Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Efficient synthesis of camphor-based polycarbonates: a direct route to degradable polymers

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1) General information

Zinc trifluoromethanesulfonate ($Zn(OTf)_2$, 98%), magnesium chloride ($MgCl_2$, 99%), (1*R*,3*S*)-1,2,2-trimethyl-1,3-cyclopentanedicarboxylic acid ((1*R*,3*S*)-(+)-camphoric acid, 98%+), 1,3-propanediol (99%) and diethyl carbonate (DEC, 99%) were purchased from Alfa Aesar. Lithium aluminum hydride ($LiAlH_4$, 95%) was provided by Acros Organics. 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride ((TMP)MgCl·LiCl, 1.0 M in THF), dianhydro-D-glucitol (D-isosorbide, 98%) were provided by Sigma-Aldrich. Tetrahydrofuran (THF, HPLC grade) was obtained from CARLO ERBA Reagents. H_2SO_4 (95%), $MgSO_4$ (95%) and all other solvents were purchased from VWR. $MgCl_2$ was ground in a mortar and dried under vacuum overnight before use. $Zn(OTf)_2$, (TMP)MgCl·LiCl were stored under argon atmosphere in a glovebox. Other commercial compounds were used as received.

NMR spectra were recorded at 300 K on a Bruker Avance400 spectrometer with reference to the residual solvent peaks. Size exclusion chromatography (SEC) of the polymers was performed in THF at 35°C using an Agilent 1260 Infinity Series GPC (ResiPore 3 µm, 300 x 7.5 mm, 1.0 $ml{\cdot}min^{-1}$, UV (250 nm) and RI (PLGPC 220) detectors). The number average molecular masses ($\bar{M}_n$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) of the polymers were calculated with reference to a universal calibration vs. polystyrene standards (limits $\bar{M}_w$ = 200 to 400 000 $g{\cdot}mol^{-1}$). Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments DSC25, under nitrogen with heating / cooling / heating rates of $10°C{\cdot}min^{-1}$. T_g was measured at the midpoint during the second heating, in order to erase the thermal history of the polymers. Thermogravimetric analysis (TGA) measurement was performed on a TA Instruments TGA55 under nitrogen at a heating rate of $10°C{\cdot}min^{-1}$. The 5% weight loss temperature was recorded as $T_d^{5\%}$.

Synthesis of (1*R*,3*S*)-(+)-*cis*-1,2,2-trimethylcyclopentane-1,3-dimethanol) (TCDM)

A suspension of lithium aluminum hydride (2.277 g, 4 eq., 60 mmol) in 75 mL anhydrous tetrahydrofuran (THF) was placed in a 250-mL three-necked flask equipped with a reflux condenser. Then a solution of (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid (3.000 g, 1 eq., 15 mmol) in 75 mL THF was added dropwise over 30 min in an ice bath (10°C). The ice bath was then removed and the mixture was allowed to reach room temperature. The gray suspension was refluxed overnight. The excess lithium aluminum hydride was carefully quenched with distilled water and an aqueous solution of 5% H_2SO_4, then the white slurry was filtered and washed with diethyl ether. The aqueous layer was extracted three times with diethyl ether and the combined organic layer was washed with brine, dried with $MgSO_4$, concentrated under vacuum to give the crude product. Further sublimation (90°C, dynamic vacuum) of the crude product gave 2.120 g of white solid TCDM, yield: 82%. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm), 0.79 (s, 3H); 1.01 (s, 3H); 1.02 (s, 3H); 1.38 (m, 2H, *J* = 40 Hz); 1.59 (m, 1H, *J* = 32 Hz); 1.95 (m, 1H, *J* = 36 Hz); 2.08 (m, 1H, *J* = 32 Hz); 3.52 (m, 3H, *J* = 48 Hz); 3.73 (m, 1H, *J* = 16 Hz).

Typical procedure for the reaction of TCDM with DEC

TCDM (0.344 g, 1 eq., 2 mmol), DEC (0.59 g, 2.5 eq., 5 mmol) and (TMP)MgCl·LiCl (40 µl of 1 M in THF, 0.02 eq., 0.04 mmol) were added in a Schlenk tube. The reaction mixture was stirred at the desired temperature and monitored by ^{1}H NMR spectroscopy. After achieving complete conversion of TCDM, the volatile components are carefully removed under reduced pressure and the resulting reaction mixture is analyzed by ^{1}H NMR spectroscopy.

Synthesis of (1*S*,5*R*)-1,8,8-trimethyl-3-oxabicyclo[3.2.1]octane

Following the previously described procedure, the complete conversion of TCDM to the corresponding cyclic ether ((1*S*,5*R*)-1,8,8-trimethyl-3-oxabicyclo[3.2.1]octane) was achieved using $Zn(OTf)_2$ as catalyst (Figure S1). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm), 0.72 (s, 3H); 0.88 (s, 3H); 1.08 (s, 3H); 1.71 (m, 5H, *J* = 148 Hz); 3.07 (d, 1H, *J* = 10.8 Hz); 3.41 (dd, 1H, *J* = 2.4, 10.4 Hz); 3.41 (dd, 1H, *J* = 0.8, 10.8 Hz); 4.00 (d, 1H, *J* = 10.8 Hz).

Typical procedure for the two-step polycondensation in a one-pot process

In a typical one-pot polycondensation procedure, TCDM (0.344 g, 1 eq, 2 mmol) alone or with the appropriate amount of 1,3-propanediol or/and isosorbide, DEC (0.59 g, 2.5 eq., 5 mmol or 2.5 eq. of all diols) and (TMP)MgCl·LiCl (40 µl of 1 M in THF, 0.02 eq, 0.04 mmol, or 0.02 eq. of all diols) were stirred in a Schlenk tube at 130 ° C until complete conversion of the diol monomers. The temperature was then fixed at 180 ° C while the pressure was gradually reduced to 10^{-2} mbar within 1 h. The polycondensation was continued as long as the viscosity of the solution allowed stirring (typically 3~5 h). The resulting polymer was purified by precipitation in diethyl ether after dissolution in chloroform and dried under vacuum overnight.

Typical procedure for methanolysis degradation

In a Schlenk tube under an argon atmosphere, 30 µL (TMP)MgCl·LiCl (1M in THF) was added to a solution of the selected polycarbonate (20 mg) in MeOH (2 mL) or in a MeOH/THF mixture (volume ratio 0.1 mL : 2 mL). The solution was then stirred at 100 ° C for the required time (3 h for MeOH or 72 h for MeOH/THF), during which small aliquots were periodically taken, dried under vacuum, and analyzed by SEC-RI. Since light scattering (LS) detection requires a precise concentration of the purified polymers to obtain accurate results, refractive index (RI) detection was preferred in our case. To compensate for the inaccuracy of the RI method due to calibration with polystyrene standards, the results were recorded in relative loss of $\bar{M}_\mathrm{w}$.

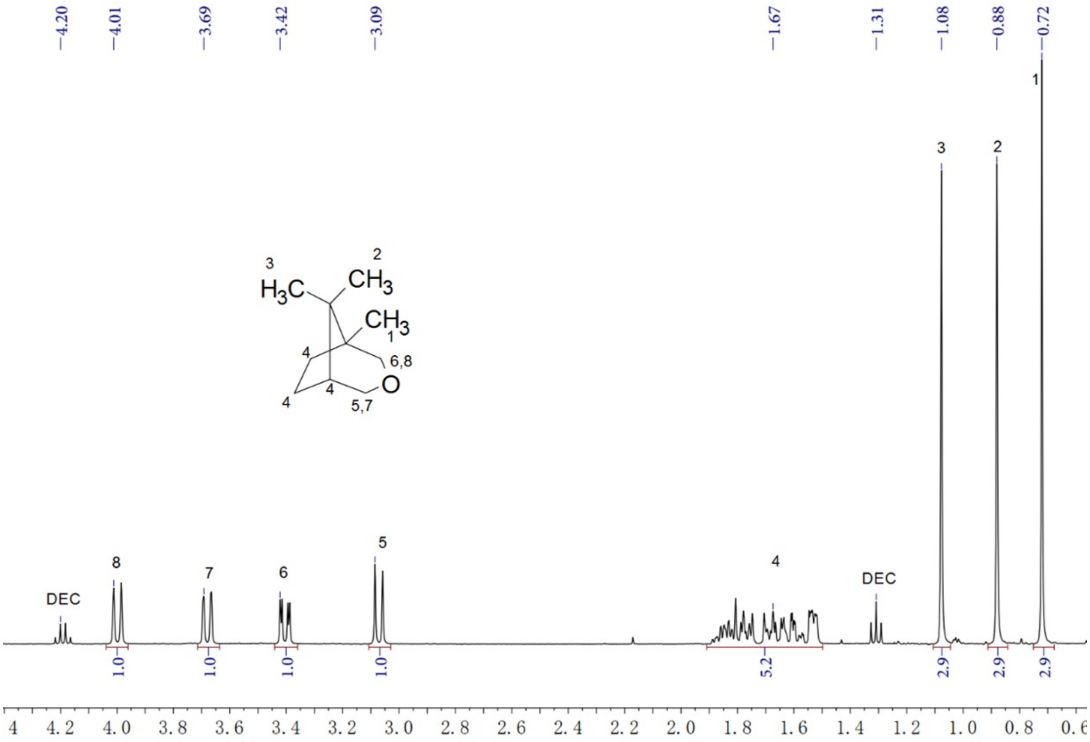

Figure S1. ^{1}H NMR spectrum of (1*S*,5*R*)-1,8,8-trimethyl-3-oxabicyclo[3.2.1]octane

