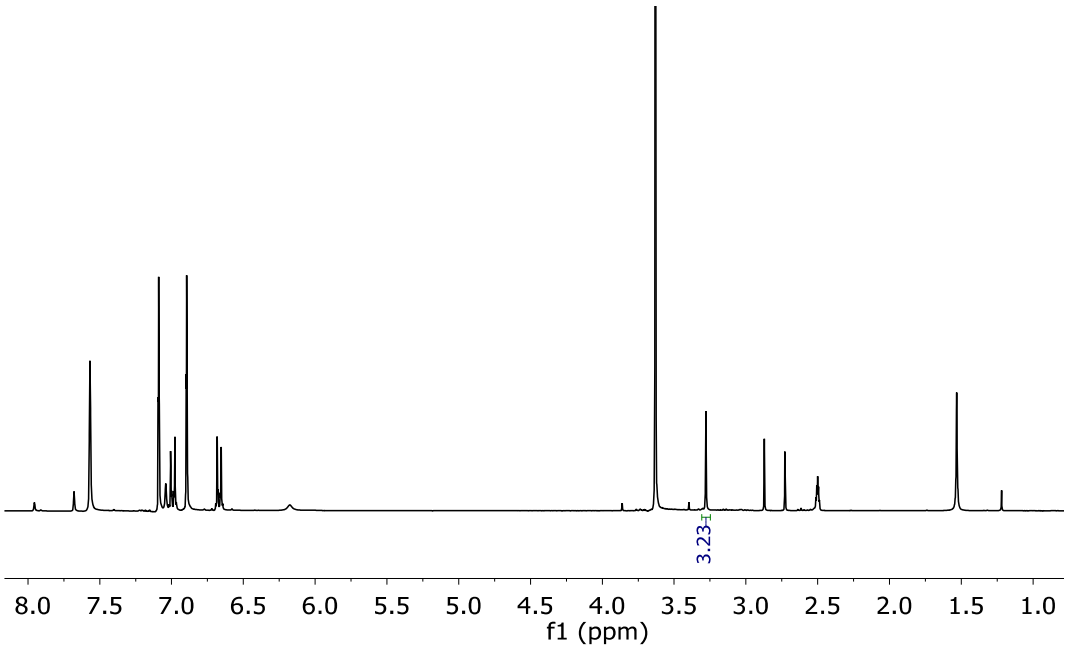


Figure S30. ^{1}H NMR spectrum of the crude product of the depolymerisation of BPA-PC carried out with 1 eq. of imidazole as catalyst, 1.05 eq. of ethylenediamine as nucleophile and 10 eq. of 1-methylimidazole as solvent, after 3 h at 50 °C.

^{1}H NMR (400 MHz, DMSO-d_6, 298K) δ (ppm) 3.27 (s, 4H, J = 5.2 Hz, CH_2).

References

(1) Tan, E. W. P.; Hedrick, J. L.; Arrechea, P. L.; Erdmann, T.; Kiyek, V.; Lottier, S.; Yang, Y. Y.; Park, N. H. Overcoming Barriers in Polycarbonate Synthesis: A Streamlined Approach for the Synthesis of Cyclic Carbonate Monomers. *Macromolecules* 2021, *54* (4), 1767–1774. https://doi.org/10.1021/acs.macromol.0c02880.

(2) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*, CRC Press.; CRC Press: Boca Raton, 2007. https://doi.org/10.1201/9781420006834.