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Aryloxy ‘biometal’ complexes as efficient catalysts for the synthesis of poly(butylene adipate terephthalate)

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S1. NMR spectra of the aryloxy complexes of Mg, Zn and Al

As mentioned in the manuscript, all aryloxy complexes of 'biometals' were obtained using published methods. ^{1}H NMR spectra, presented below, reflect the grade of purity of the catalysts used in the synthesis of PBAT.

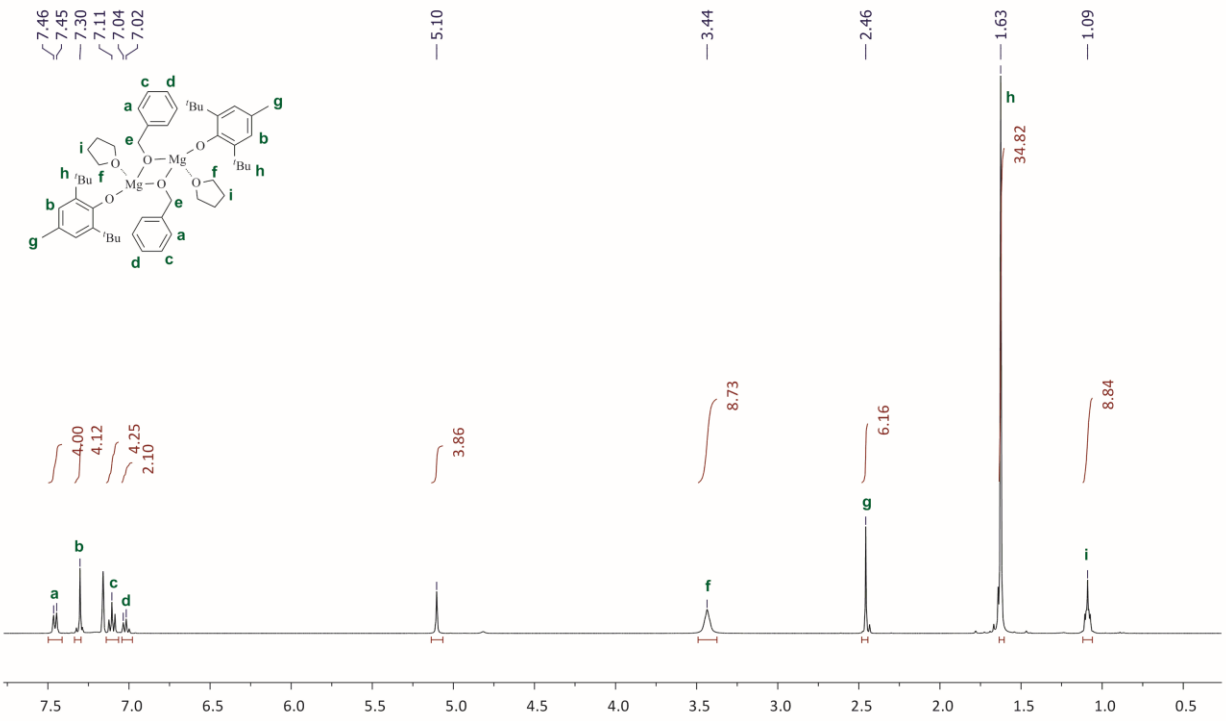


Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **1**.

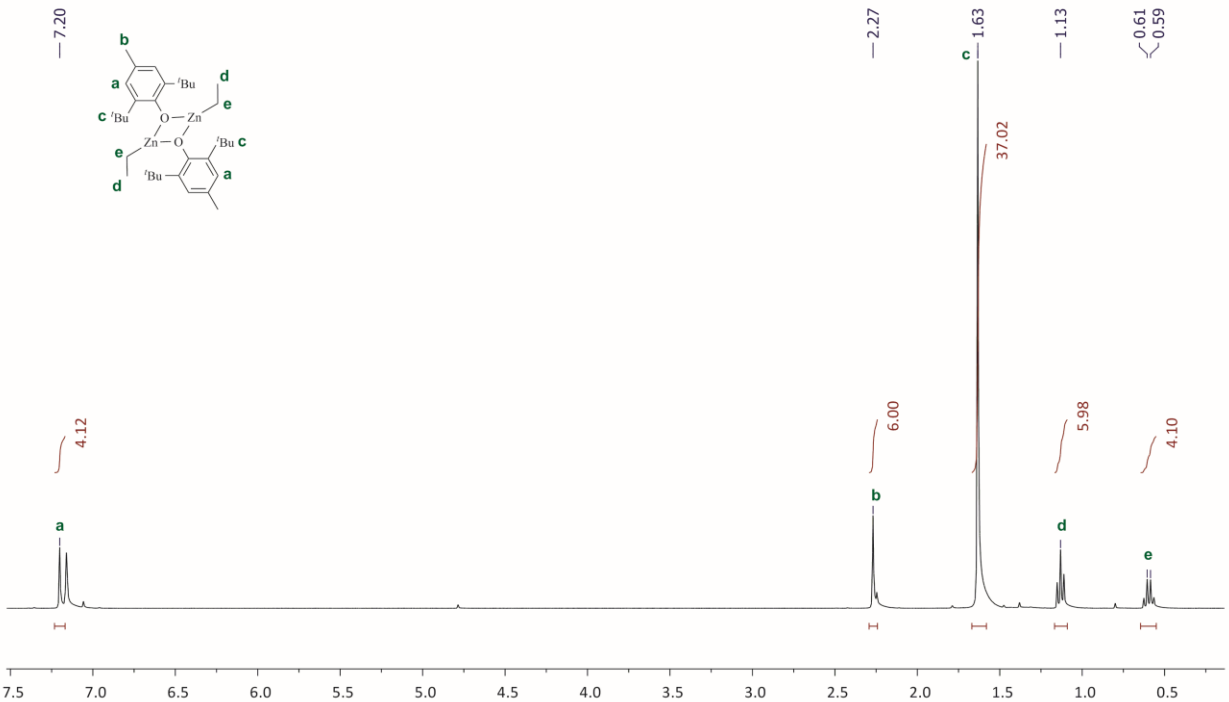


Figure S2. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **2**.