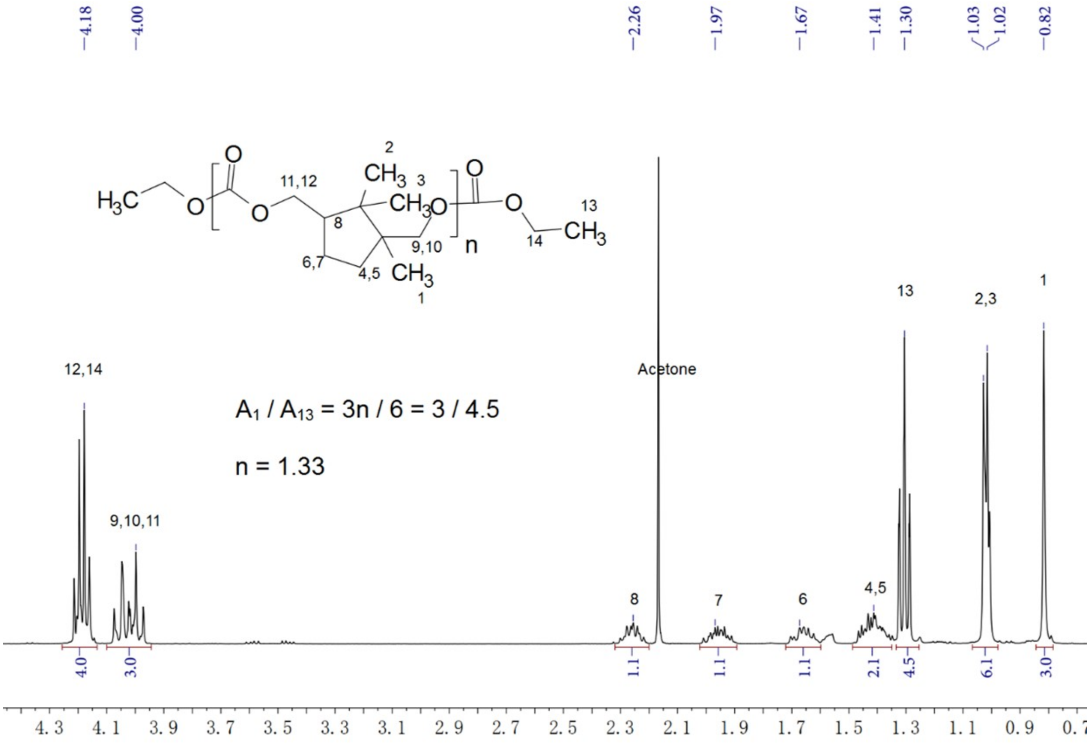

Figure S2. ^{1}H NMR spectrum of TCDM-based carbonate oligomer

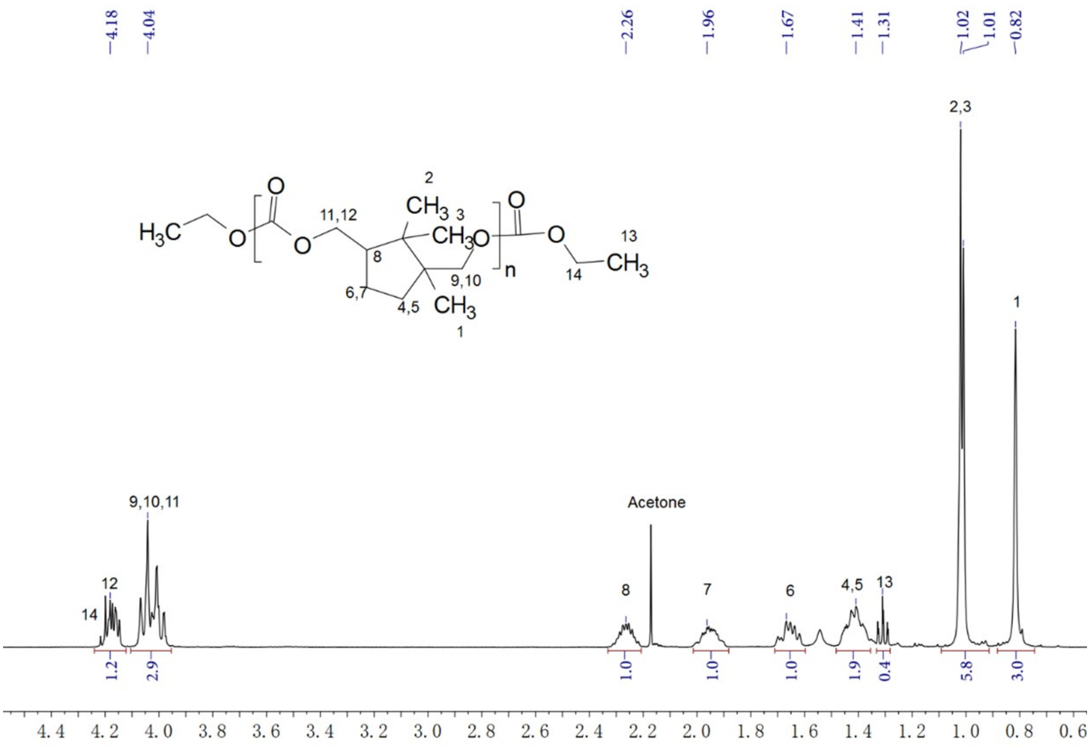

Figure S3. ^{1}H NMR spectrum of TCDM-based PC

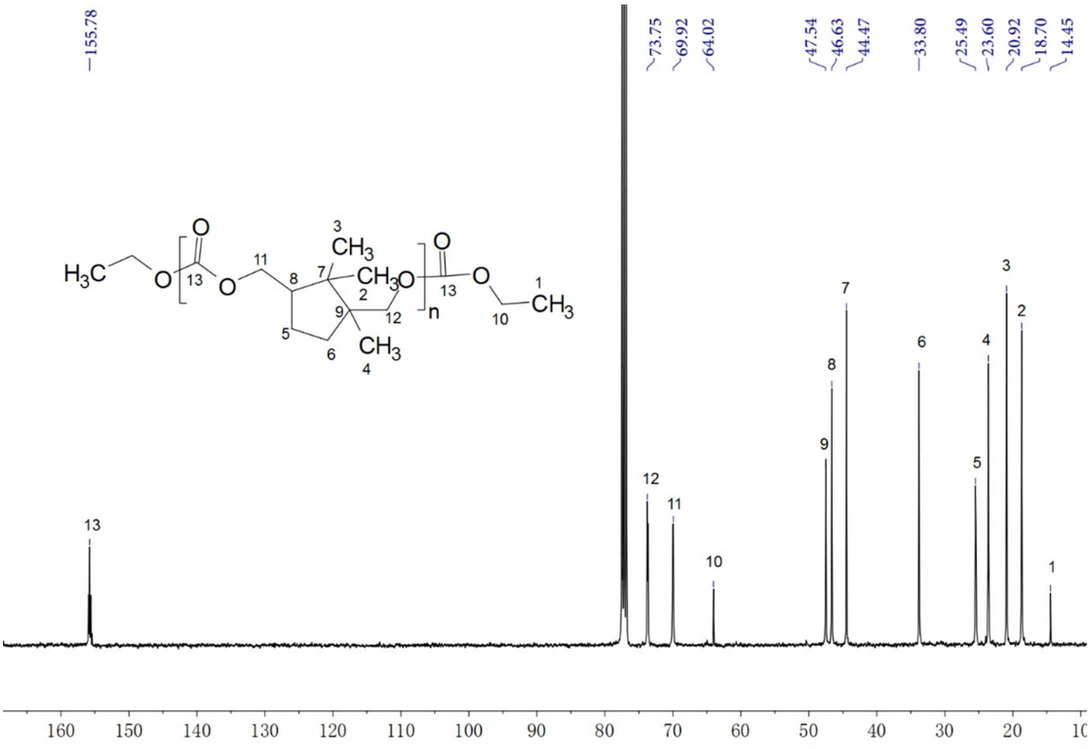

Figure S4. ^{13}C NMR spectrum of TCDM-based PC

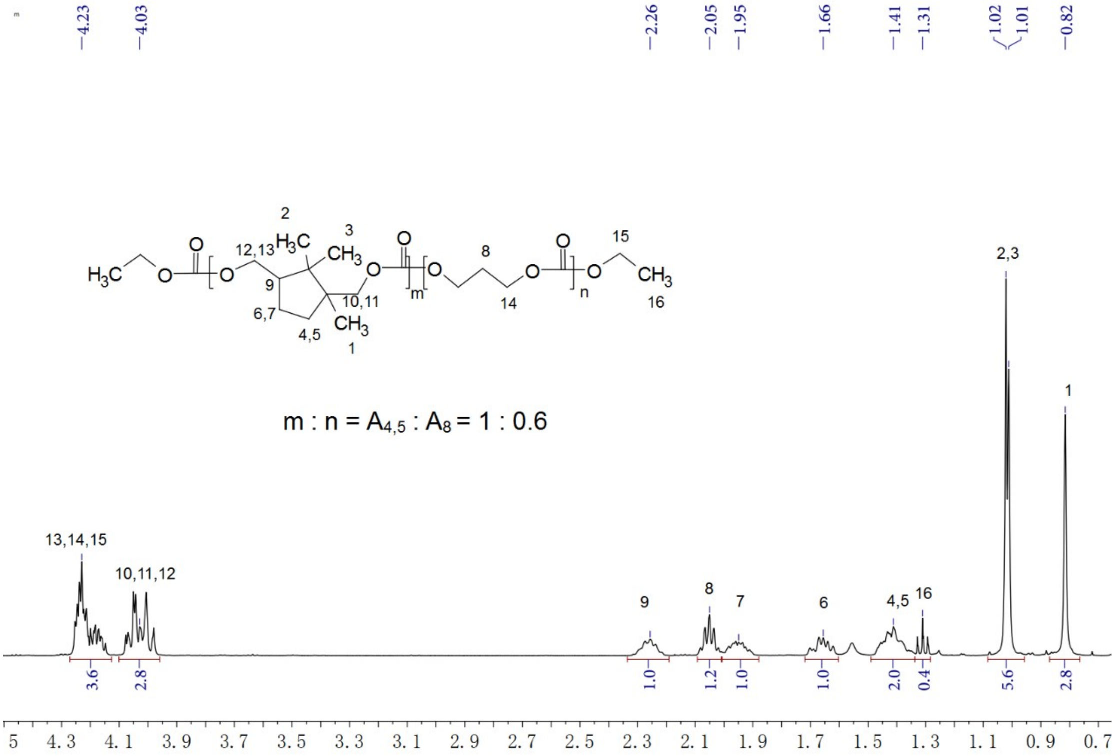

Figure S5. ^{1}H NMR spectrum of representative TCDM and 1,3-propanediol copolymer (TCDM-*co*-PD0.6)

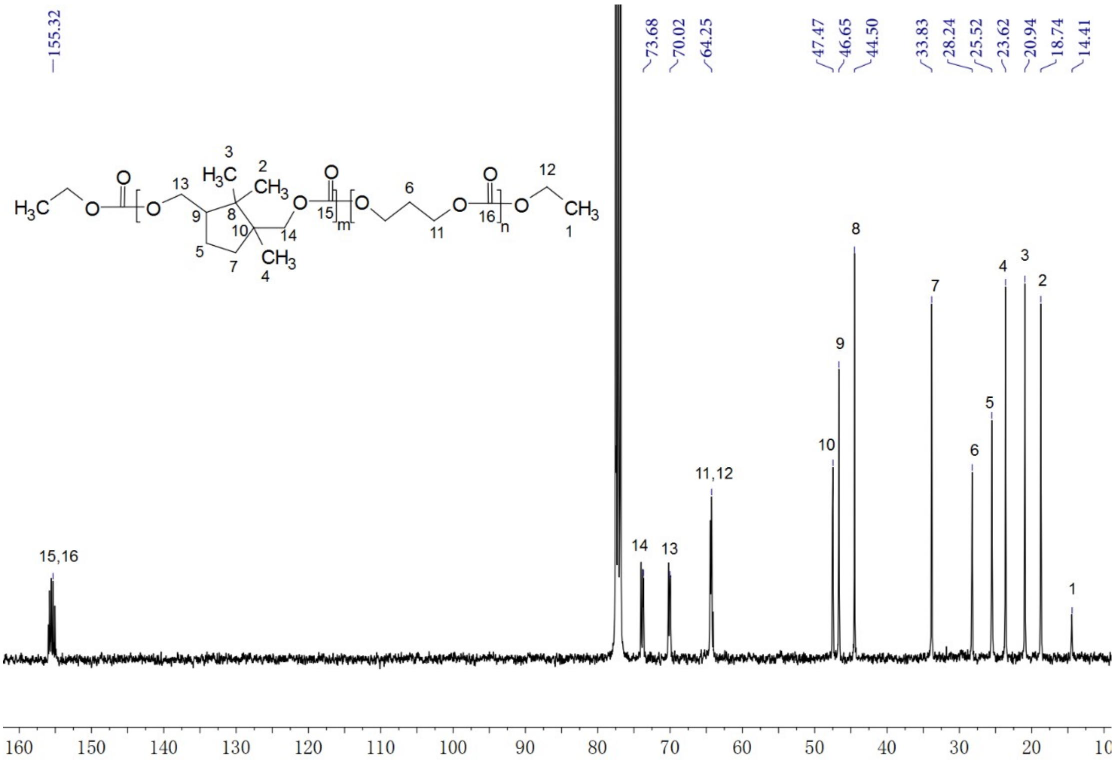

Figure S6. ^{13}C NMR spectrum of representative TCDM and 1,3-propanediol copolymer (TCDM-*co*-PD0.6)

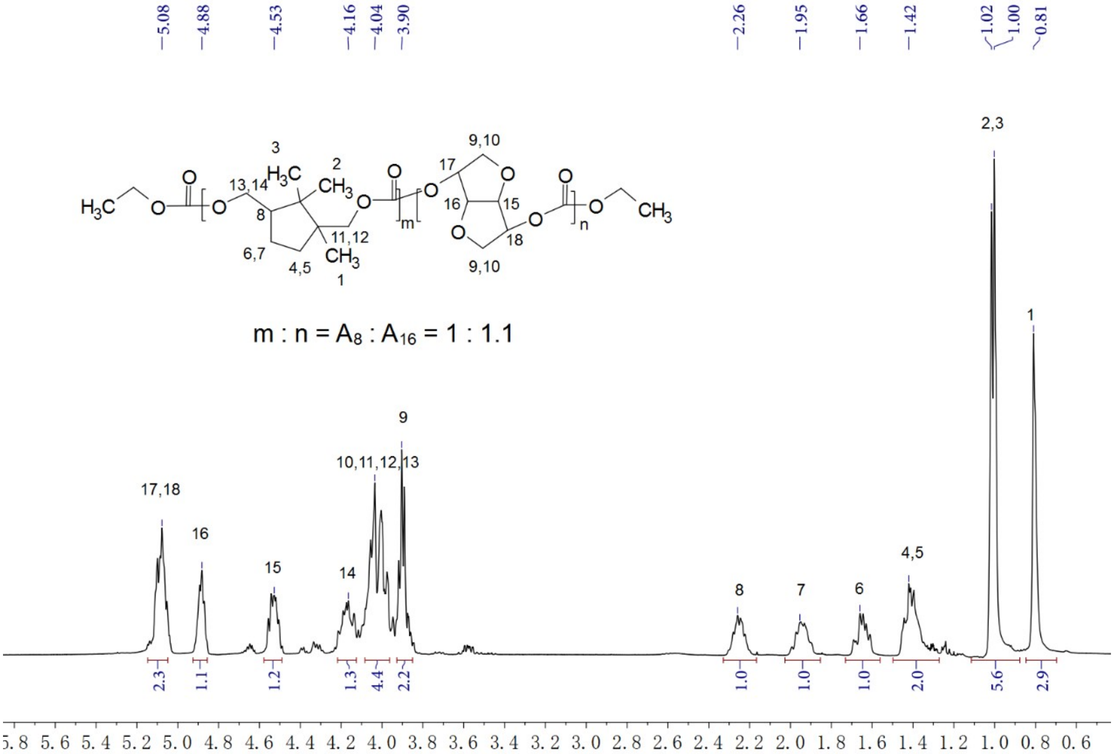

Figure S7. ^{1}H NMR spectrum of representative TCDM and isosorbide copolymer (TCDM-*co*-IS1.1)

