Electronic Supplementary Information (ESI)

Biocatalytic and solvent-free synthesis of a bio-based bis-cyclocarbonate

D. S. Wunschik[1,2,3], Kim N. Ingenbosch[1,2,3], M. Zähres[3], J. Horst[1], C. Mayer[3], M. Jäger[1], V. Strehmel[1], M. Dornbusch[1] and K. Hoffmann-Jacobsen[1,*]

[1] Niederrhein University of Applied Sciences, Department of Chemistry, Adlerstr. 32, 47798 Krefeld, Krefeld

[2] Deutsches Textilforschungszentrum Nord-West gGmbH, Adlerstraße 1, 47798 Krefeld, Germany

[3] Institute of Physical Chemistry and CENIDE (Center for Nanointegration), University Duisburg-Essen, Universitätsstraße 5, 45117 Essen, Germany

1. Infrared Spectra

Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Vector 22 spectrometer equipped with an attenuated total reflectance (ATR) diamond module in reflection mode. All ATR-FTIR spectra were collected at a resolution of 4 cm^{-1} with 32 scans per recording.

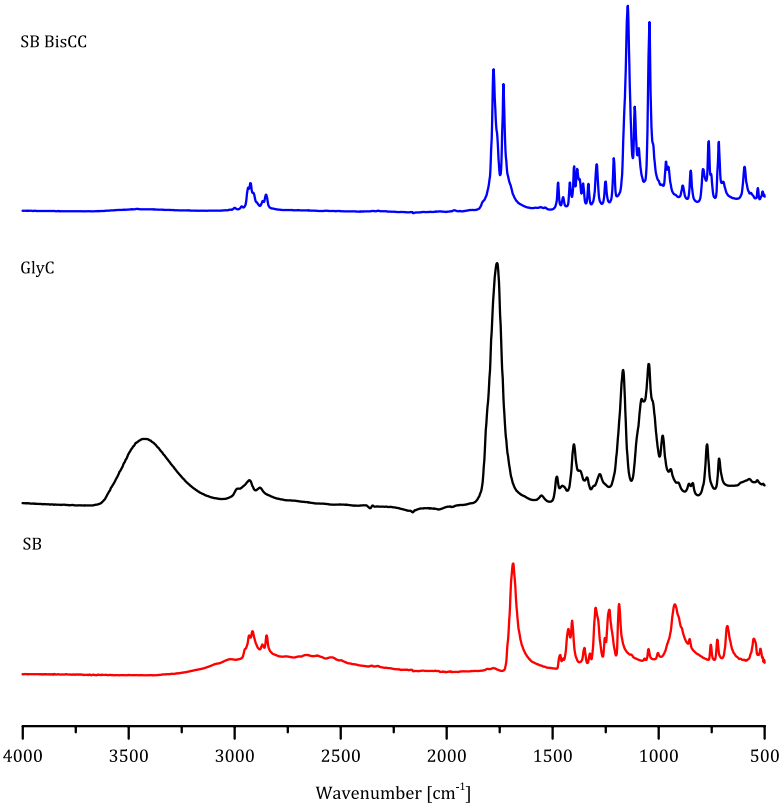

Fig. S1: FTIR spectra of sebacic biscyclocarbonate (SB BisCC) in comparison to the reactants glycerol carbonate (GlyC) and sebacic acid (SB)

2. Mass Spectrometry

Mass spectra were acquired with a Q-ToF LC/MS system from Agilent (Agilent 6530, Santa Clara, USA) using a Polaris Amid C18 column (Agilent, Santa Clara, USA). The mass spectrometer was equipped with a Jet-Stream Electron-Spray-Ion-source (ESI), which was operated in positive detection mode. Mass spectrometer and HPLC system were controlled via MassHunter Workstation B.06.00. Chromatograms and mass spectra were processed using the same software. For the analysis of product purity, the purified product was dissolved in acetonitrile and injected directly into the ToF analyzer (method A). The samples of the raw product were introduced as acetonitrile/water (90:10) solutions containing 0.1% of formic acid at a flow rate of 0.3 mL/min (method B). The source temperature was kept at 300 °C, the drying gas flow at 8 L/h and the fragmentor voltage at 175 V for both methods. The capillary and cone voltage were increased for

the detection of oligomers in the raw product (method B). This leads to stronger fragmentation in the instrument.

