Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information (SI)

Branched Polyesters from Radical Ring-Opening Polymerization of Cyclic Ketene Acetals: Synthesis, Chemical Hydrolysis and Biodegradation

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Supplementary Information

Hydrolysis calculations:

The degree of hydrolysis was calculated from ^{1}H-NMR by comparing the integral of -OC$\underline{H_2}$- (around 4.1 ppm) in the polymer with the integral of HOC$\underline{H_2}$-(around 3.6 ppm) after hydrolysis using the formula: Degree of hydrolysis: $Int_{HOC\underline{H2}\text{-}}/(Int_{\text{-}HOC\underline{H2}\text{-}}+Int_{\text{-}OC\underline{H2}\text{-}})$

Peaks from other hydrolysis products may overlap with the peak at 3.6 ppm and therefore interfere with hydrolysis calculations

NMR

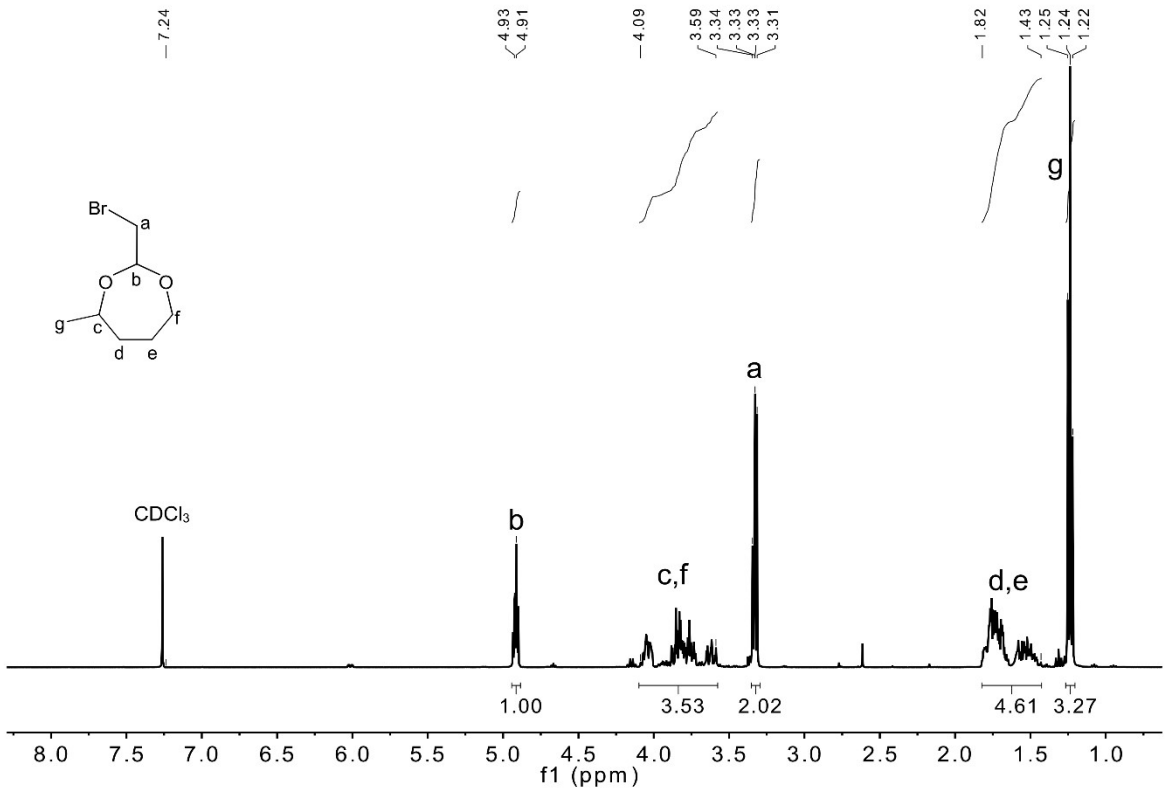


Fig. S1 ^{1}H-NMR of 2-(bromomethyl)-4-methyl-1,3-dioxepane in $CDCl_3$.

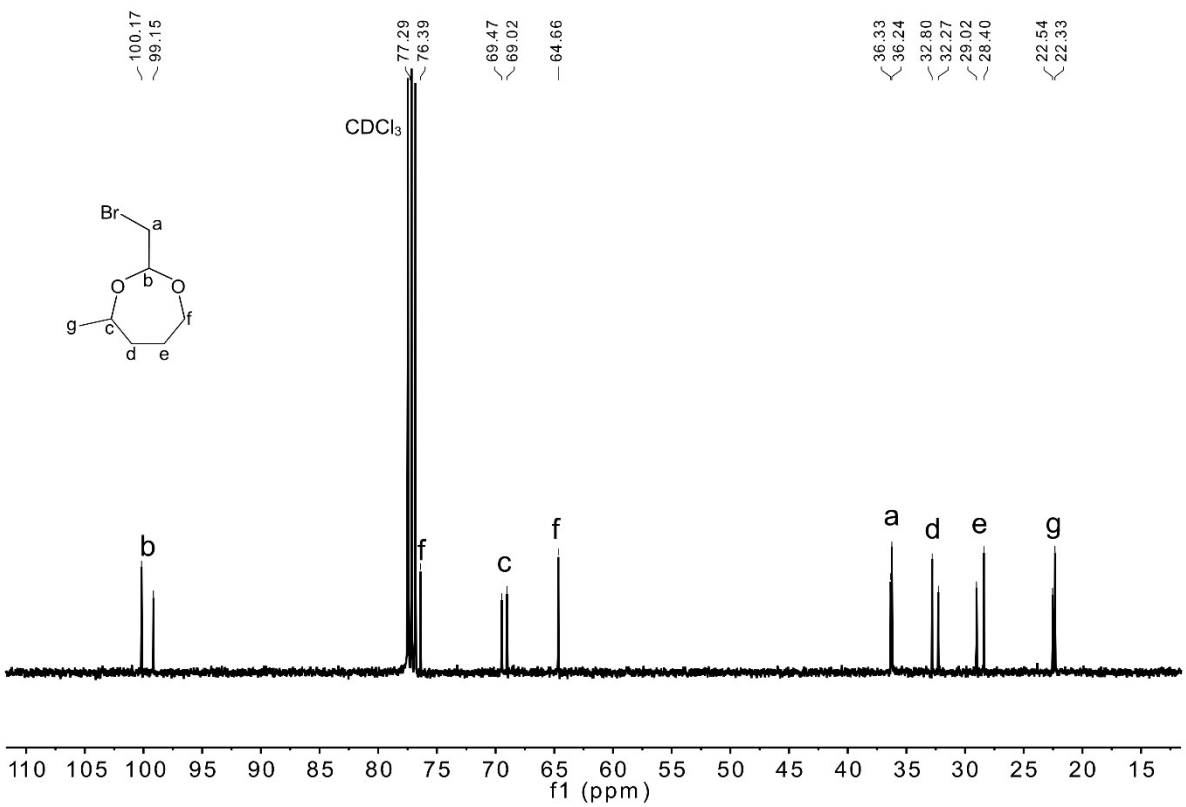


Fig. S2 ^{13}C-NMR of 2-(bromomethyl)-4-methyl-1,3-dioxepane in $CDCl_3$.