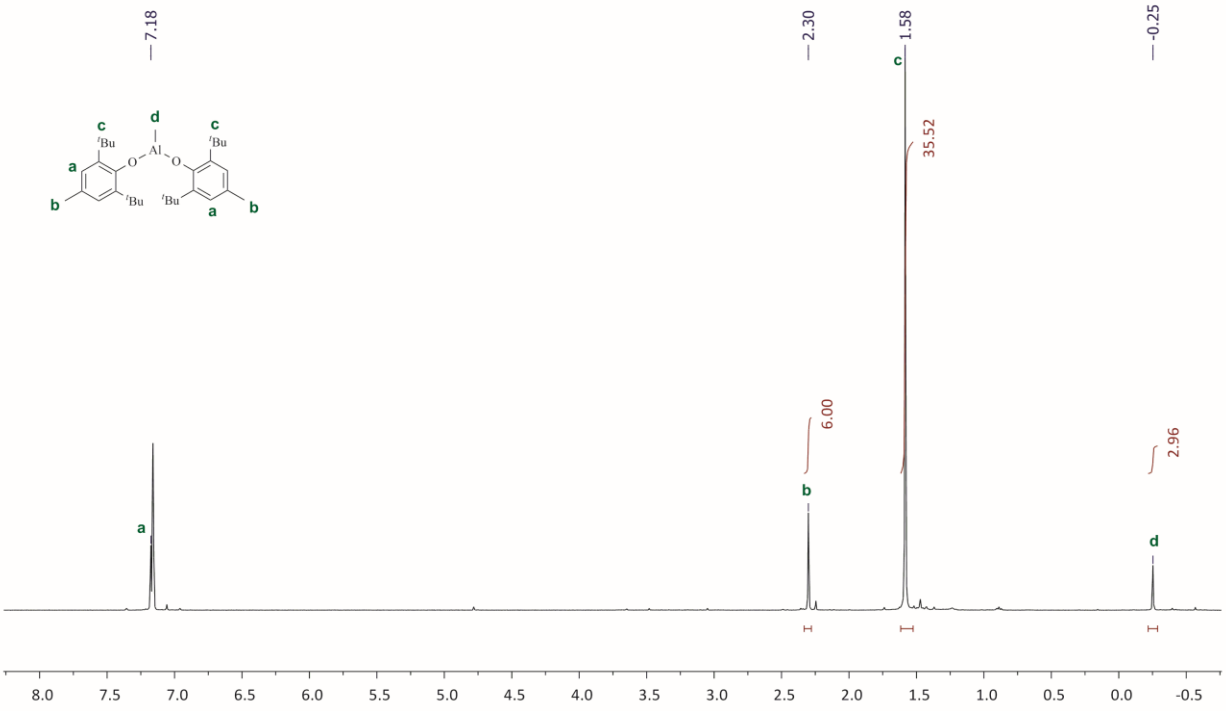


Figure S3. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **3a**.

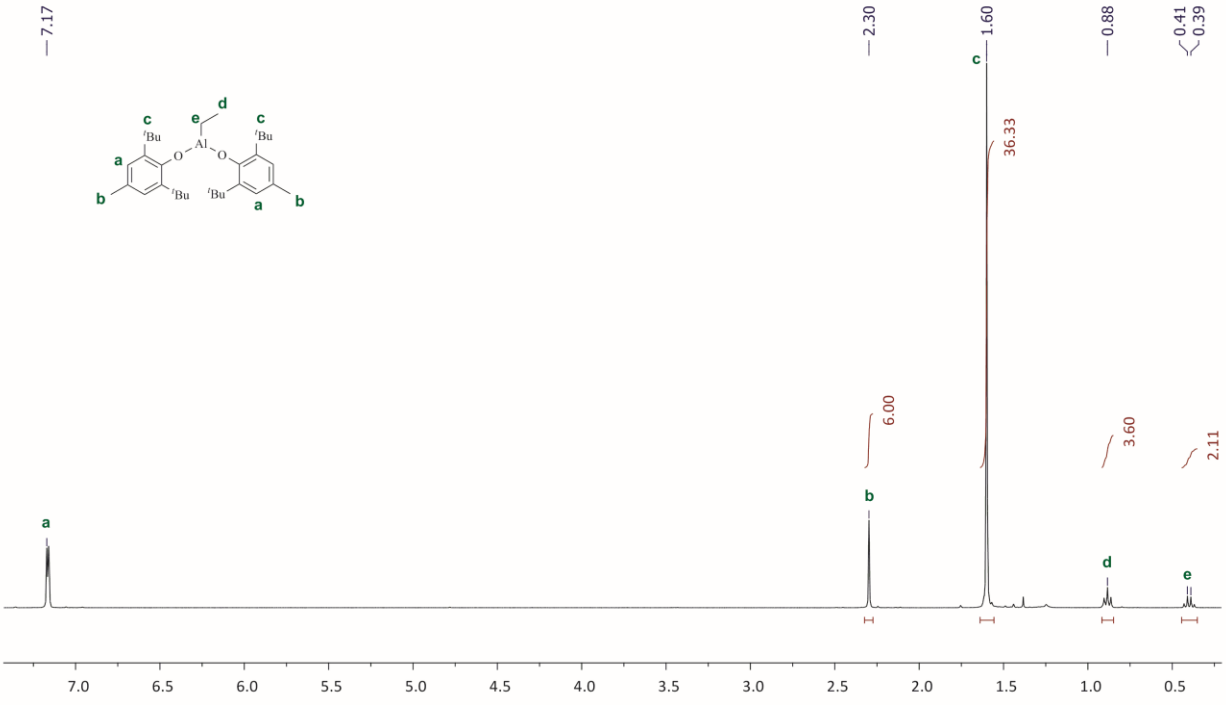


Figure S4. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **3b**.

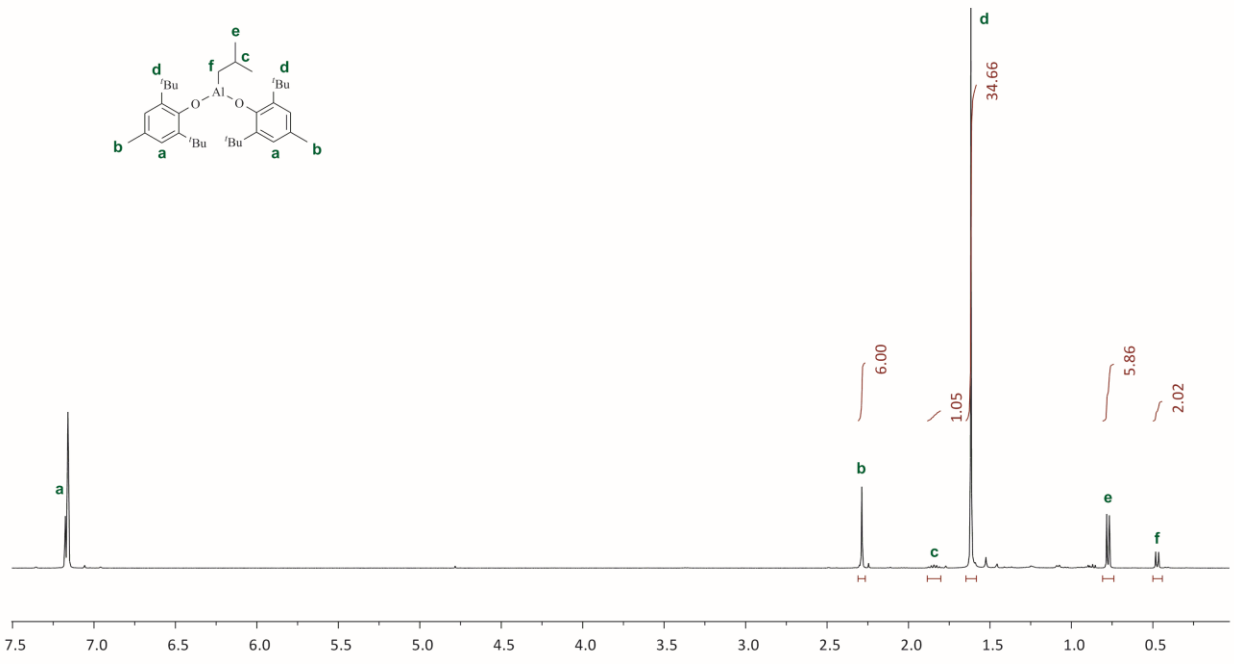


Figure S5. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **3c**.