Fig. S2 shows the mass spectra of the purified product with both methods. With method A, the molecular ion peak is detected as Na^+ adduct (m/z 425). Method B reveals the presence of a small amount of oligomer impurities in the product but the molecular ion peak is diminished in the spectra acquired and fragments, especially upon loss of quasi-molecular ion carbon dioxide, are observed instead (m/z 376). The most prominent impurity peak at m/z of 715 is in line with an oligomer consisting of three sebacic acid units lacking the final carbonate functionalization.

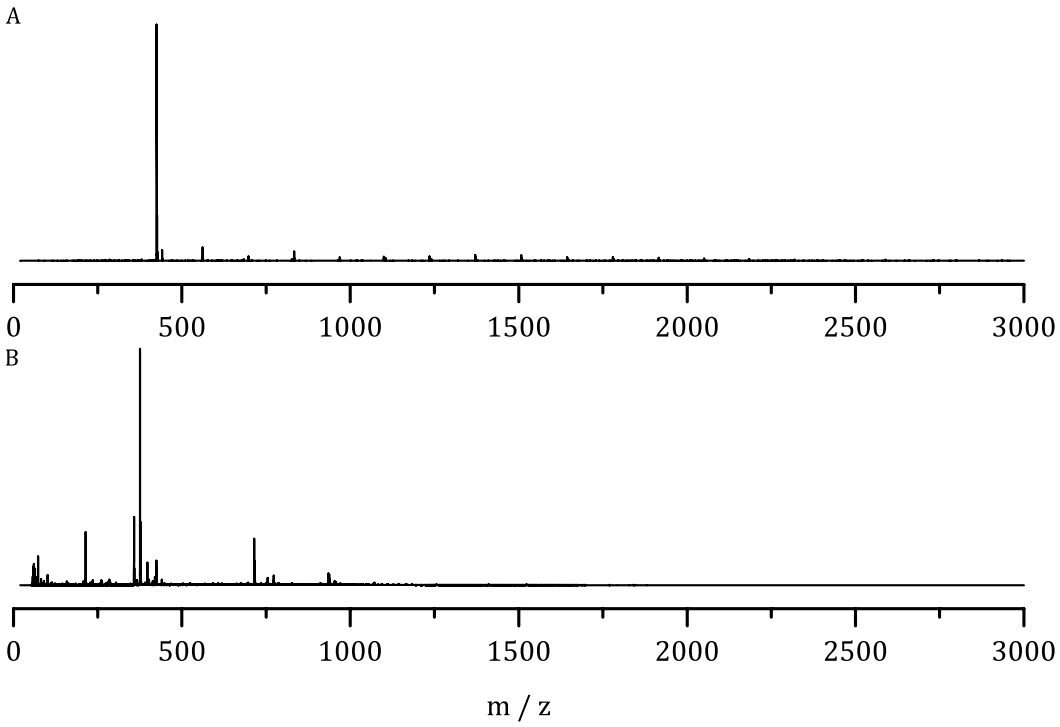

Fig. S2: ESI-ToF mass spectra of the purified product obtained with method A and method B respectively.