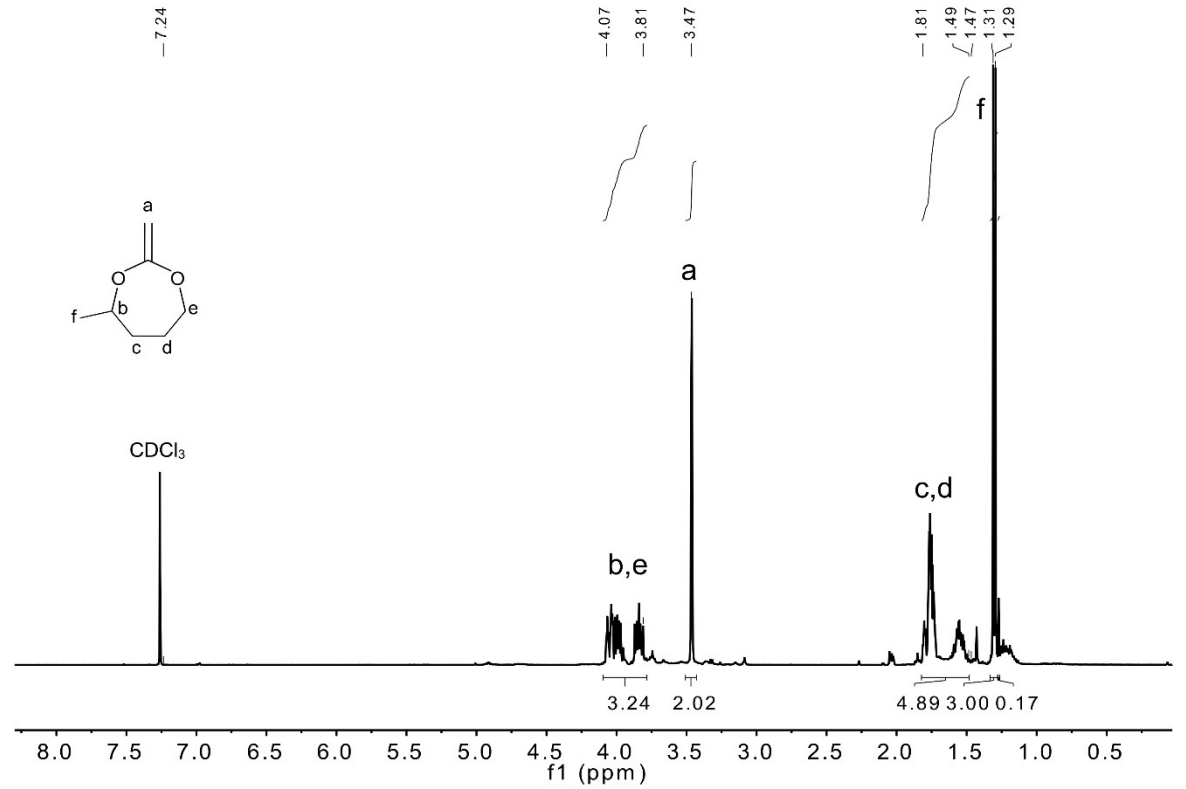


Fig. S3 ^{1}H-NMR spectrum of Me-MDO in $CDCl_3$.

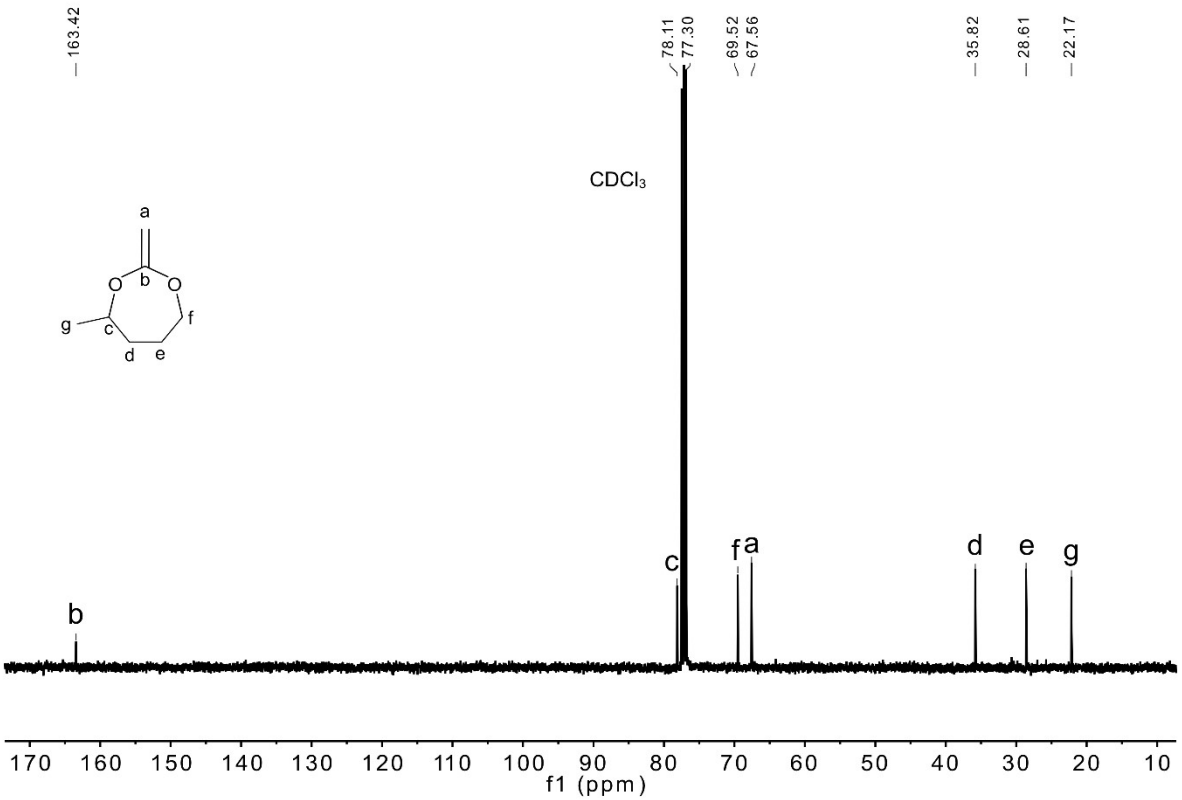


Fig. S4 ^{13}C-NMR spectrum of Me-MDO in $CDCl_3$.