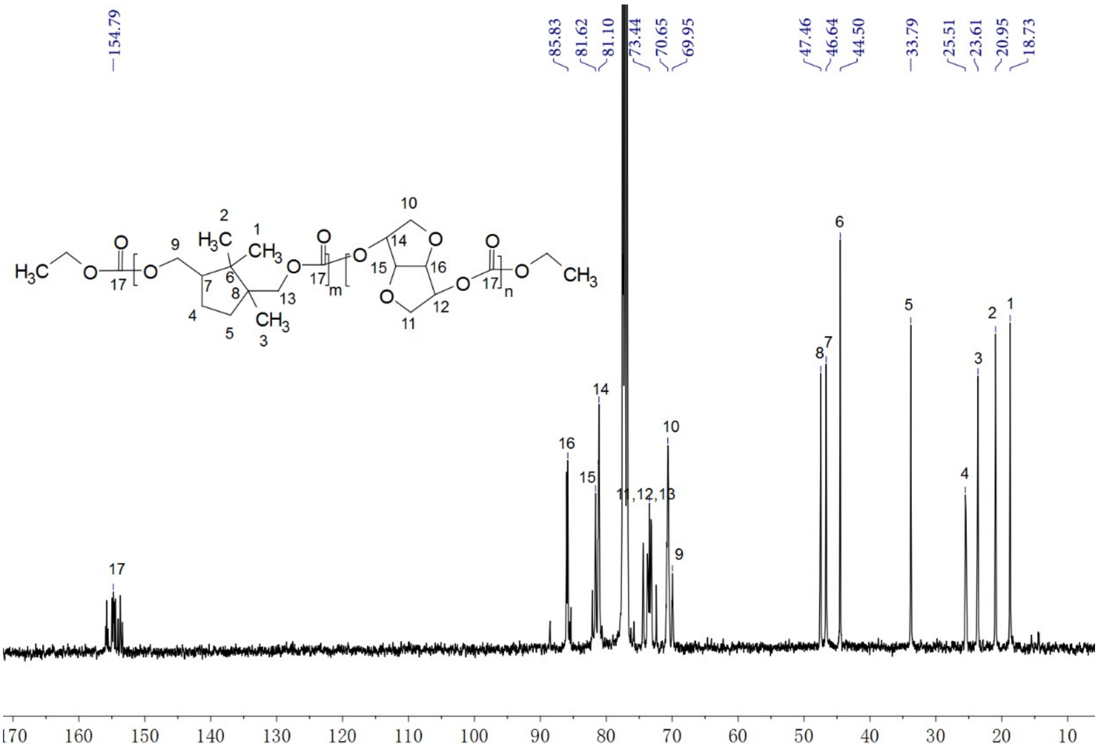

Figure S8. ^{13}C NMR spectrum of representative TCDM and isosorbide copolymer (TCDM-*co*-IS1.1)