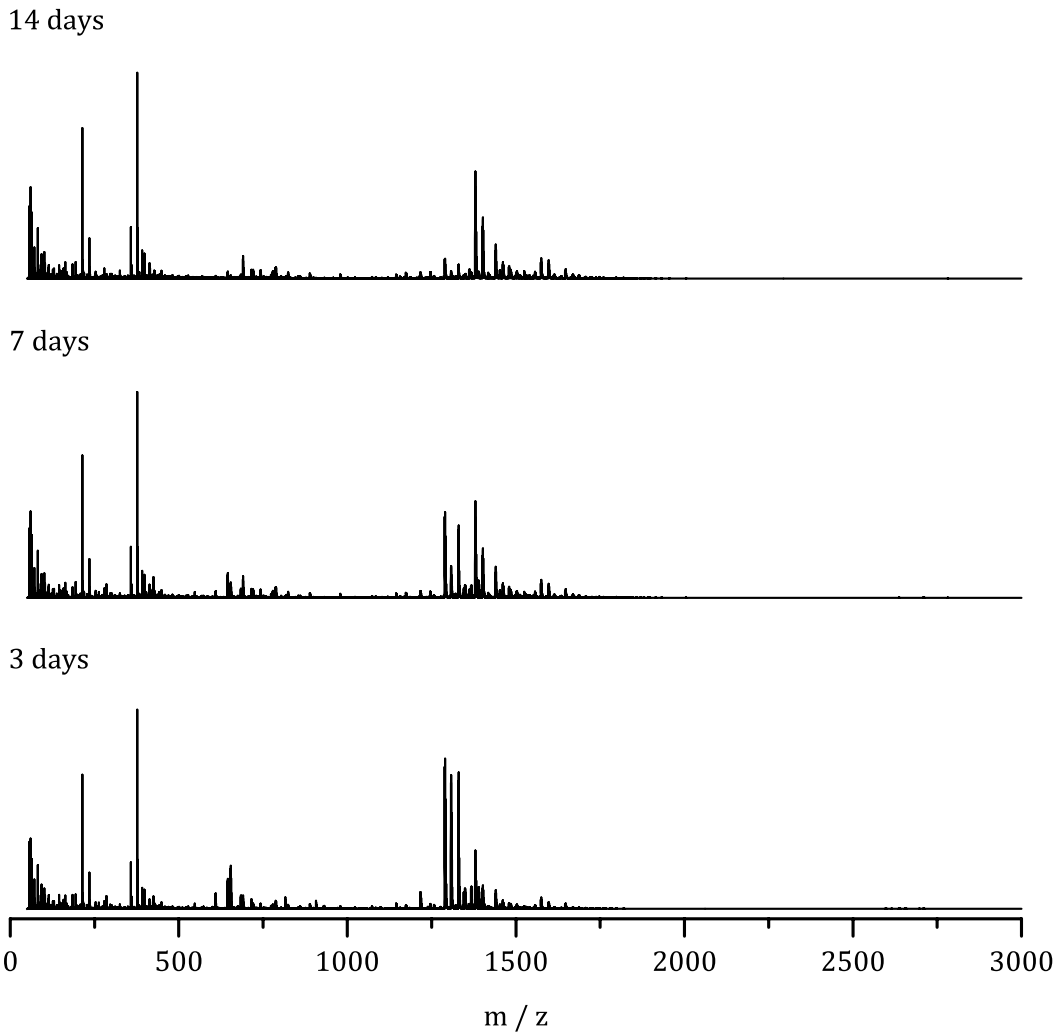

Fig. S3: ESI-ToF spectra of the raw product after the indicated reaction time (method B).

Fig. S3 depicts the mass spectra of the raw product for reaction times of 3, 7 and 14 days acquired with method B. The spectra illustrate the presence of oligomers in the raw product, which are subjected to fragmentation in the instrument. The most prominent oligomeric peaks are found at m/z 1289 and 1380. A mass of 1380 g/mol is in line with a linear pentamer as sketched in Fig. 1 after elimination of two carbon dioxide molecules upon fragmentation. The peak at m/z 1289 coincides with the molecular mass of a pentamer after internal esterification of the primary alcohol group formed by ring opening. It should be mentioned that the size of the observable oligomers and the relative peak intensities are suspected to depend on the raw product isolation, dissolution in acetonitrile and the applied voltages. However, the mass spectra provide direct evidence for the formation of oligomers.

3. NMR Spectroscopy

H-C HMQC-NMR and DEPT 135 spectra of the product obtained from the optimized synthesis were recorded on a Bruker Avance 3 Fourier 400 spectrometer at 400 MHz and 100 MHz ^{1}H and ^{13}C Larmor frequency.