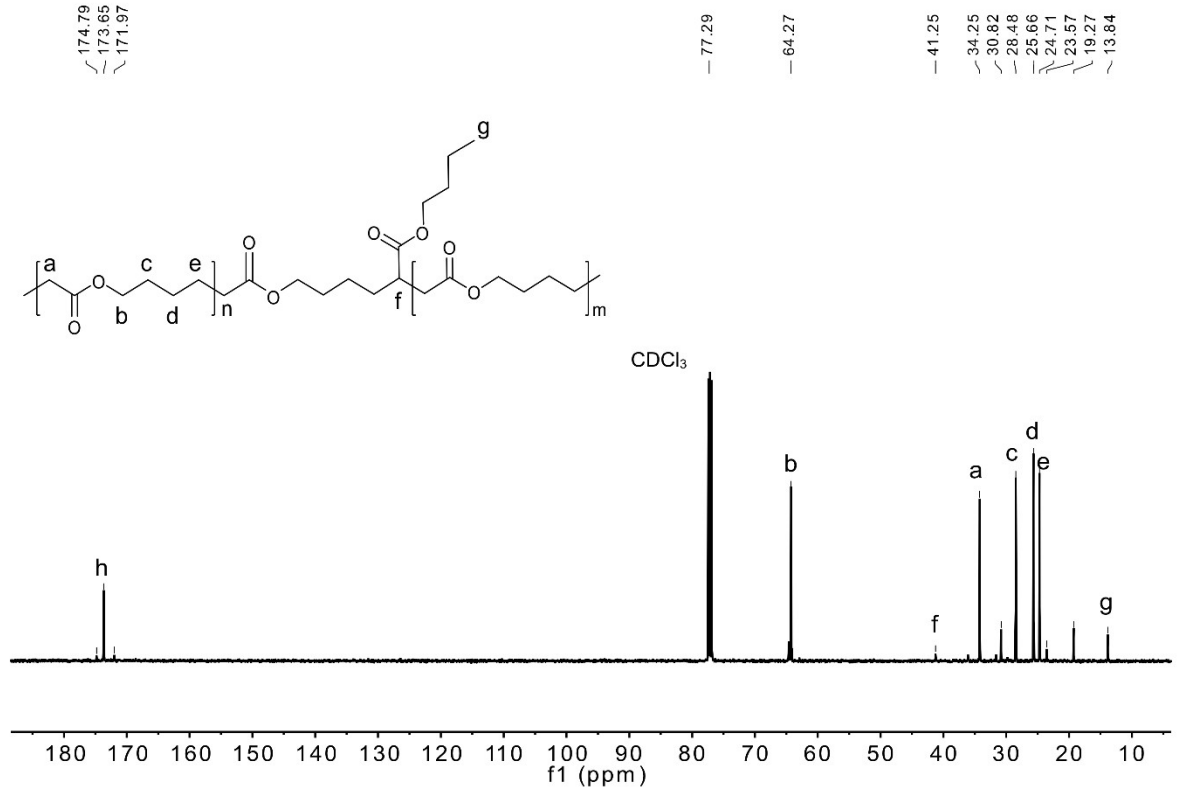


Fig. S5 ^{13}C-NMR spectrum of PMDO in $CDCl_3$.

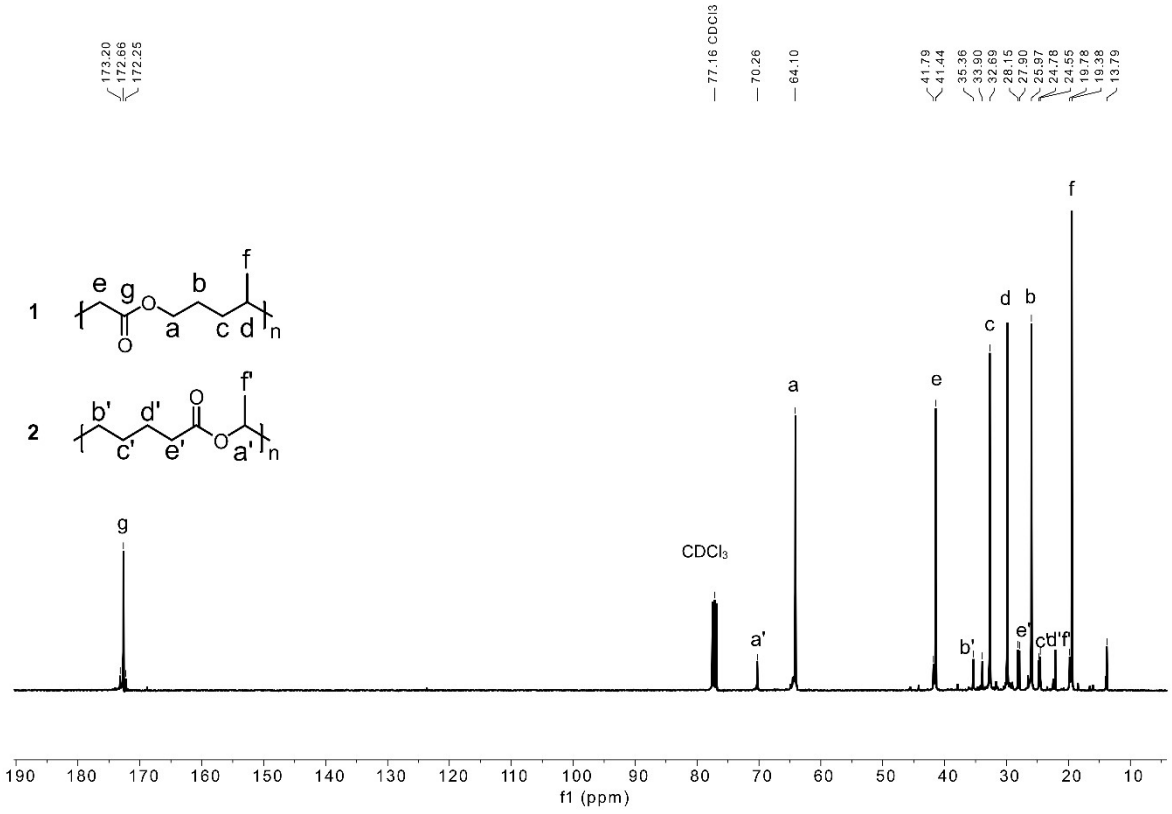


Fig. S6 ^{13}C-NMR spectrum of PMe-MDO in $CDCl_3$.