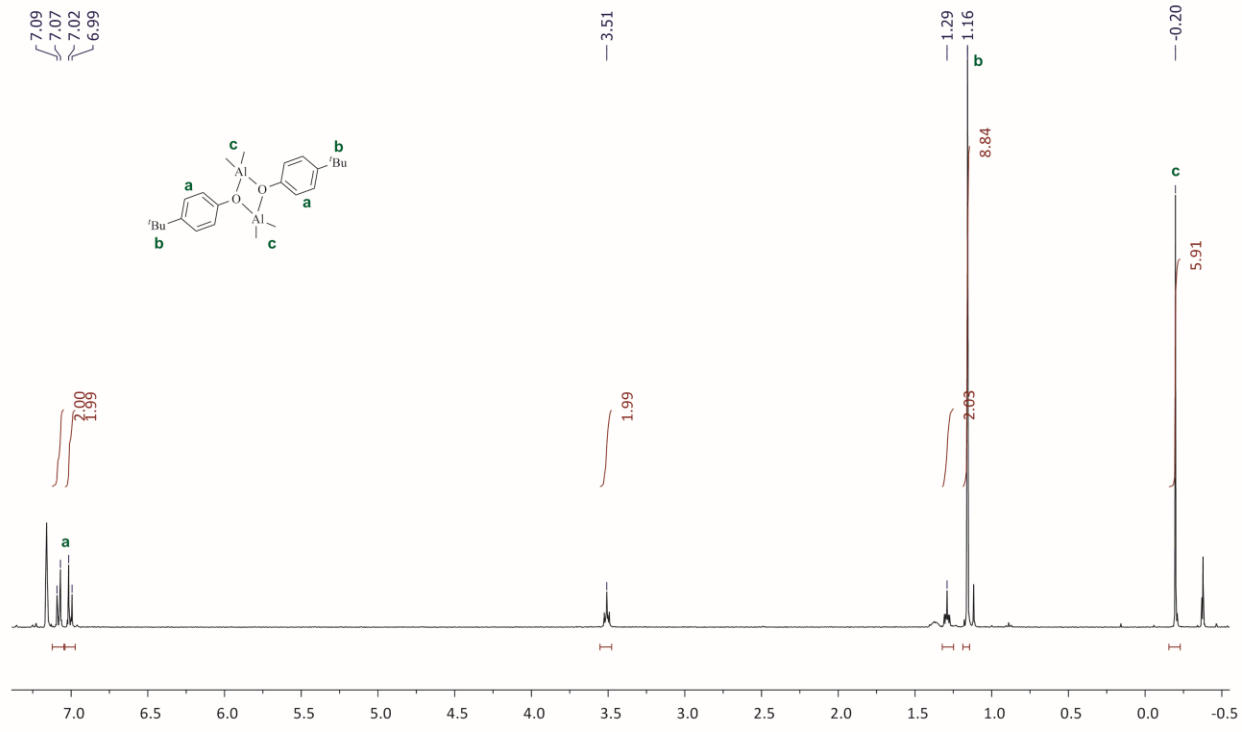


Figure S6. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **4a**.

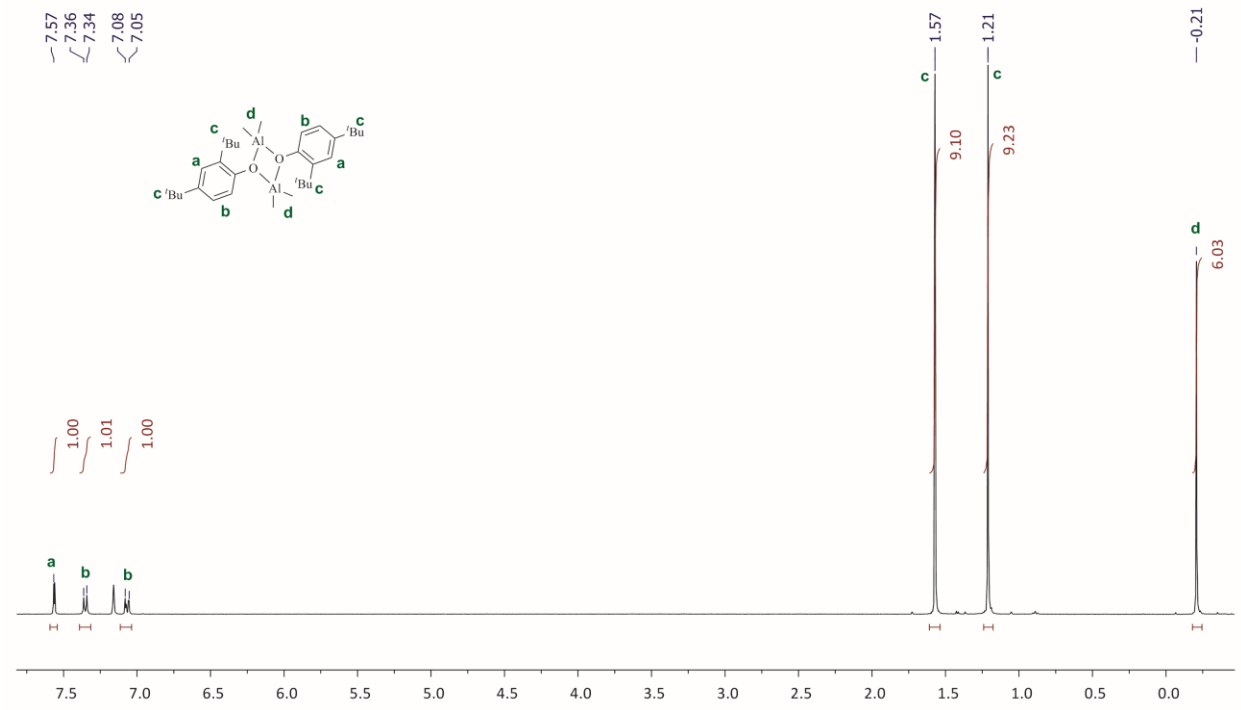


Figure S7. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of **4b**.

S2. Chemicals and equipment

All solvents were supplied by Merck (Darmstadt, Germany). Tetrahydrofuran and toluene were distilled from Na/benzophenone/dibenzo-18-crown-6. 2,6-Di-*tert*-butyl-4-methylphenol (BHT-H, ≥99%), 2,4-di-*tert*-butylphenol, 4-*tert*-butylphenol, di-*n*-butylmagnesium (1.0 M solution in heptane), diethylzinc (1.0 M solution in hexanes), trimethylaluminium (1.0 M solution in heptane), triethylaluminium (1.0 M solution in heptane), triisobutyaluminium (1.0 M solution in hexanes) (Merck, Darmstadt, Germany) were used as purchased.

$CDCl_3$ and C_6D_6 (99.8 at% D, Cambridge Isotope Laboratories, Tewksbury, MS, USA) were used as purchased. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer (Bruker Corporation, Billerica, MS, USA) at 20 °C, with chemical shifts reported in ppm relative to residual solvent peaks. Fourier transform infrared (FT-IR) spectra were recorded using an IFS 66v/S spectrometer (Bruker, Billerica, MA, USA) equipped with a DLaTGS detector. The following experimental parameters were used: attenuated total reflection method, ZnSe crystal, spectral range 600–4000 cm^{-1}, resolution 2 cm^{-1}, 15 scans.