2) Thermal characterizations of camphor-based polycarbonates

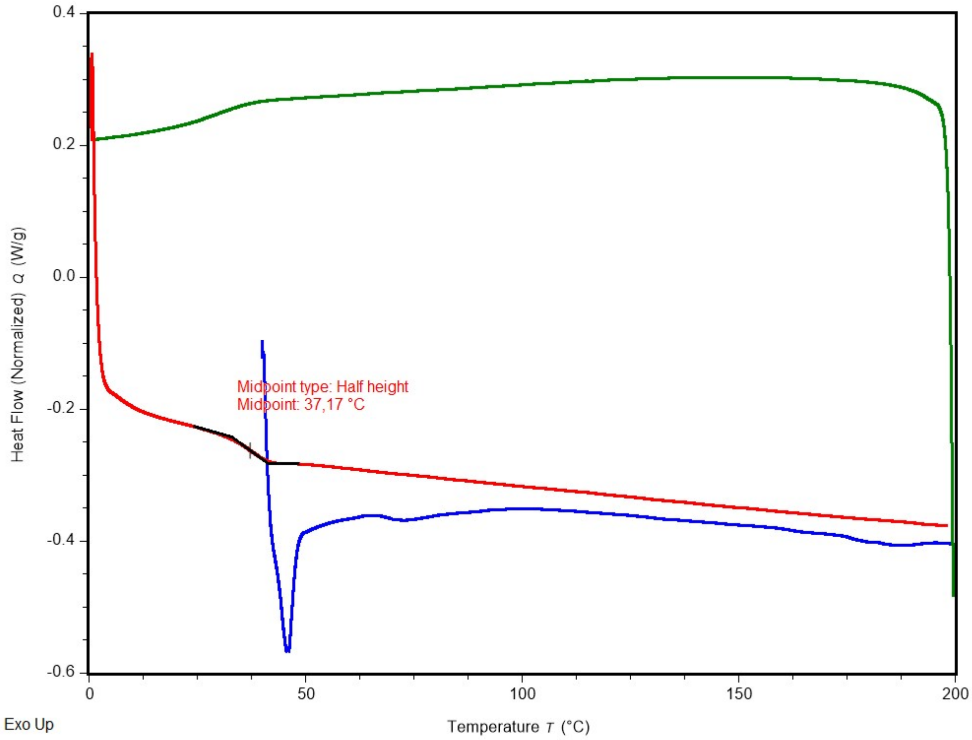

Figure S9. DSC diagram of TCDM-based PC

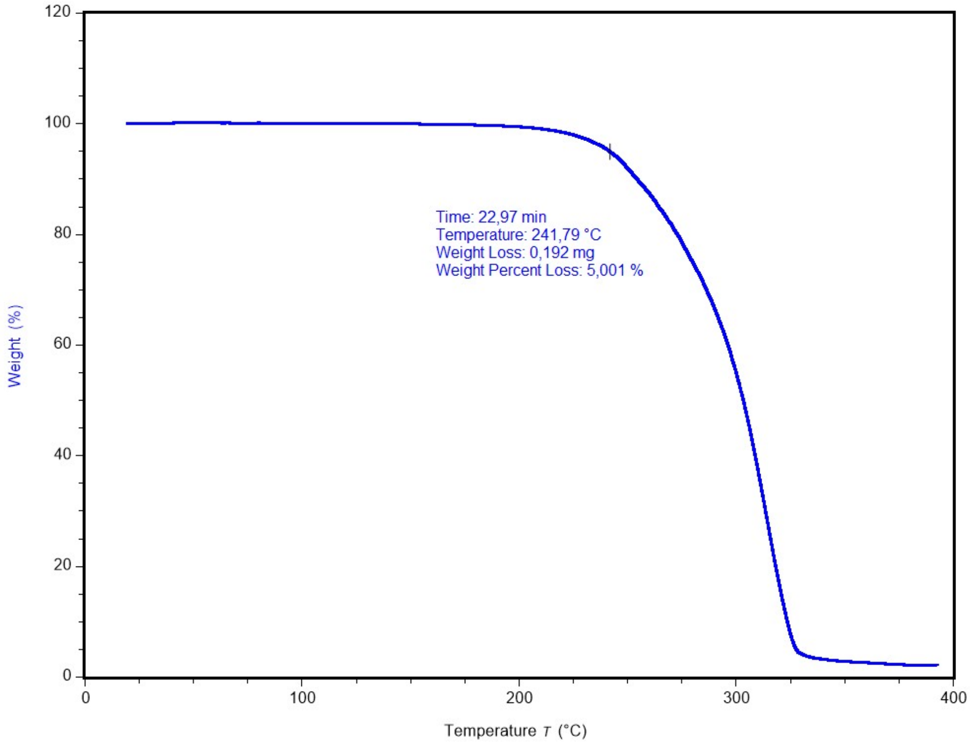

Figure S10. TGA diagram of TCDM-based PC

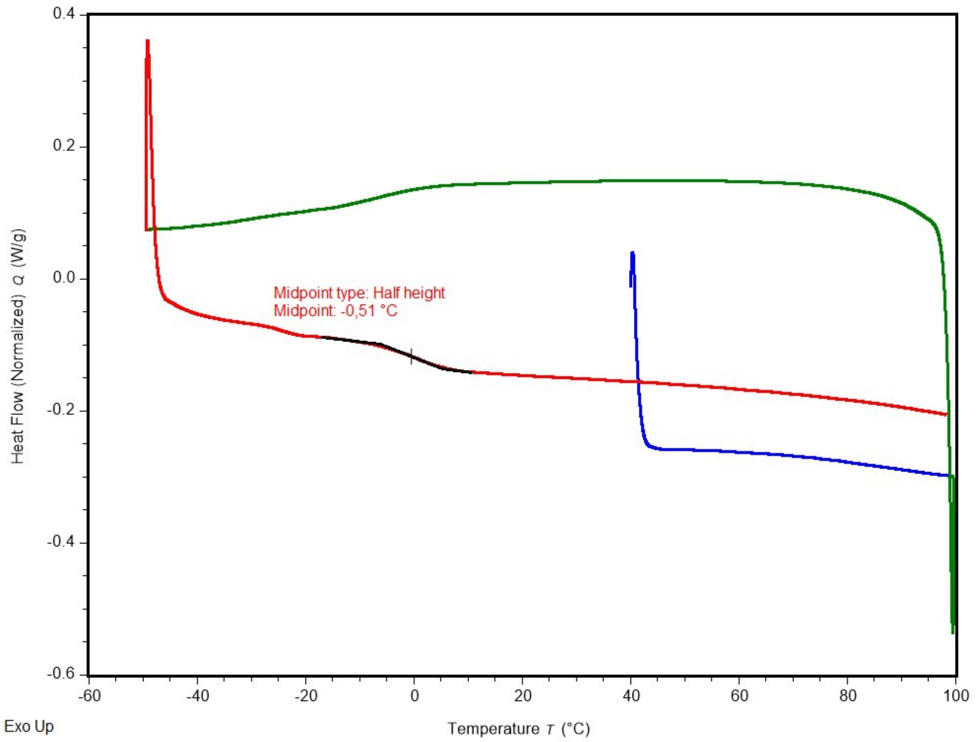

Figure S11. DSC diagram of TCDM-*co*-PD1.3

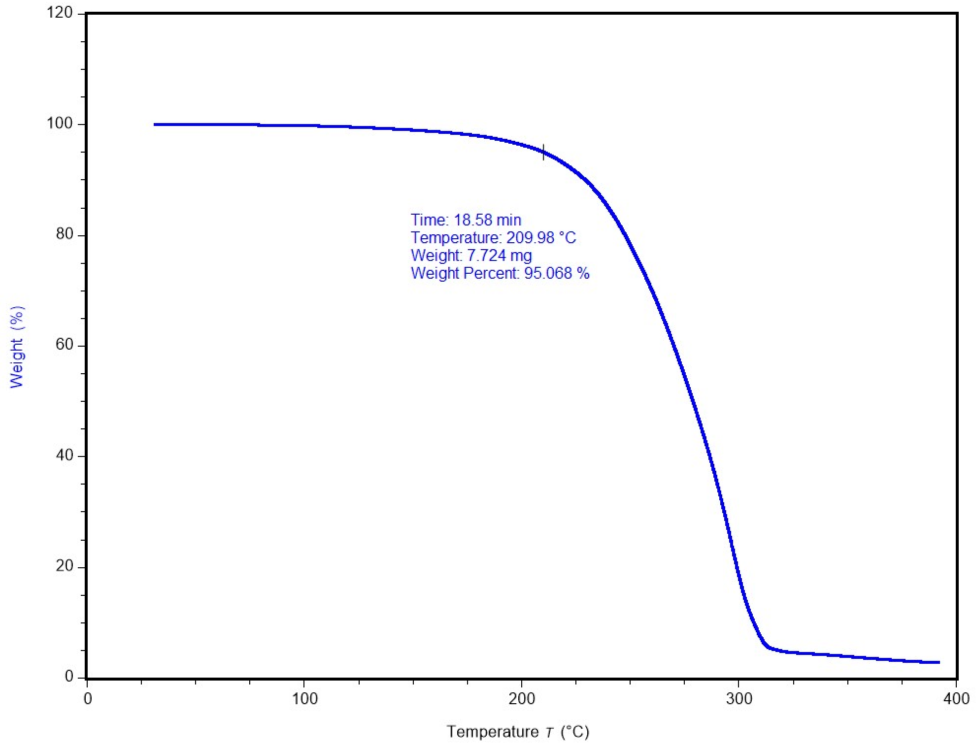