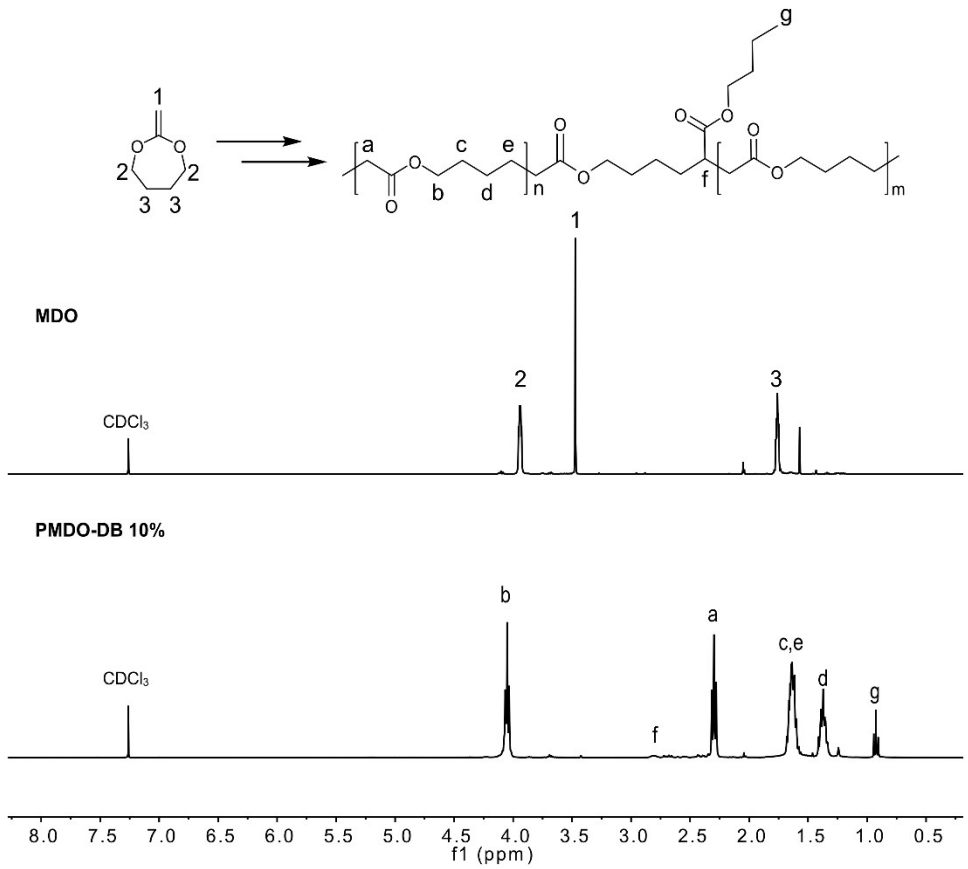


Fig. S7 ^{1}H-NMR spectra of MDO and PMDO-DB 10% in $CDCl_3$.

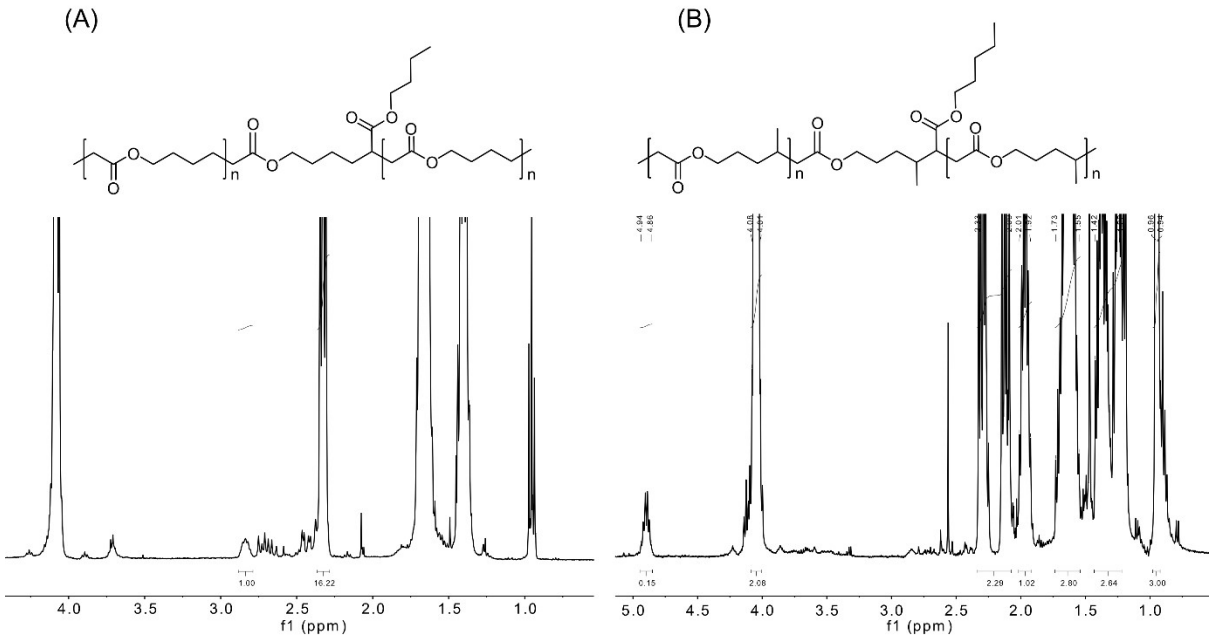
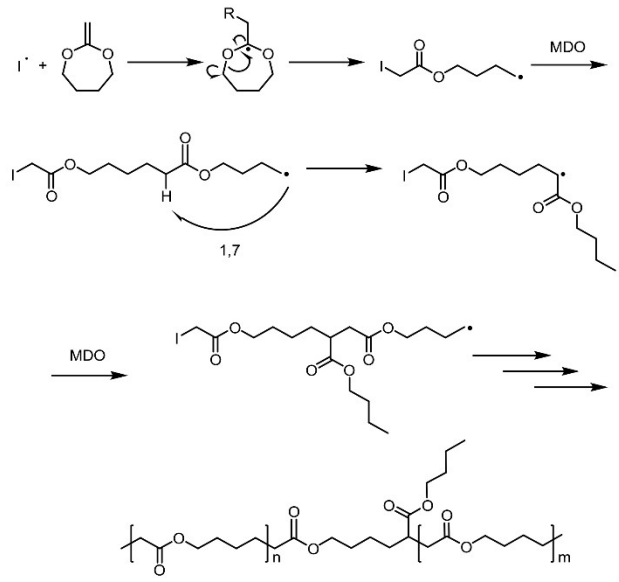


Fig. S8 Enlarged ^{1}H-NMR spectra of (A) PMDO and (B) PMe-MDO in $CDCl_3$.



Scheme S1 rROP of MDO leading to branch formation randomly along the polymer chain.[24, 39]