Elemental analysis (C, H, N, O) was performed using a Perkin Elmer Series II CHNS/O Analyzer 2400 (Perkin Elmer, Waltham, MS, USA).

Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1 ml min^{-1} and at 50 °C using an 1260 Infinity II (Agilent Technologies, Santa Clara, CA, USA) integrated instrument equipped with a PLgel MIXED-C column (2 × 102 – 2 × 106 Da), an autosampler, and an refractive index detector. Calibration was achieved using polystyrene standards.

S3. Synthesis of PBAT

Synthesis of low-MW copolymer

Titanium(IV) tetrabutoxide (60 mg, 0.176 mmol) was added to a mixture of dimethyl terephthalate (194 g, 1 mol) and butane-1,4-diol (226 g, 2.51 mol). The mixture was heated with stirring to 150–160 °C, the volatiles were distilled off within 2.5 h. Adipic acid (179 g, 1.23 mol) was added, and the mixture was heated at 170-180 °C for 3.5 h with removing water by distillation. Next, the mixture was heated for 12 h at 0.5 Torr, and cooled to room temperature. The reaction product (for NMR spectrum, see Figure S8) was used in further experiments.

Synthesis of PBAT

Low-MW polycondensation product (60 g) was fused, heated to 200 °C, and catalyst (20 mmol) was added with stirring. The temperature was raised to 245 °C, and the mixture was stirred for 7 h at 0.1 Torr. The hot copolymer melt was transferred into PTFE cuvette, cooled, ground and analyzed.

S4. NMR spectra of PBAT

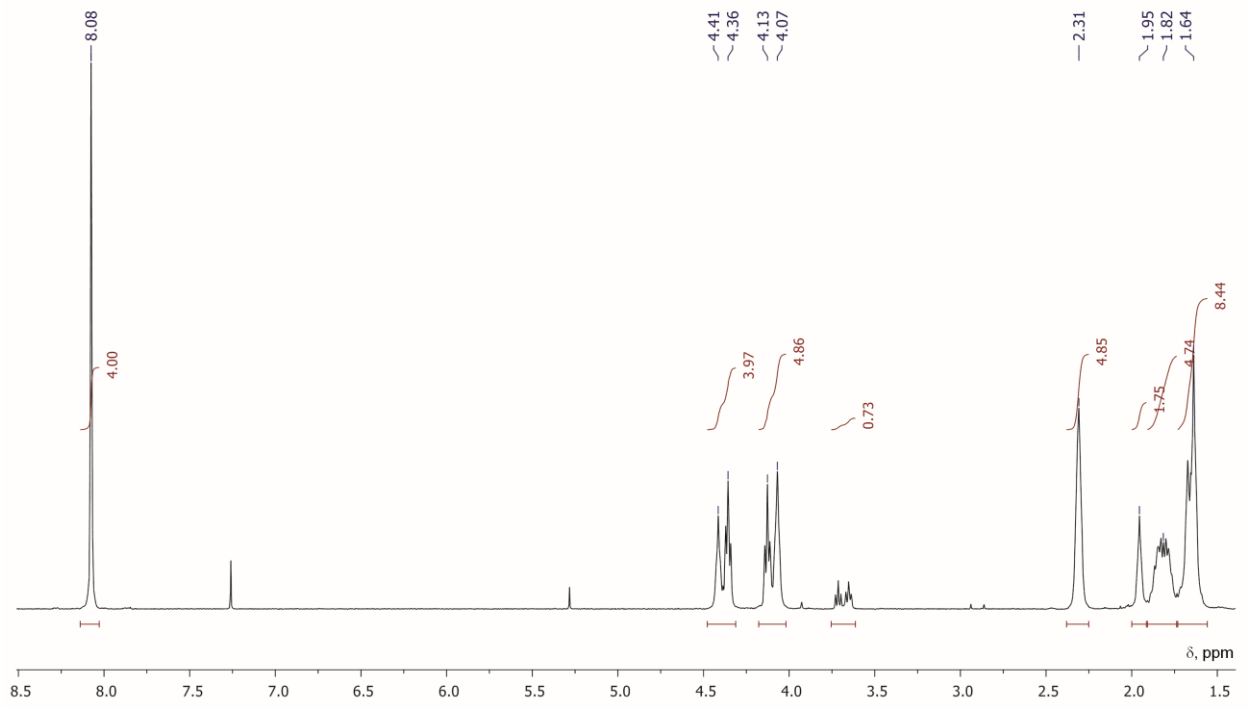


Figure S8. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of low-MW copolymer.

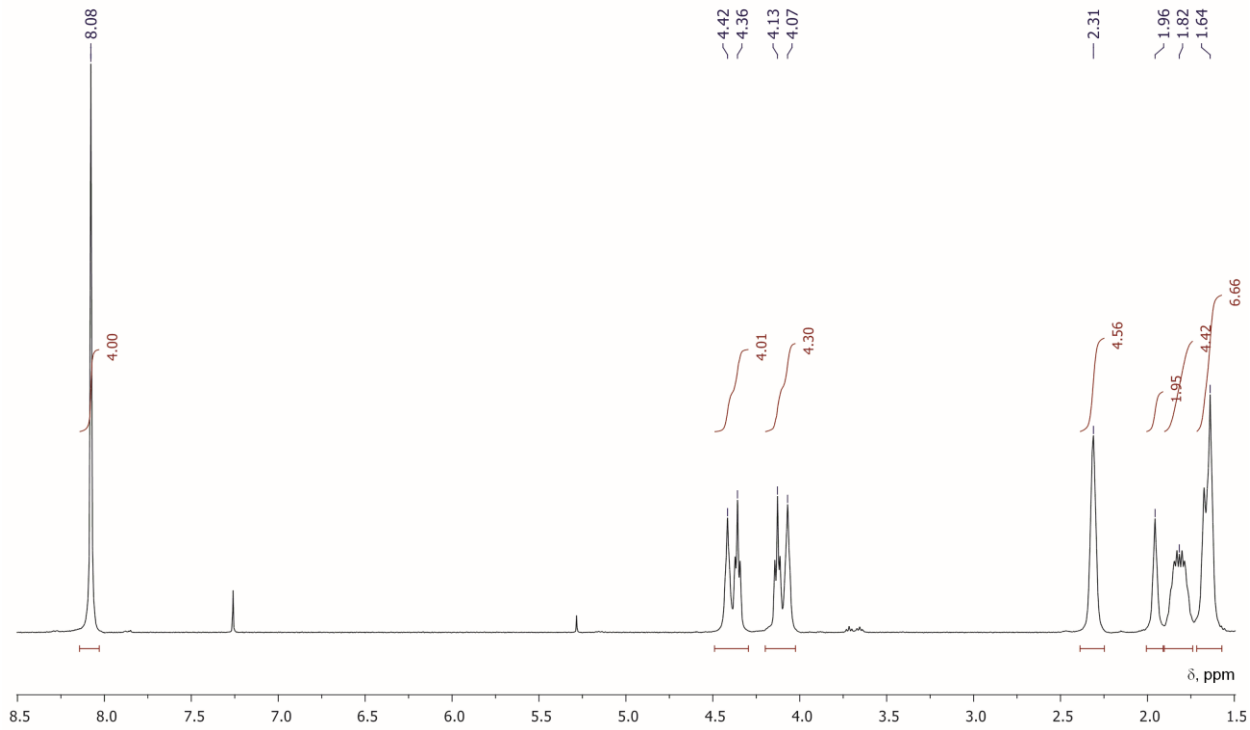


Figure S9. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of **3a** (see main text, Table 1, entry 3).