Figure S12. TGA diagram of TCDM-*co*-PD1.3

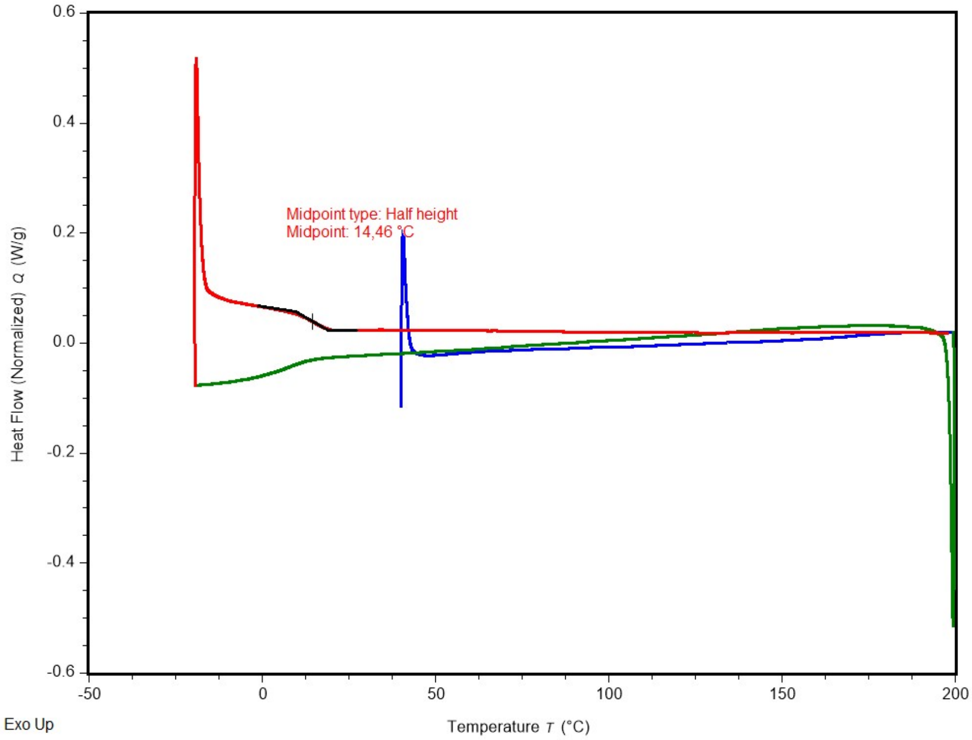

Figure S13. DSC diagram of TCDM-*co*-PD0.6

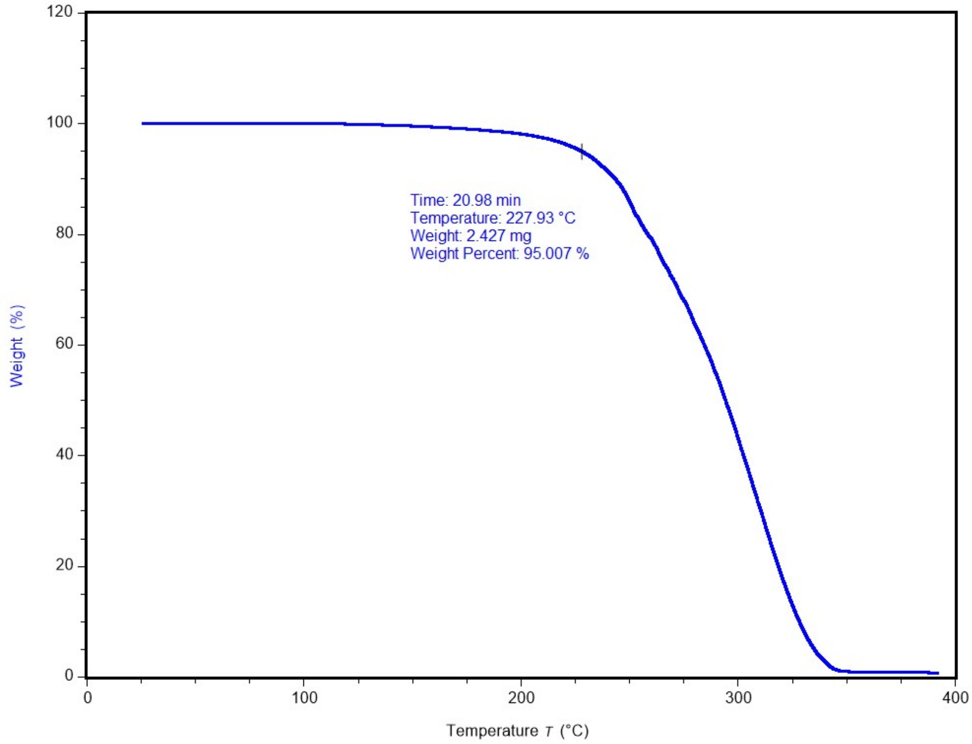

Figure S14. TGA diagram of TCDM-*co*-PD0.6

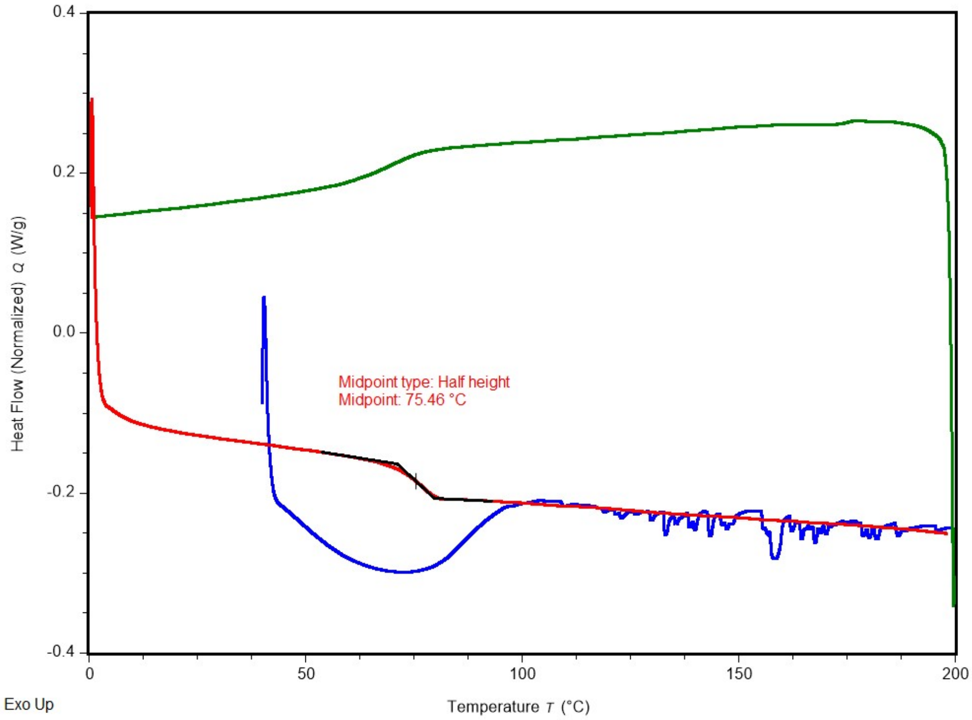

Figure S15. DSC diagram of TCDM-*co*-IS0.6

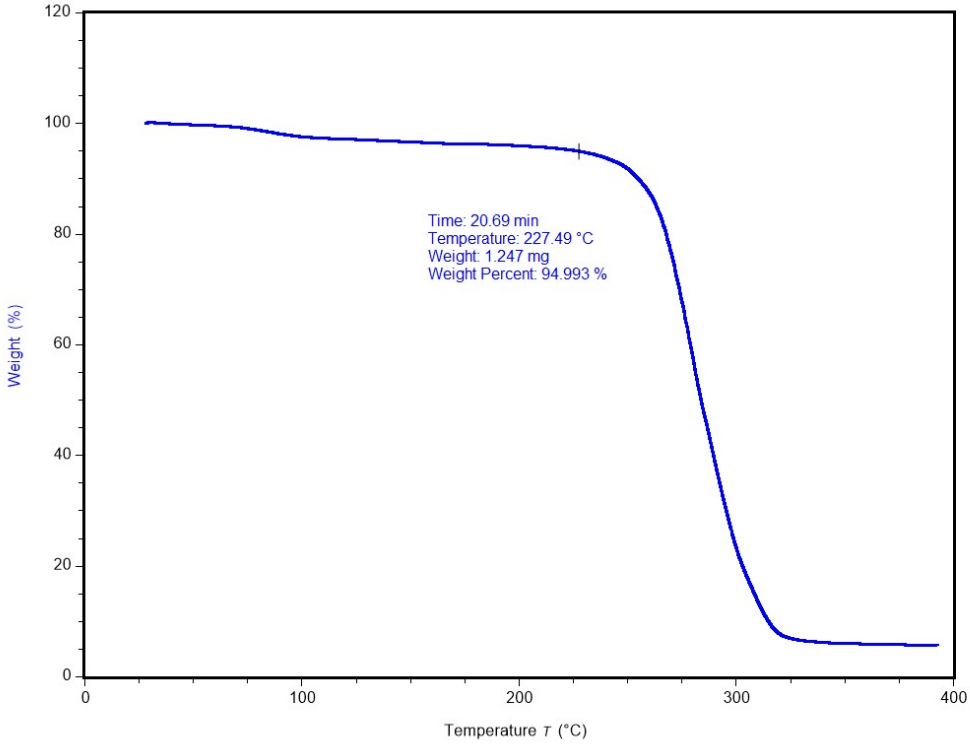

Figure S16. TGA diagram of TCDM-*co*-IS0.6