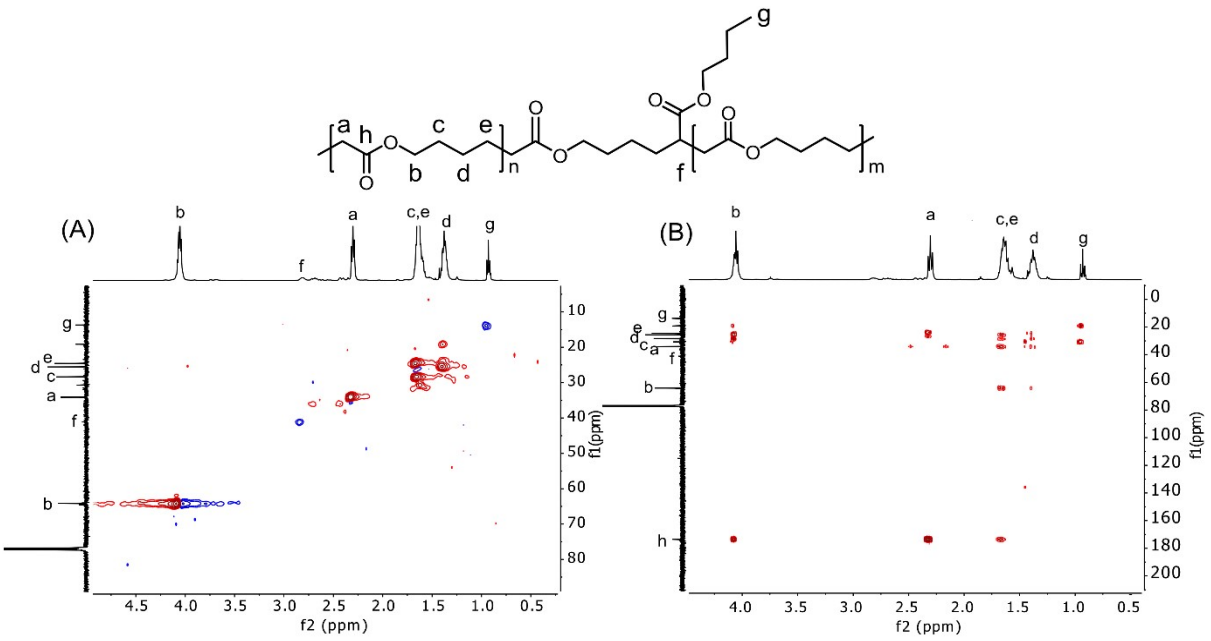


Fig. S9 (A) HSQC of PMDO showing the direct H-C correlation. (B) HMBC of PMDO showing the two or three H-C bond correlation in $CDCl_3$.

DSC

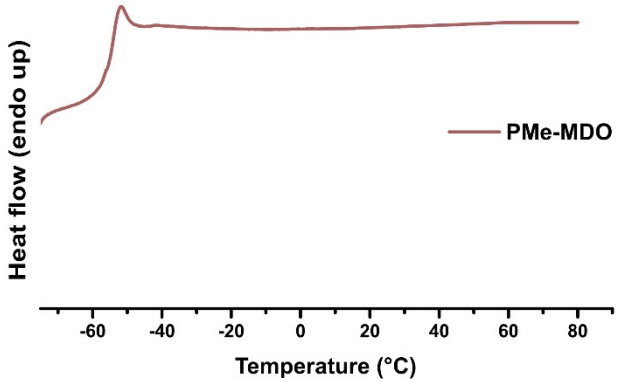


Fig. S10 DSC thermogram of PMe-MDO.

SEC traces

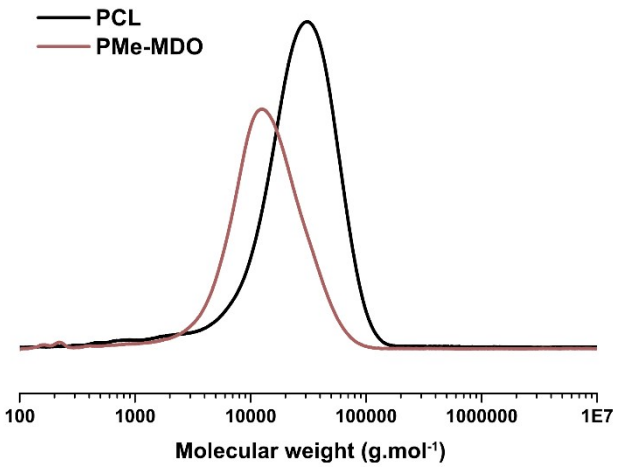


Fig. S11 SEC chromatograms of PCL and PMe-MDO

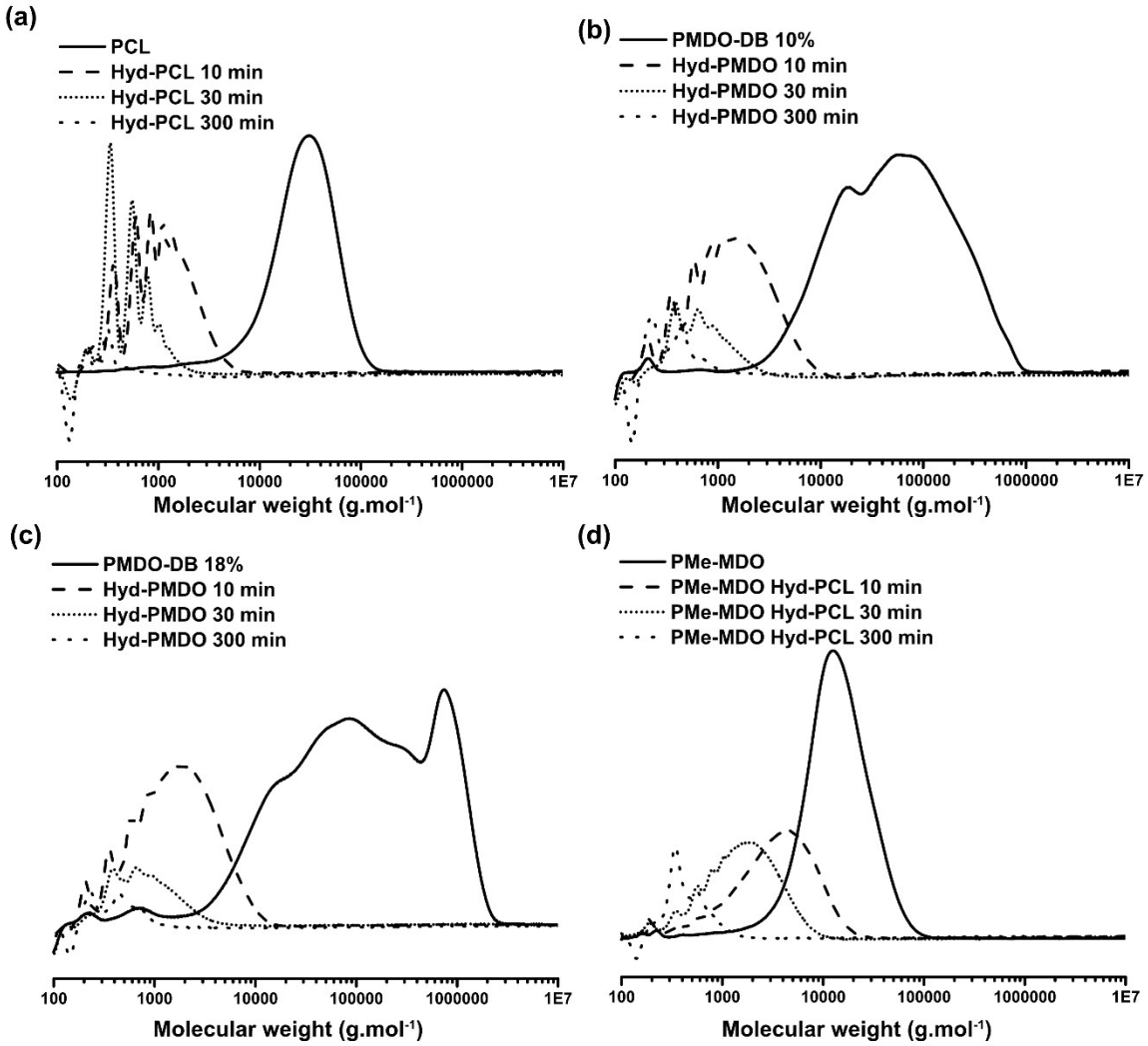


Fig. S12 SEC chromatogram of the different polyesters and their hydrolysis products after 10, 30 min and after 300 min (A) PCL, (B) PMDO-DB 10%, (C) PMDO-DB 18% and (D) PMe-MDO.