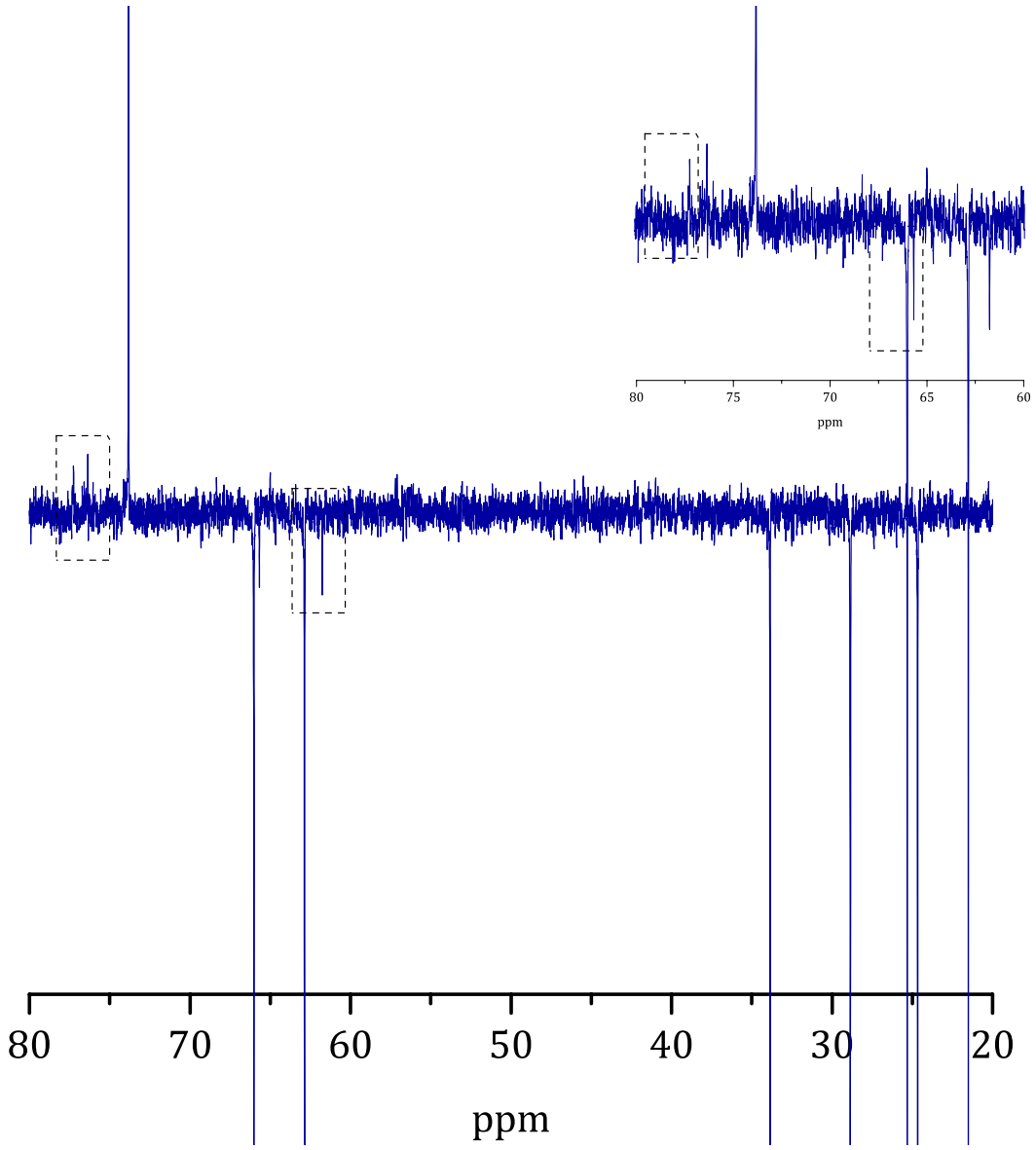

Fig. S4: DEPT 135 spectrum of SB BisCC. The impurity signals are marked with boxes.