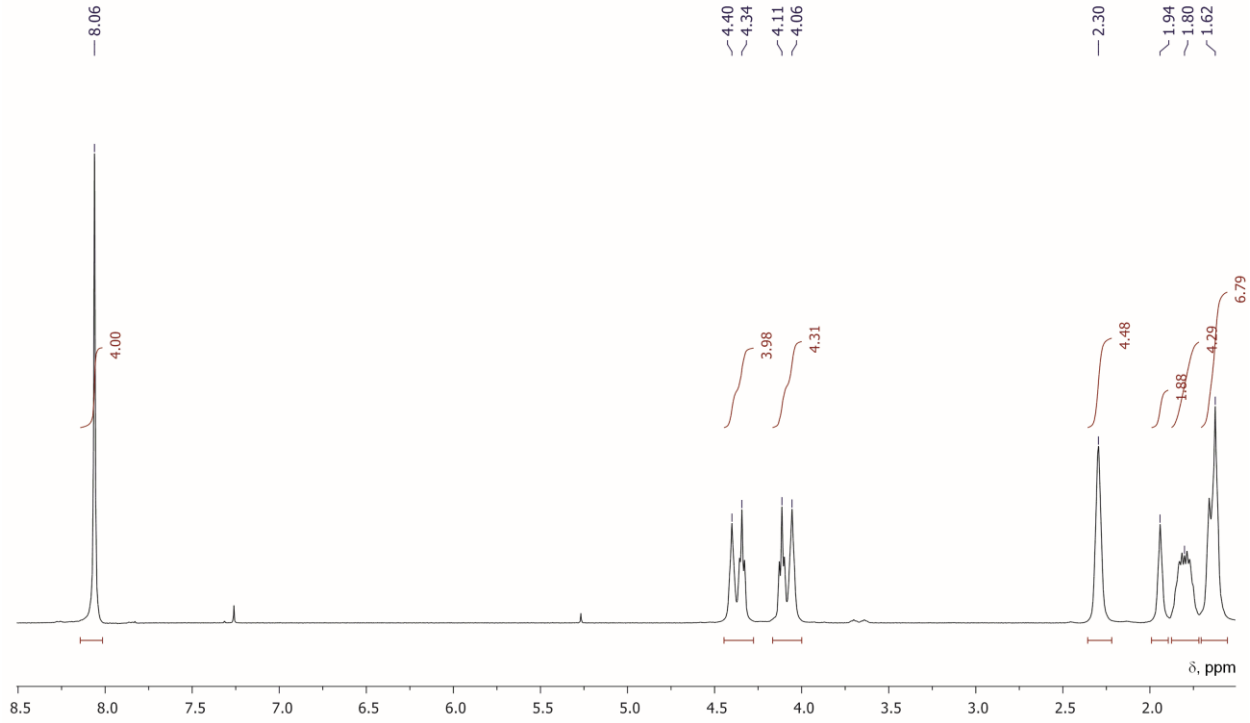


Figure S10. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of **3b** (see main text, Table 1, entry 4).

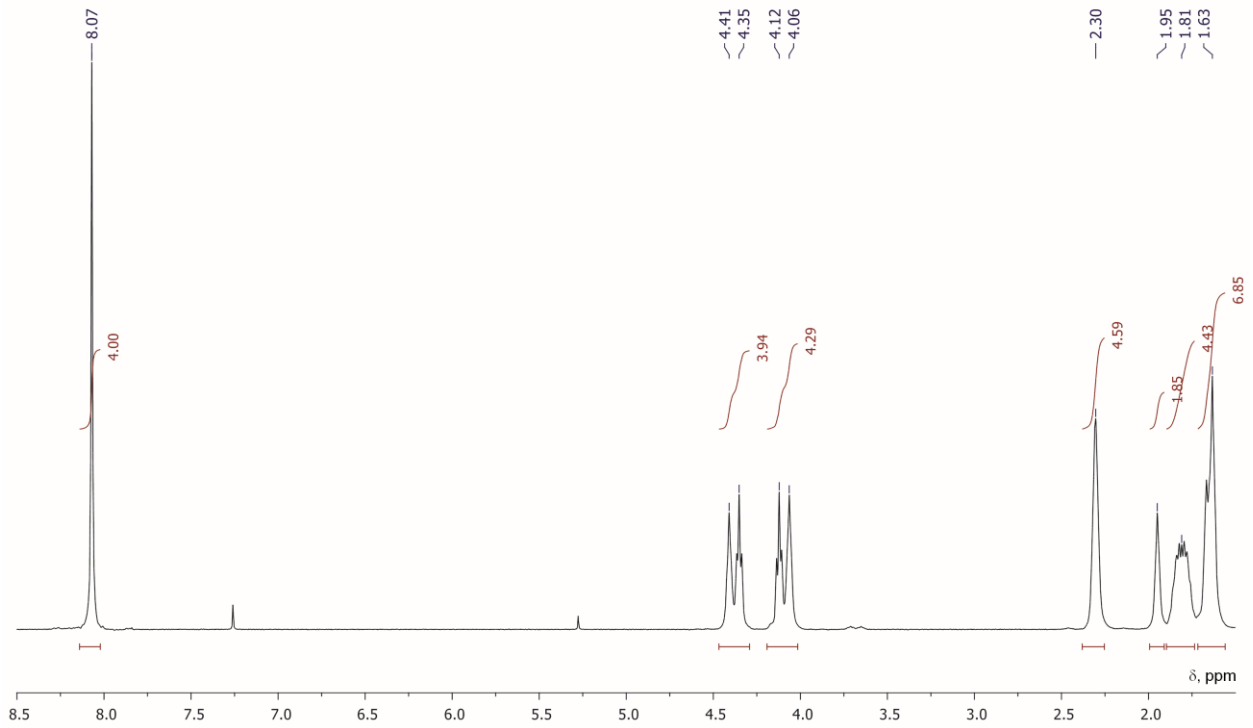


Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of **3c** (see main text, Table 1, entry 5).