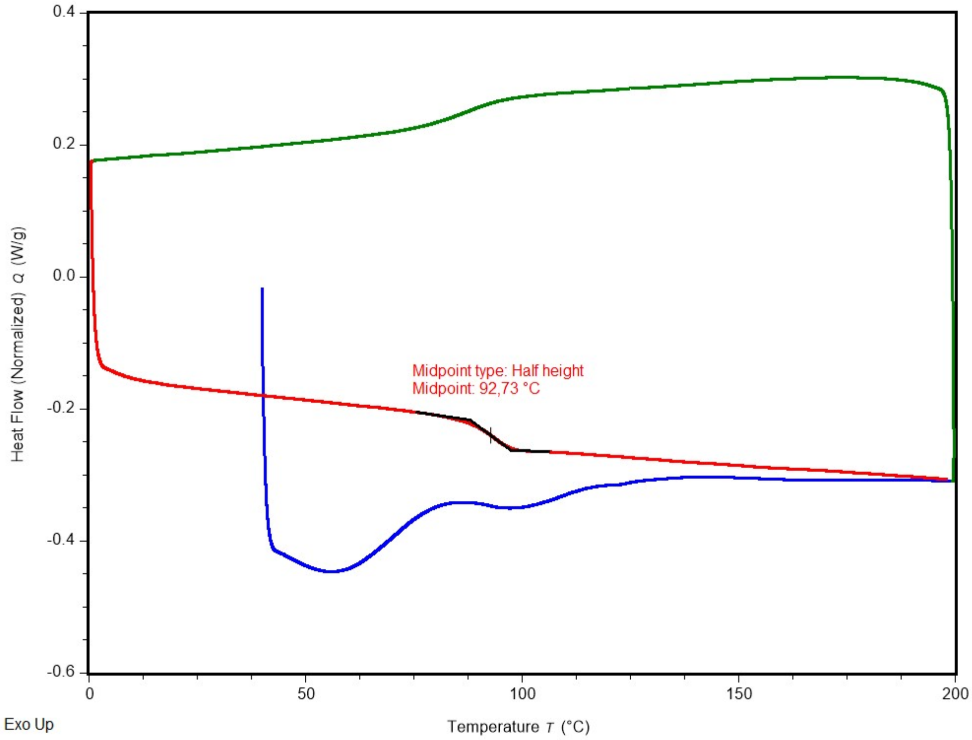

Figure S17. DSC diagram of TCDM-*co*-IS1.1

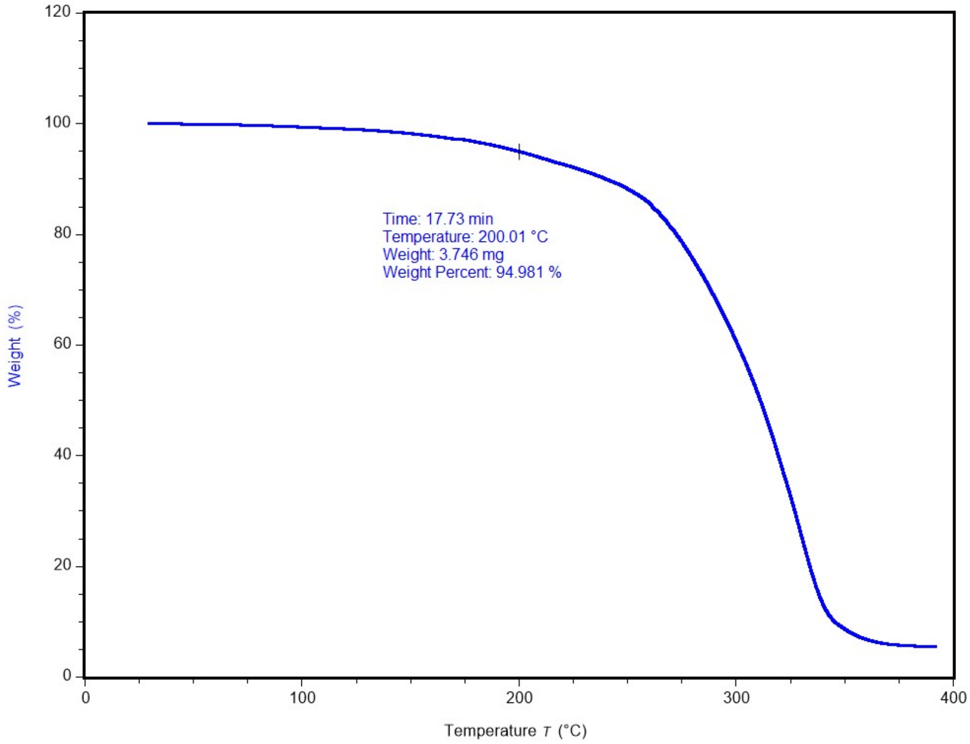

Figure S18. TGA diagram of TCDM-*co*-IS1.1

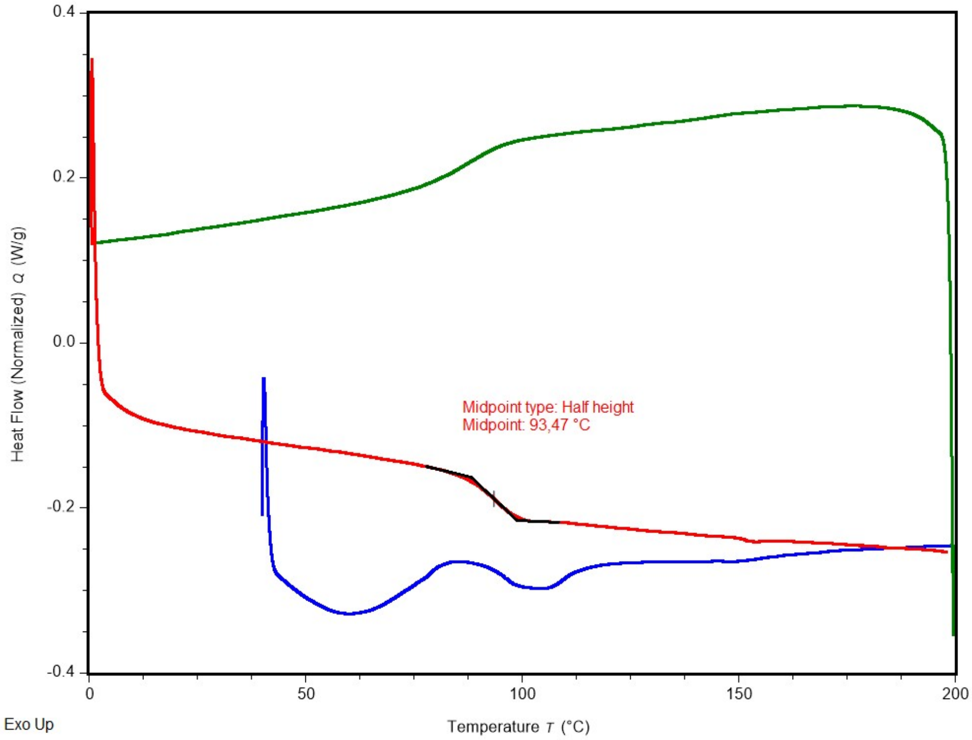

Figure S19. DSC diagram of TCDM-*co*-IS1.3

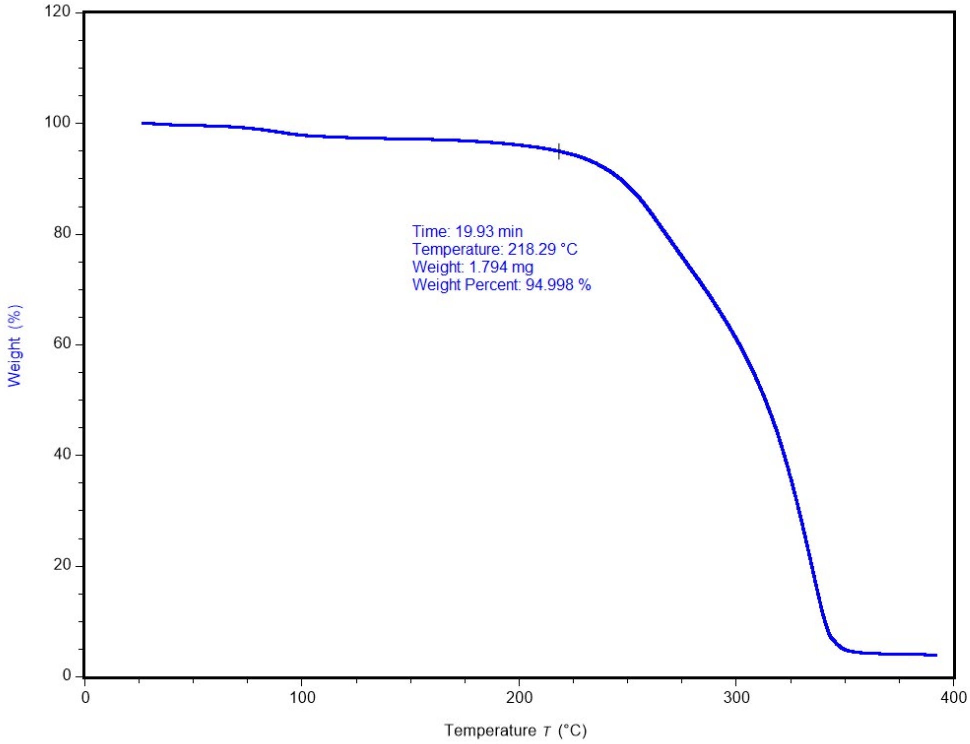

Figure S20. TGA diagram of TCDM-*co*-IS1.3