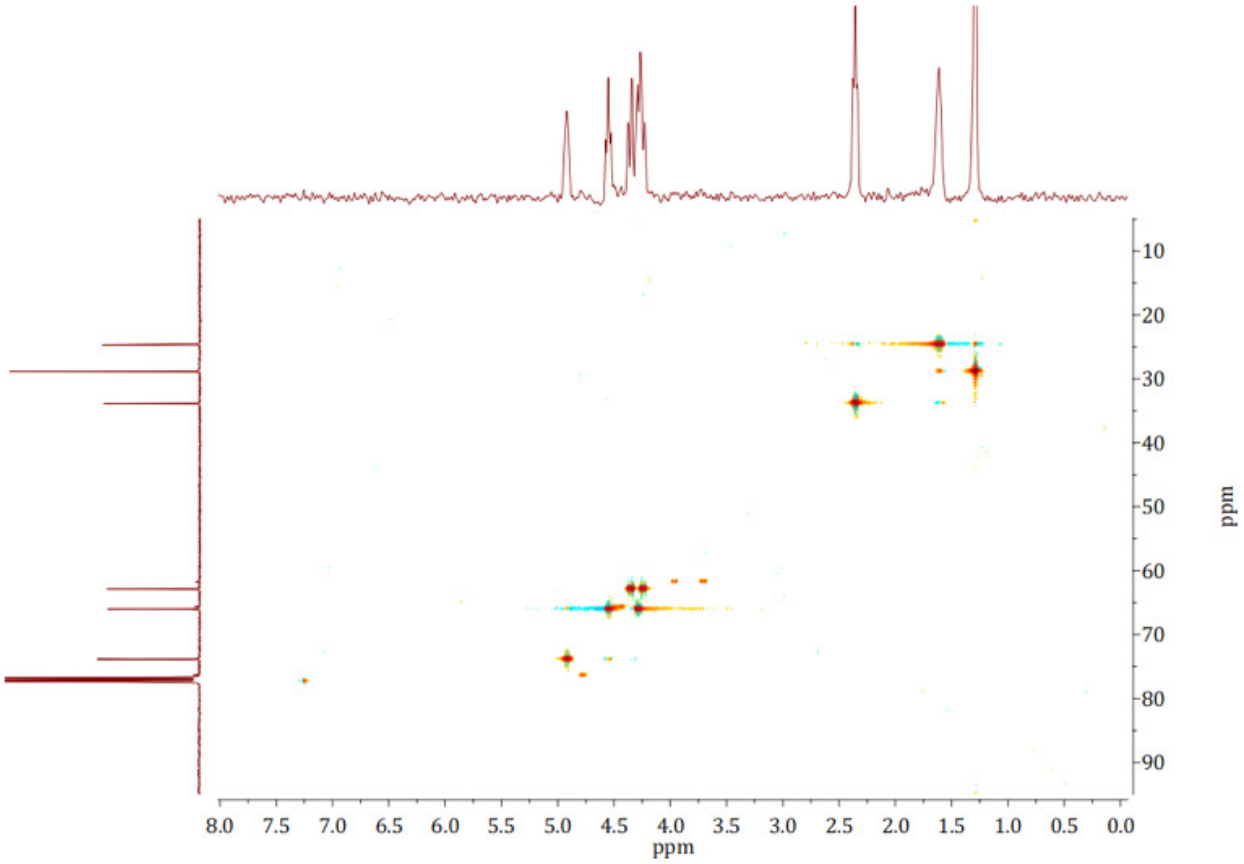

Fig. S5: H-C HMQC-NMR spectrum of SB BisCC

The impurity signals at 3.7-3.9 ppm and 4.6 ppm were further characterized by DEPT 135- and H-C HMQC-NMR to confirm the predicted by-product (*2*). Therefore, a DEPT 135 was performed and correlated with a ^{1}H-NMR. The correlation at 4.77/76.35 ppm indicates -O-CH_2-C*H*-CH_2-OH whereas 3.70-3.97/61.76 suggest -O-CH_2-CH-C*H*$_2$-OH.