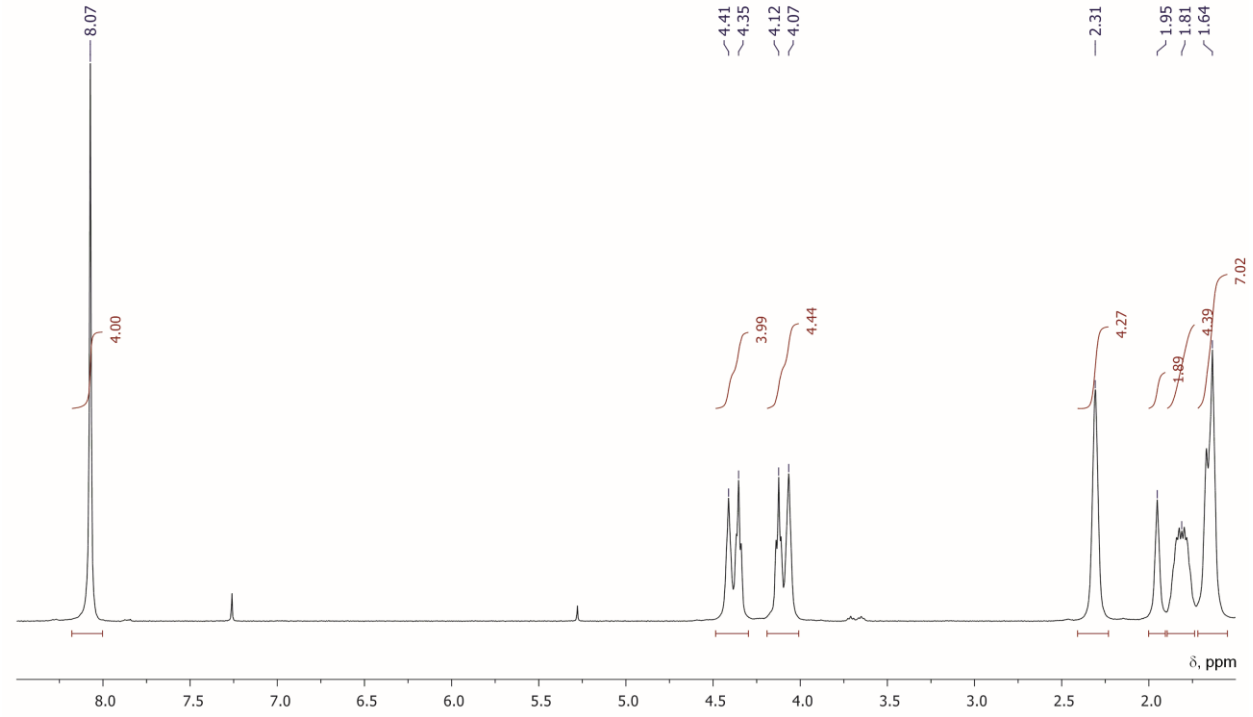


Figure S12. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of **4a** (see main text, Table 1, entry 6).

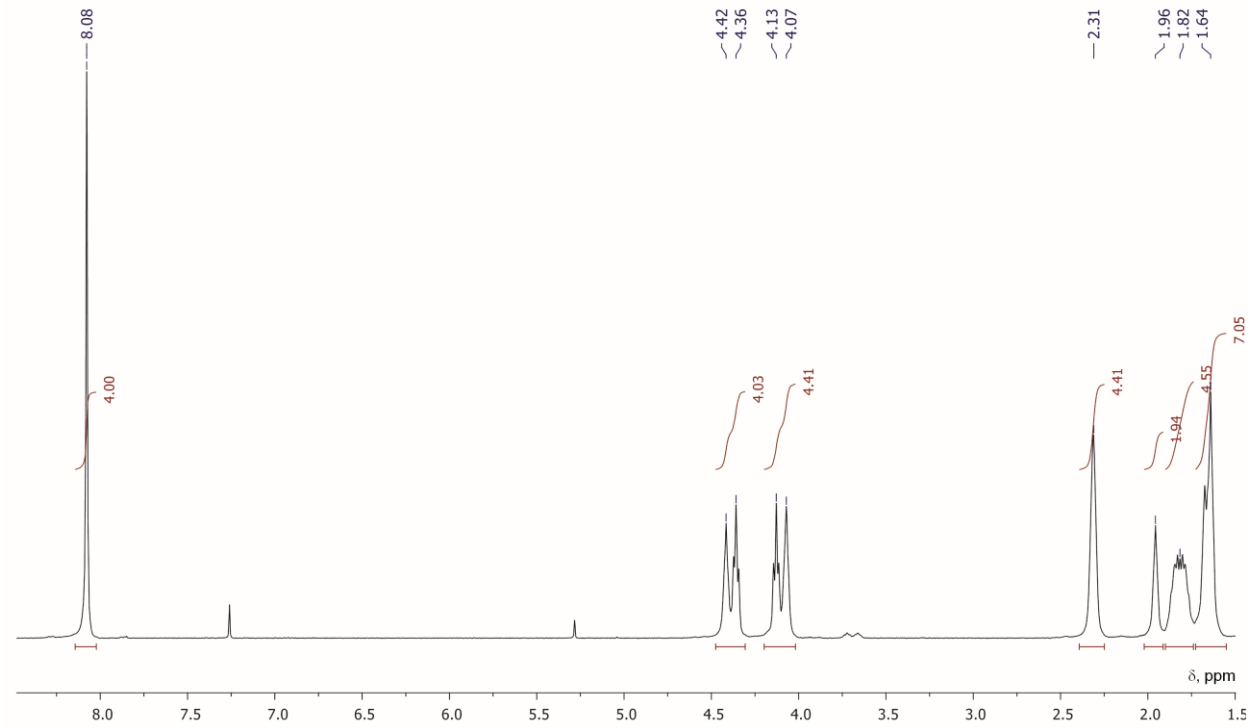


Figure S13. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of **4b** (see main text, Table 1, entry 7).

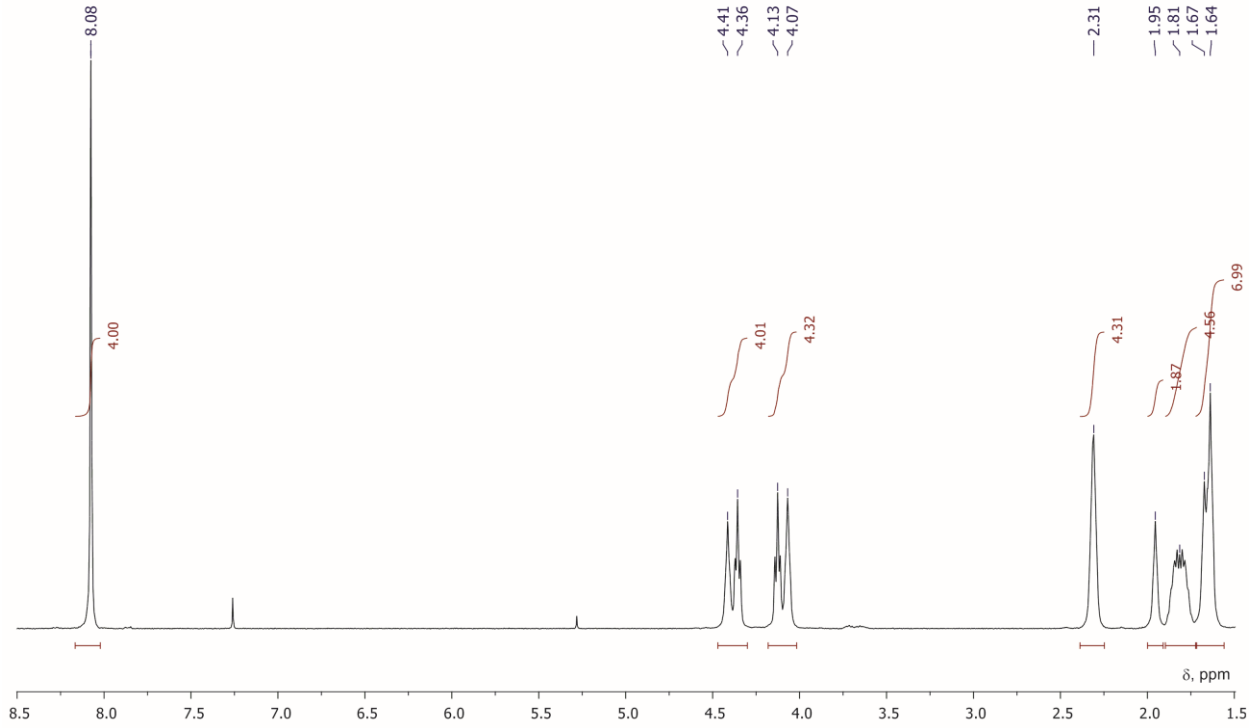


Figure S14. ^{1}H NMR spectrum (400 MHz, C_6D_6, 20 °C) of PBAT obtained in the presence of $Ti(OBu)_4$ (see main text, Table 1, entry 8).