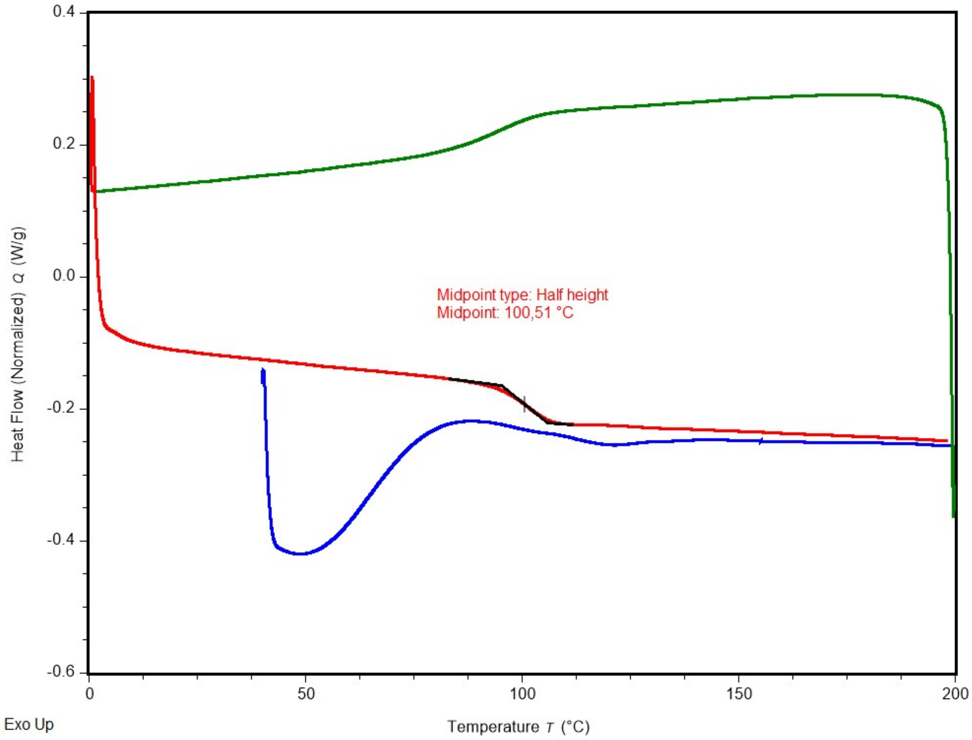

Figure S21. DSC diagram of TCDM-*co*-IS2.9

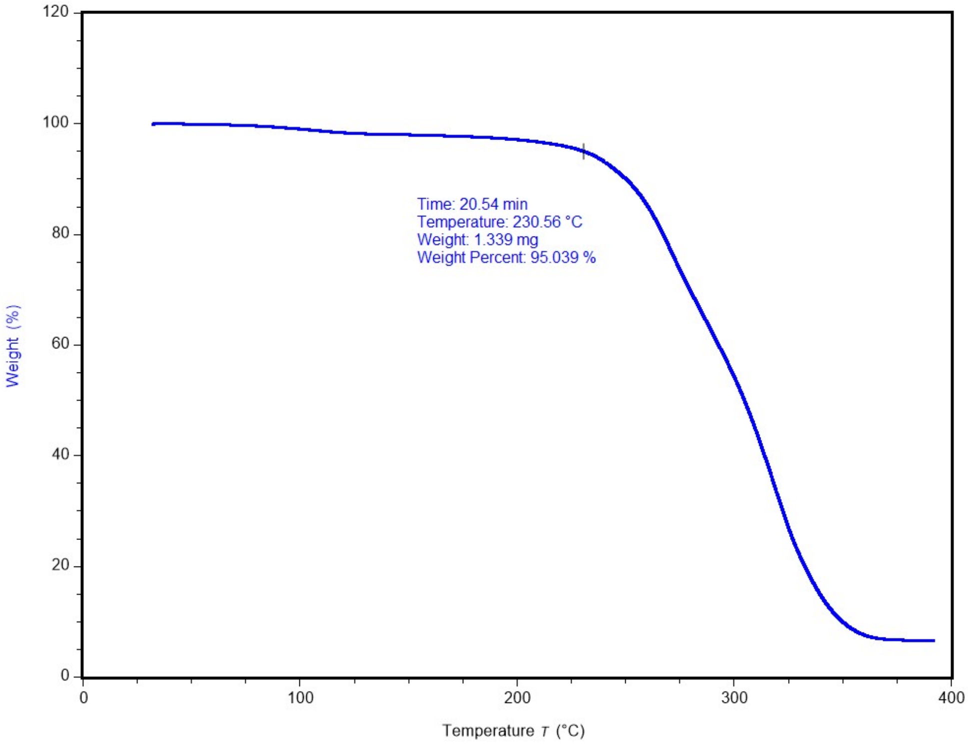

Figure S22. TGA diagram of TCDM-*co*-IS2.9

3) Degradation studies

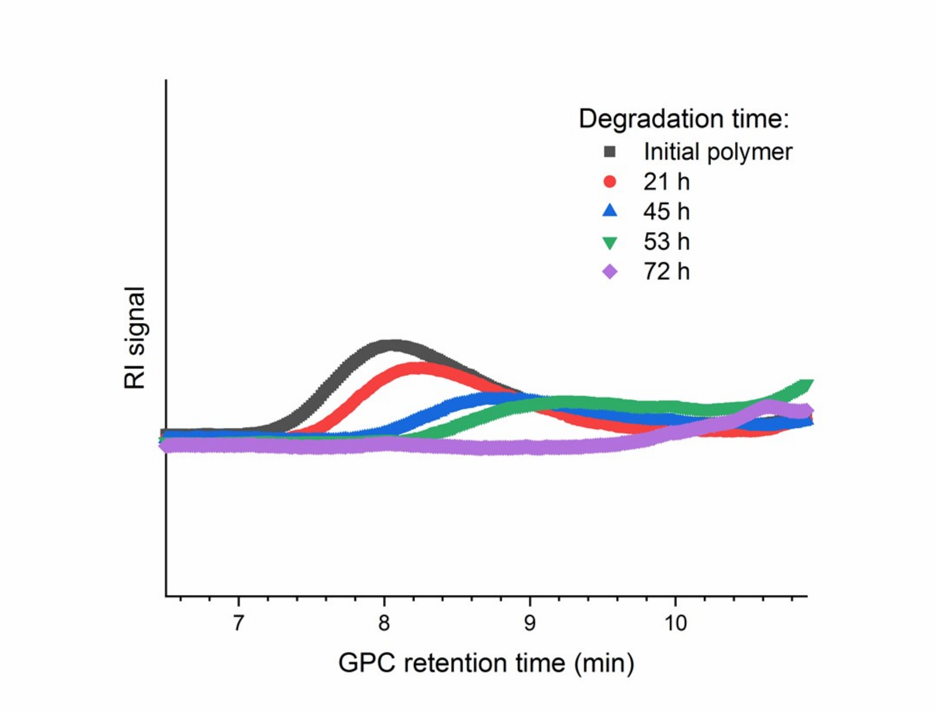

Figure S23. SEC-RI traces of (TMP)MgCl·LiCl catalyzed TCDM-co-PD0.6 methanolysis over time in MeOH/THF (volume ratio 1 : 20) at 100°C