NMR-hydrolysis

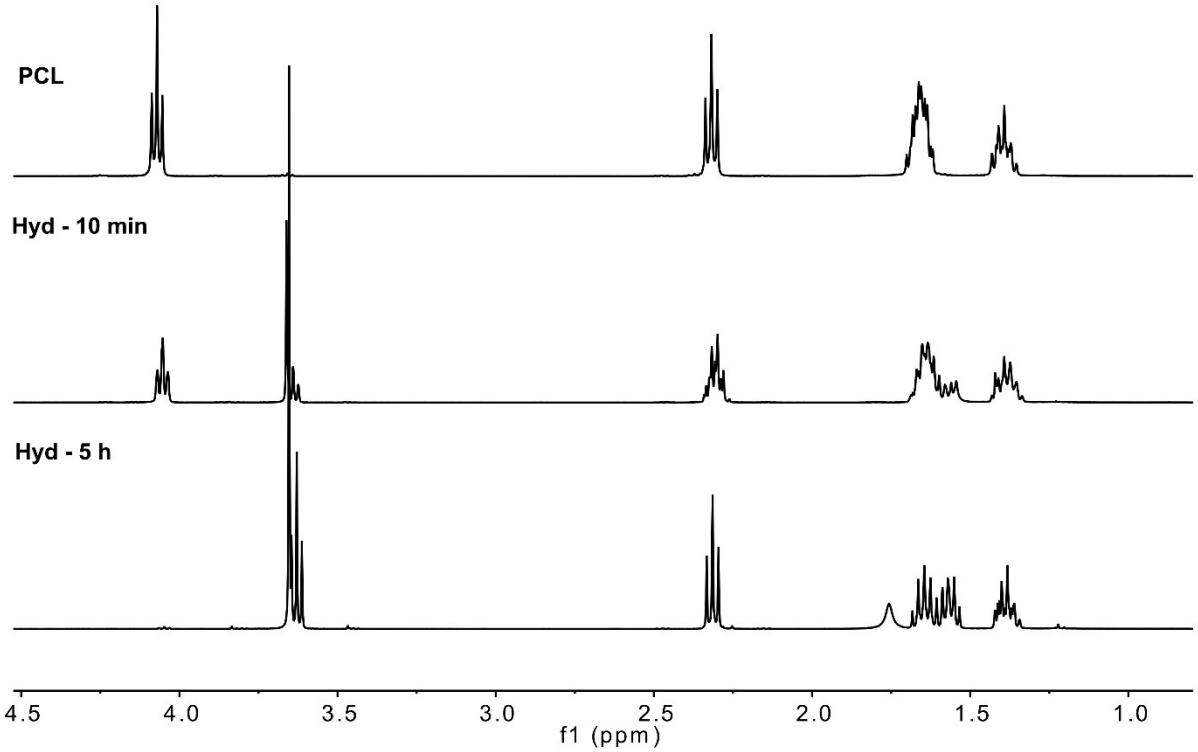


Fig. S13 ^{1}H-NMR of PCL and the hydrolysis products of PCL after 10 min and after 5 h, respectively in $CDCl_3$.

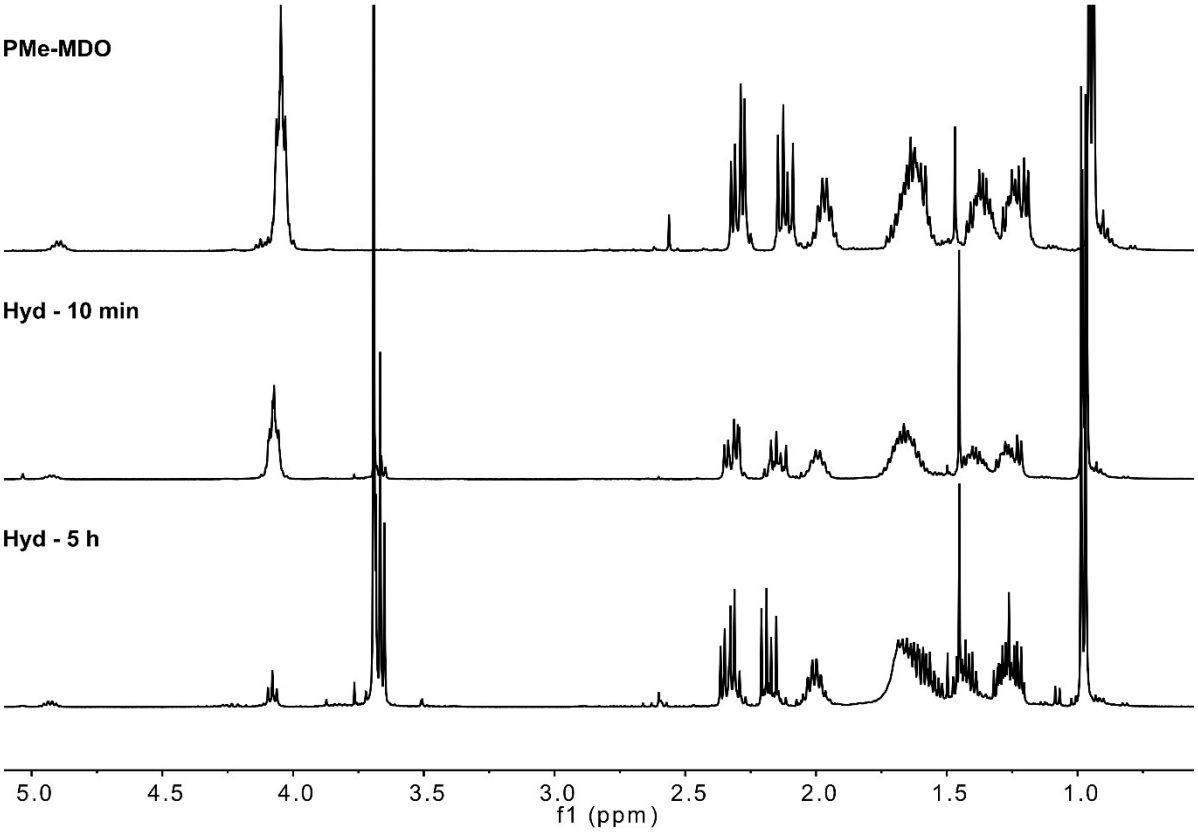


Fig. S14 ^{1}H-NMR of PMe-MDO and the hydrolysis products of PMe-MDO after 10 min and after 5 h, respectively in $CDCl_3$.