S5. Characterization of 1,6-dioxacyclododecane-7,12-dione (DCDD)

DCDD represents colorless crystalline compound. M. p. 94 °C. For $C_{10}H_{16}O_4$ calc. (%) C, 59.98; H, 8.05; O, 31.96; found C, 59.94; H, 8.07; O, 31.98.

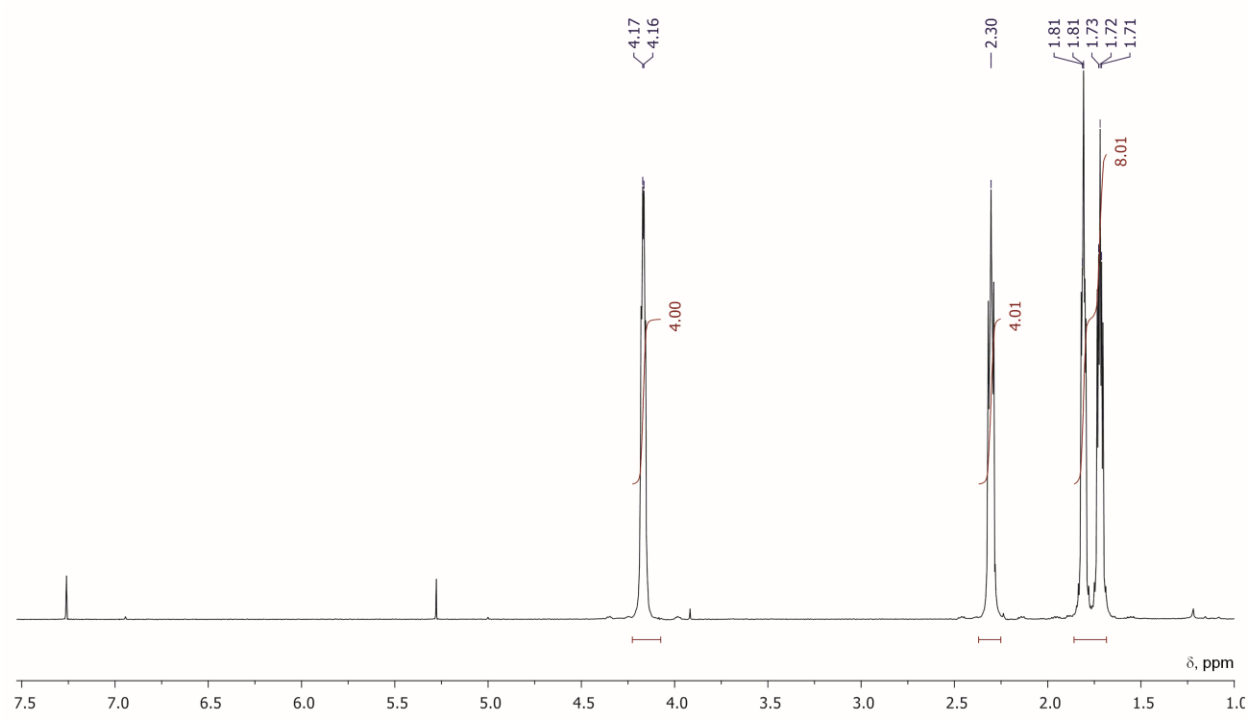


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of DCDD.

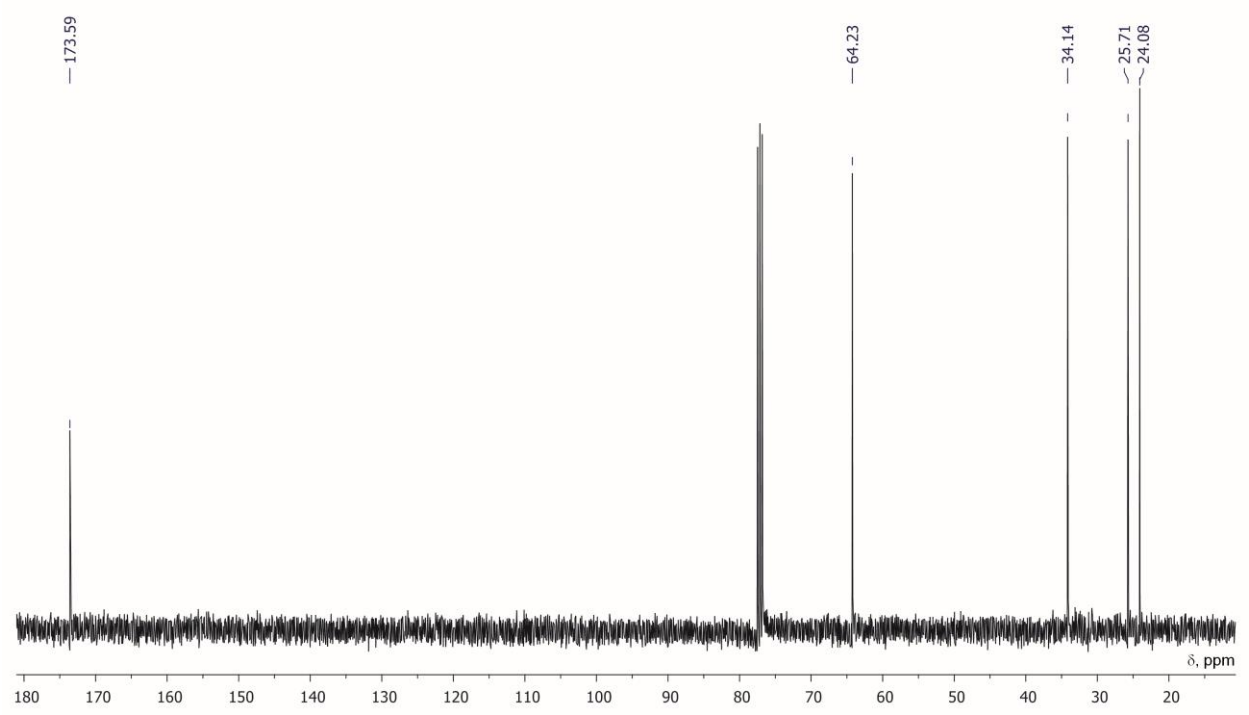


Figure S16. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 20 °C) of DCDD.