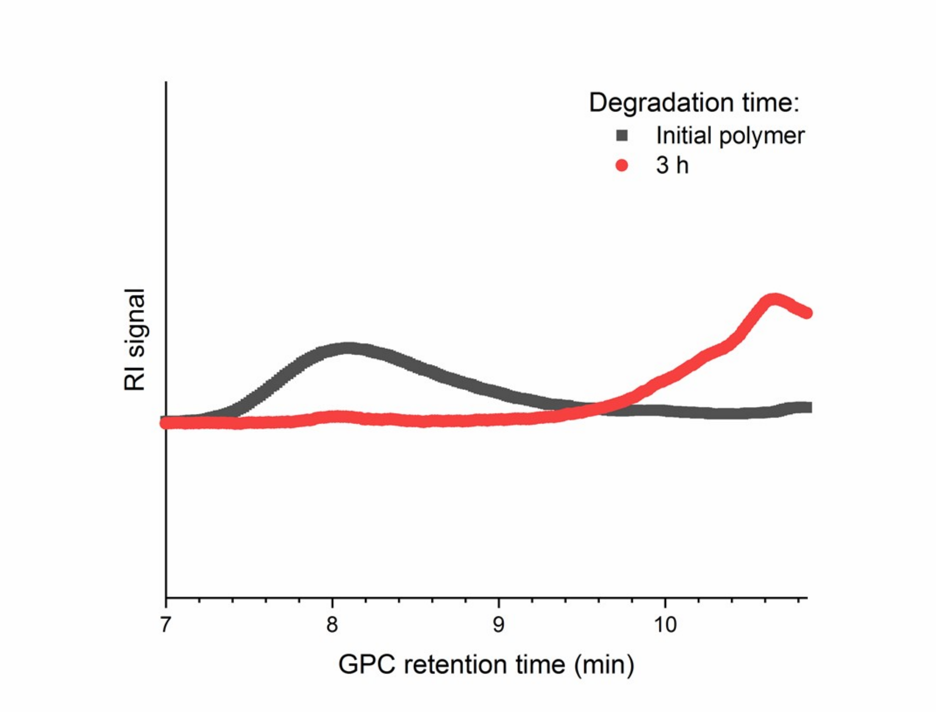

Figure S24. SEC-RI traces of (TMP)MgCl·LiCl catalyzed TCDM-*co*-PD0.6 methanolysis over time in MeOH at 100°C

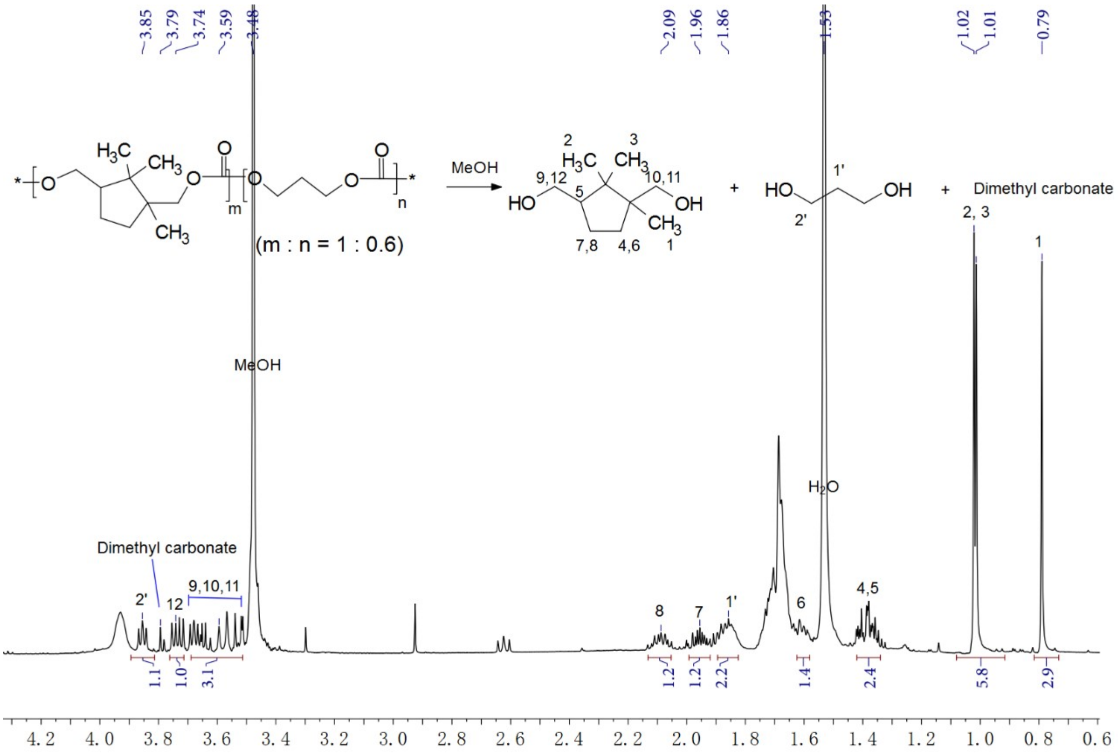

Figure S25. ^{1}H NMR spectrum of the crude after solvent evaporation in the TCDM-*co*-PD0.6 methanolysis reaction at 100°C after 3 h using MeOH

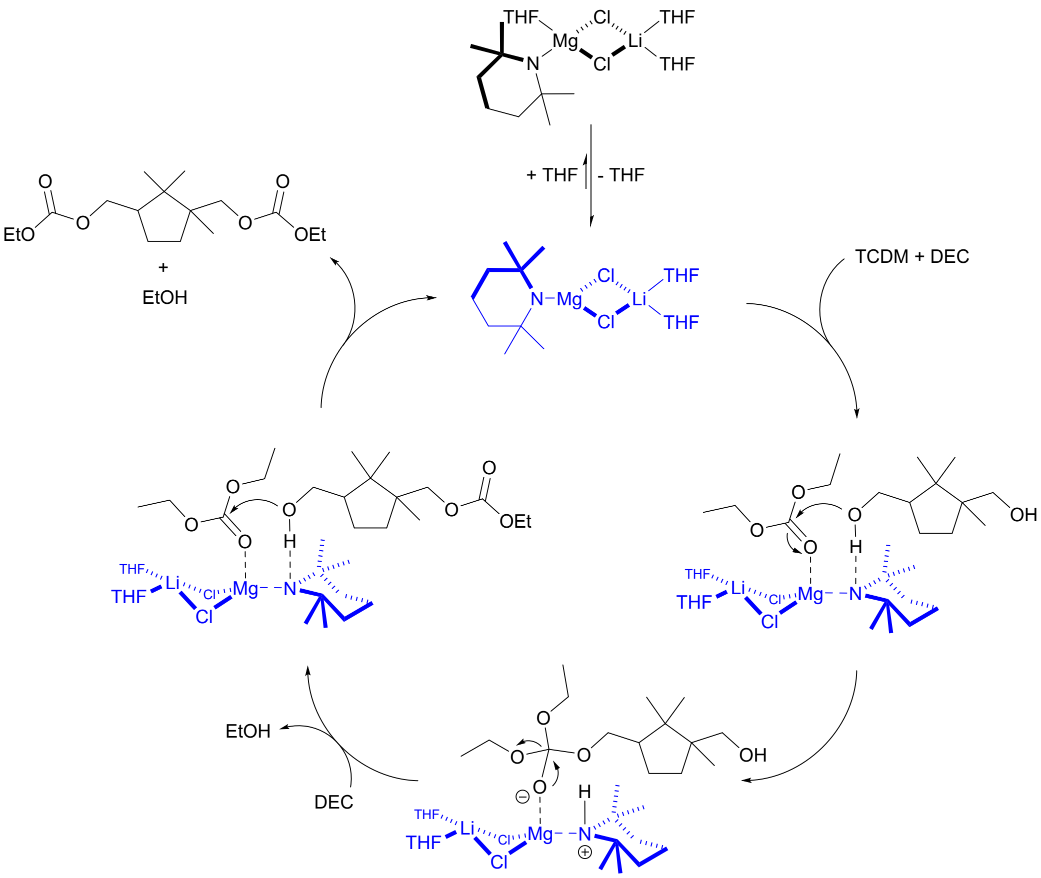

Figure S26. Envisaged mechanism for the reaction of TCDM with DEC catalyzed by (TMP)MgCl·LiCl