Biodegradation test

Biodegradation test inocula

River water was collected from the river Rhine near Heveadorp, The Netherlands (51◦58'26.8'' N, 5◦49' 26.4'' E). The nearest WWTP to this sampling point is 3 km upstream and is treating predominantly domestic wastewater. To reduce the endogenous respiration in the Closed Bottle test the river water was aerated for 7 days before use and particles were removed by sedimentation and decantation.

Activated sludge was collected from the wastewater treatment plant (WWTP) in Duiven, The Netherlands. WWTP Nieuwgraaf is an activated sludge plant consisting of mechanical and biological stages for the treatment of predominantly domestic wastewater. The activated sludge was preconditioned to reduce the endogenous respiration rates in the Closed Bottle test. To this end the inoculum was diluted in aerated Closed Bottle test medium to 0.4 g dry weight L^{-1} of activated sludge and aerated for one week. The preconditioned sludge was homogenized before use by pressing it through a sterile needle with a syringe. The homogenized sludge was subsequently diluted further to 2 mg dry weight L^{-1} concentration in the bottles.

Calculation of the theoretical oxygen demand (ThOD), biological oxygen demand (BOD) and the biodegradation percentage

Table S1 Average molecular formula, polymer purity, and theoretical oxygen demand used to calculate the biodegradation of the polyesters in the OECD 301D test.

Polyester	Purity (%)	Average molecular formula	$ThOD_{NH3}$[a] (mg oxygen/mg substance)
PCL	100	(C6H10O2)n	2.10
PMDO-DB 10%	100	(C6H10O2)n	2.10
PMDO-DB 18%	100	(C6H10O2)n	2.10
PMe-MDO	100	(C7H12O2)n	2.25

[a]The theoretical oxygen demands (ThOD) of the polyesters were calculated from their molecular formula and molecular weight (MW) as follows (OECD 301, 1992):

$$ThOD_{NH3}(mgO_2/mg)=\frac{16(2C+0.5(H-Cl-3N)+3S+2.5P+0.5Na-O)}{MW}$$

Calculation of the biochemical oxygen demand (BOD)

Provided the oxygen concentrations in all bottles are equal at the start of the test, the amounts of oxygen consumed (BOD) in the test were calculated as follows:

Oxygen consumption (mg/L) test substance = mean oxygen concentration (mg/L) in control bottles - mean oxygen concentration (mg/L) in the test bottles

The biological oxygen demand (BOD) mg/mg of the polyesters were calculated by dividing the oxygen consumption by the polyester concentration used in the Closed Bottles.

Calculation of the biodegradation percentages

The biodegradation percentages were calculated by the ratio of the biochemical oxygen demand (BOD) to the theoretical oxygen demand and multiply with 100.

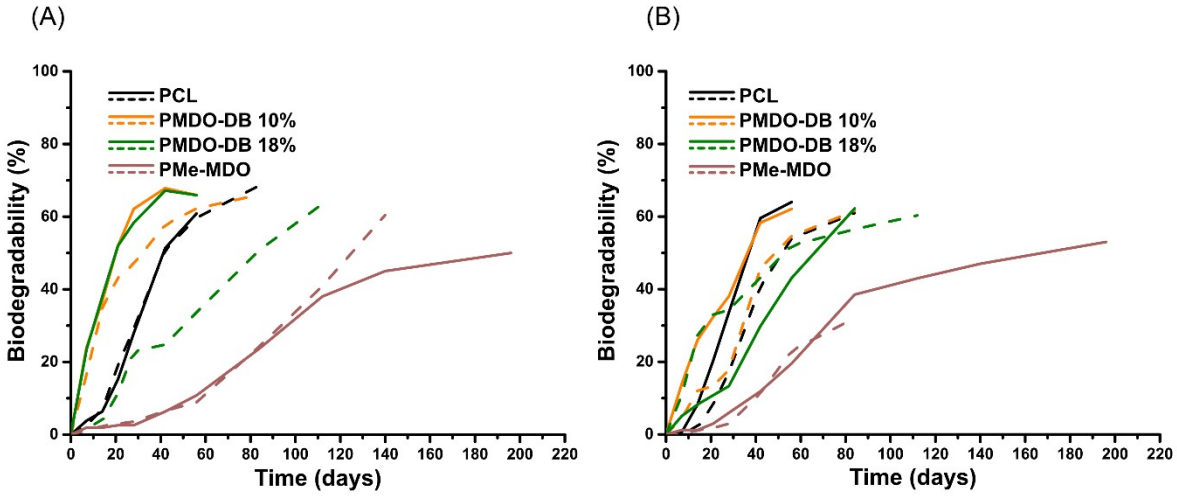


Fig. S15 OECD 301 D Closed Bottle Test biodegradability (%) results of PCL, PMDOs and PMe-MDO as a function of time in.

(____) for the first biological replicate and (_ _ _) for the second biological replicate. (a) river water and (b) activated sludge.

Degree of branching calculations:

one molecule 10H
sum of integrals = 1000 = 100 molecules
29.91/3H = 9.97mol%

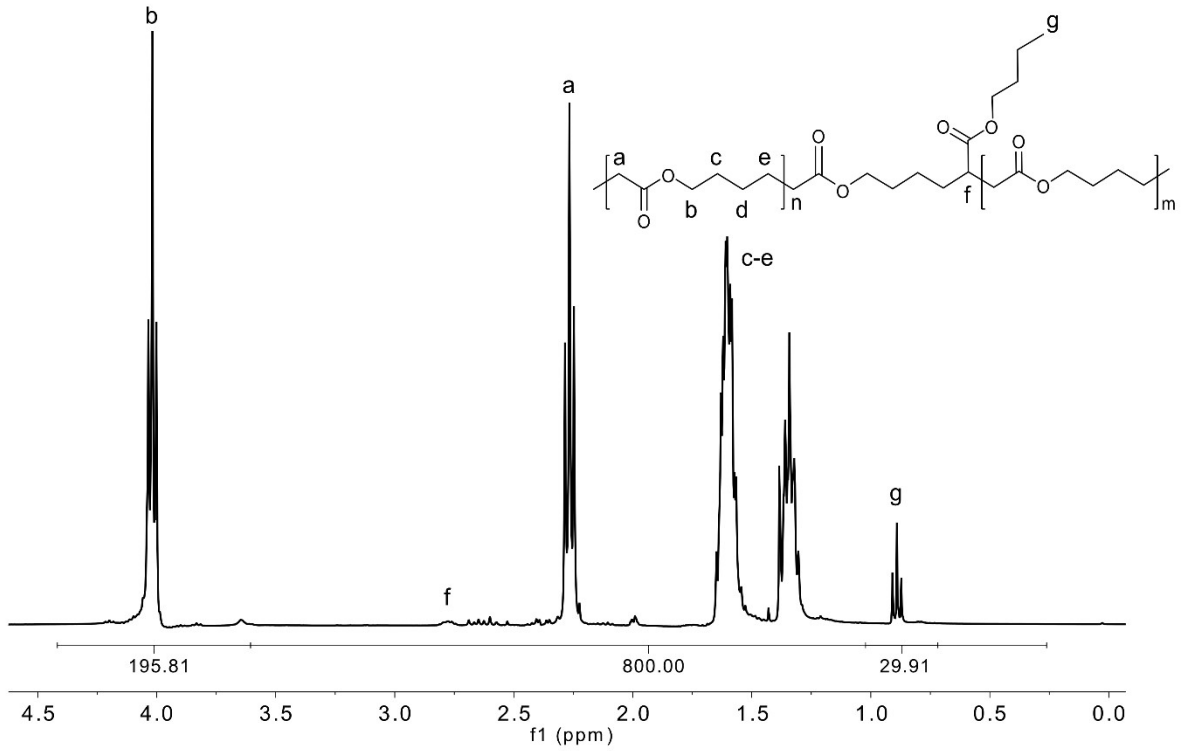


Fig. S16 ^{1}H-NMR of PMDO-DB 10% with integration for calculations of the degree of branching

Crystallinity calculation

Table S2 Crystallinity calculation where the apparent heat fusion (ΔH_f) of sample was obtained from DSC

Polymer		**mJ**	**J**	**Sample weight (mg)**	**g**	**ΔH_f of sample (J/g)**	**ΔH_f of 100% cryst. PCL**	**crystallinity= ($\Delta H_f/\Delta H_f°$)*100%**	
PCL		530	0.530	7.5	0.0075	70.75	135.31		52
PMDO-DB 8%		342	0.342	7.5	0.0075	45.63	135.31		34
PMDO- DB 10%		375	0.375	10.5	0.0105	35.74	135.31		26
PMDO-DB 15%	Tm	354	0.354	10	0.01	35.36	135.31	26	Tot. crys= 17
	Tc	118	0.118	10	0.01	11.82	135.31	9	

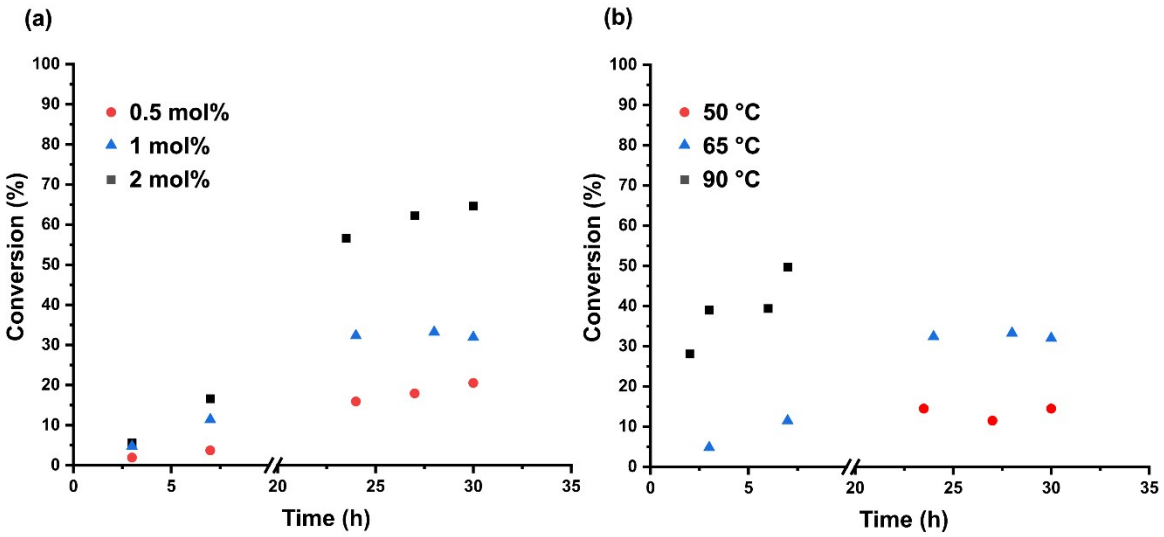


Fig. S17 Me-MDO conversion as a function of time: (a) with different AIBN concentration and (b) with different polymerization temperature

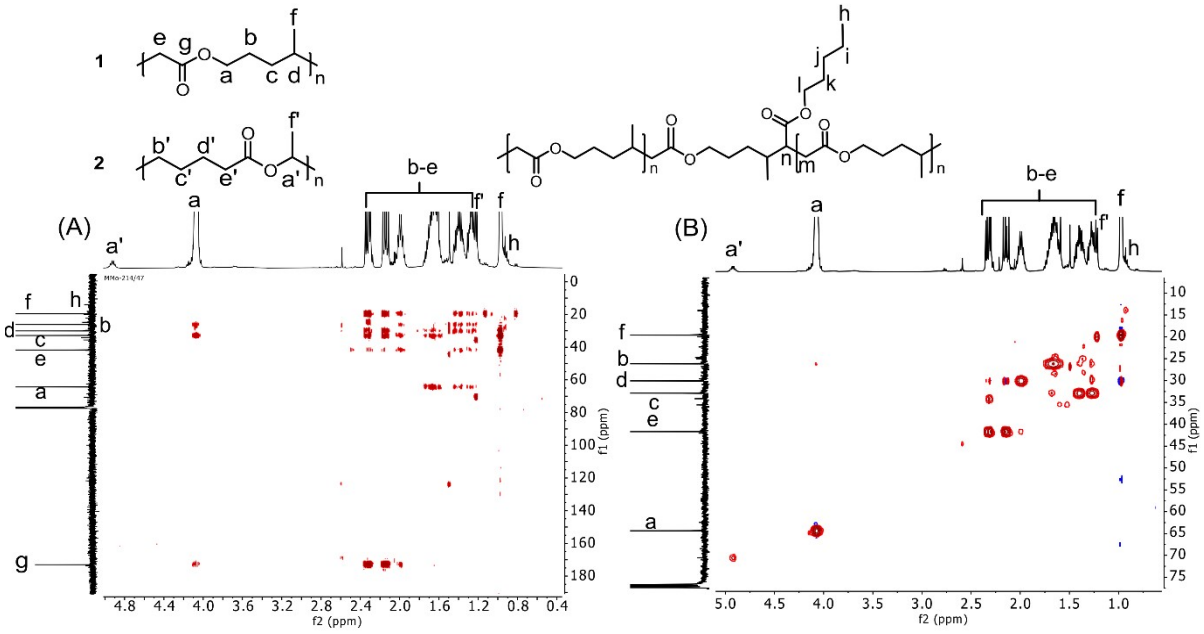


Fig. S18 (A) HMBC of PMe-MDO showing the direct H-C correlation. (B) HSQC of PMe-MDO showing the two or three H-C bond correlation in $CDCl_3$.