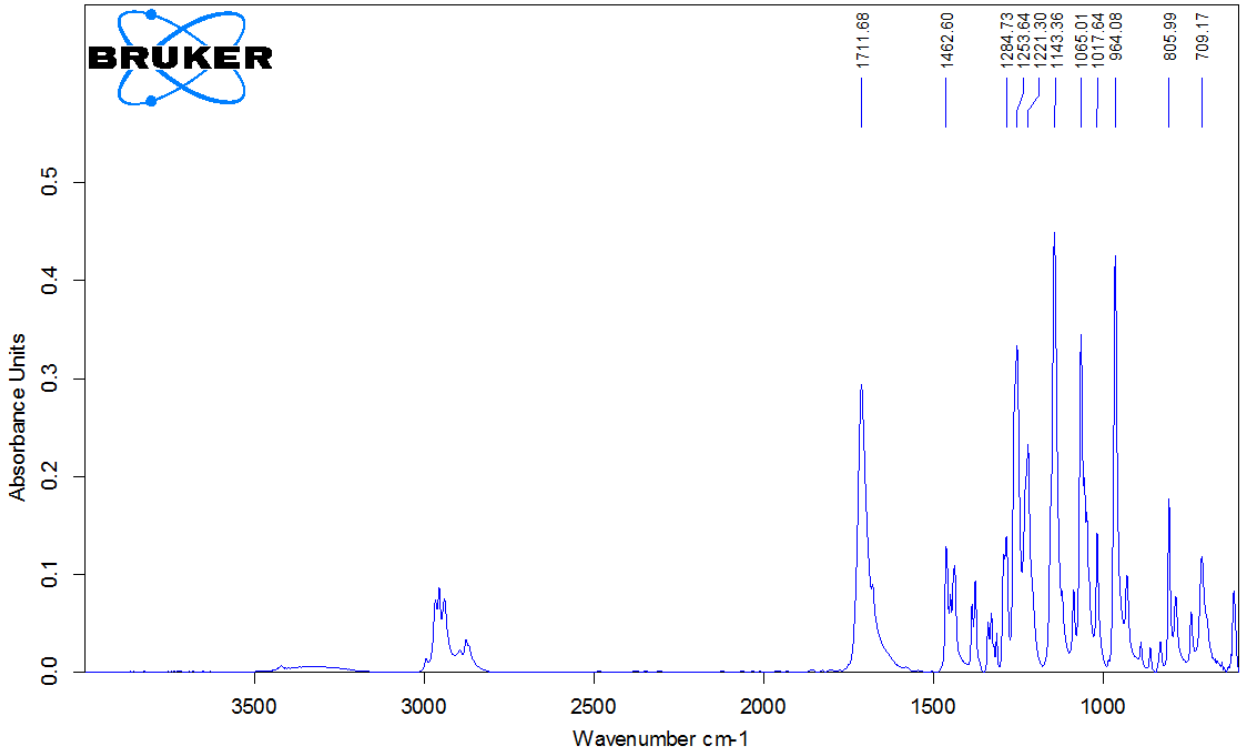


Figure S17. FT-IR spectrum of DCDD.

S6. DFT optimization of the molecular structure of DCDD

Optimization of the molecular structure of DCDD and additional DFT calcilations were conducted using PRIRODA program (version 4.0, M. V. Lomonosov Moscow University, Moscow, Russia), PBE functional and 3ζ basis [S1]. Analysis of the molecular structure of DCDD have shown the presence of only two energetically unfavorable interactions deviated from the staggered conformations (Figure S18).

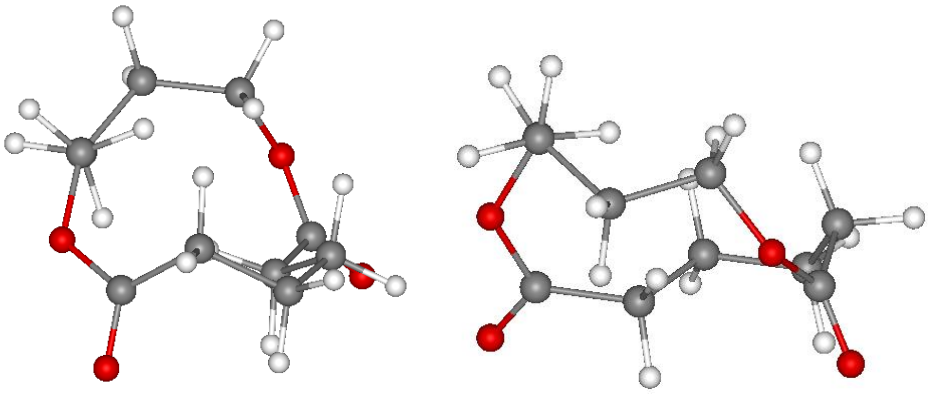
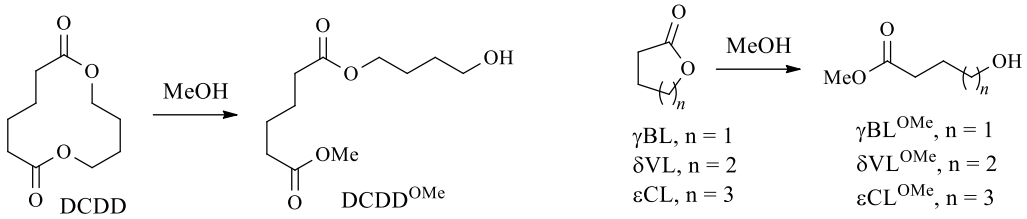


Figure S18. Unfavorable interactions in DCDD.

To estimate the ring strain in DCDD, we made calculations for the model reactions of methanolysis of DCDD and cyclic monoesters, γ-butyrolactone (γBL), δ-valerolactone (δVL) and ε-caprolactone (εCL) (Scheme S1). Among three lactones, high stability of γBL in ROP and transesterification is well-known [S2], and therefore it can be considered as a benchmark.



Scheme S1. Methanolysis of DCDD and lactones.

The results of the calculations are presented in Table S1. Methanolysis of DCDD is highly exothermic and exergonic process, as distinct from lactones. Therefore DCDD represents monomer suitable for ring-opening transesterification. It can be assumed that the problem of the formation of DCDD can be solved by collection and return of this side product into PBAT production cycle.

Table S1. DFT calculations data

Compound	MeOH	DCDD	γBL	δVL	εCL	$DCDD^{OMe}$	γBL^{OMe}	δVL^{OMe}	εCL^{OMe}
E, Hartree	-115.63072	-691.02971	-306.2572	-345.52404	-384.79288	-806.7055	-421.89691	-461.16869	-500.43946
H total, kcal/mol	33.8645	165.5114	63.7505	82.0799	100.332	199.8944	98.9787	117.1746	134.7396
G total, kcal/mol	16.8544	130.4406	41.8582	58.4295	75.2315	154.5782	69.061	84.4444	102.0688
H, kcal/mol	-72525.454	-433461.85	-192115.4	-216737.37	-241360.67	-506015.07	-264645.13	-289270.33	-313895.53
G, kcal/mol	-72542.464	-433496.92	-192137.29	-216761.02	-241385.77	-506060.39	-264675.05	-289303.06	-313928.2
ΔH, kcal/mol	–	–	–	–	–	-27.76	-4.27	-7.51	-9.41
ΔG, kcal/mol	–	–	–	–	–	-21.00	4.71	0.42	0.03

References

[S1] D. N. Laikov and Yu. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820.

[S2] R. Bernat, P. Maksym, M. Tarnacka, K. Koperwas, J. Knapik-Kowalczuk, K. Malarz, A. Mrozek-Wilczkiewicz, A. Dzienia, T. Biela, R. Turczyn, L. Orszulak, B. Hachuła, M. Paluch and K. Kamiński, *Polymer*, 2021, **233**, 124166.