

Supplementary data

Renewable-resource based poly(dodecyloate) by carbonylation polymerization

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Materials and General Considerations. Unless noted otherwise, all manipulations were carried out under an inert gas atmosphere using standard glovebox or Schlenk techniques. Pyridine was distilled from CaH_2 , and toluene from sodium under argon. Undec-10-en-1-ol supplied by ACME Synthetic Chemicals (Mumbai, India) was degassed prior to use. Carbon monoxide (3.7 grade) supplied by Air Liquide was used as received.

NMR spectra were recorded on a Bruker Avance III 600 instrument equipped with a Cryo Probe Triple resonance CPTCI, or on a Bruker AC 250 instrument. ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signal. ^1H and ^{13}C NMR assignments are supported by COSY, phase sensitive HSQC and HMBC experiments. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating/cooling rate of 10 K min^{-1} . DSC data reported are from second heating cycles. Gel permeation chromatography (GPC) was carried out on a Polymer Laboratories PL-GPC 50 with two PLgel $5\ \mu\text{m}$ MIXED-C columns and a RI-detector in THF at $40\text{ }^\circ\text{C}$ against polystyrene standards.

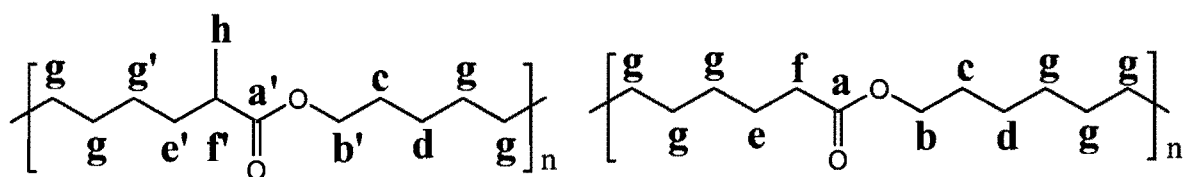
Polymerizations were carried out in a 280 mL stainless steel mechanically stirred (1500 rpm) pressure reactor equipped with a heating/cooling jacket controlled by a thermocouple dipping into the polymerization mixture.

Prior to a polymerization experiment the reactor was purged several times with argon. $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}_4(\text{CO})_{12}]$, respectively, were weighed into a dry Schlenk tube in the glovebox. Pyridine and undec-10-en-1-ol were added. The mixture was stirred until the $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}_4(\text{CO})_{12}]$, respectively, dissolved. The reaction mixture was transferred to the reactor via a teflon tube in an argon counter stream. The reactor was closed, pressurised with carbon monoxide, and heated to the desired reaction temperature (pressures given in Table 1 refer to pressure at reaction temperature). After the desired reaction time the reactor was rapidly cooled to room temperature, and vented. The solid polymer was recovered from

the reactor, dissolved in dichloromethane, and precipitated from methanol. The polymer was isolated by filtration, washed several times with methanol, and dried in vacuum at 50 °C.

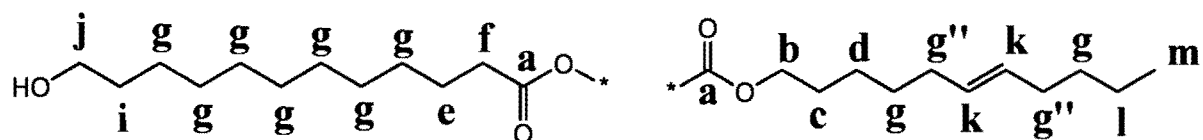
For NMR analysis residual cobalt was removed, as traces of paramagnetic impurities can impact the quality of the NMR spectra. 2 g of polymer were redissolved in 50 mL of dichloromethane. To this polymer solution were added 50 mL of an 0.1 M aqueous EDTA (ethylenediaminetetraacetate disodiumsalt) solution, 1 mL of 30 % H₂O₂, and 0.5 mL of 37 % aqueous HCl. The mixture was stirred well for one day. The pink aqueous phase formed was separated, and the polymer was precipitated from methanol, isolated by filtration, thoroughly washed with methanol, and finally dried in vacuum at 50 °C. For acquisition of ¹³C NMR spectra, a small amount of [Cr(acac)₃] was added. As an alternative or in addition to this procedure, CS₂ can be added to mask cobalt traces if required.

polyester backbone:



Key signals ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 4.01 (t, ³J_{HH} = 6.7 b-H), 2.5-2.3 (m, f'-H), 2.25 (t, ³J_{HH} = 7.6, f-H), 1.6 - 1.5 (m, e'-H, c-H and e-H), 1.35-1.18 (m, g-H), 1.1 (d, ³J_{HH} = 7.0, h-H), 1.22 (g'-H)^a, 1.29 (d-H)^a.

end groups:



Key signals ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 5.45-5.2 (m, k-H), 3.6 (t, ³J_{HH} = 6.5, j-H), 2.1 - 1.9 (m, g''-H), 0.9 - 0.8 (m-H, and CH₃ of longer branches), 1.54 (i-H)^b, 1.24 (l-H)^a

^a obscured by g-H signals, observed indirectly via HSQC and HMBC spectroscopy

^b obscured by e'-H, c-H and e-H signals, observed indirectly via COSY

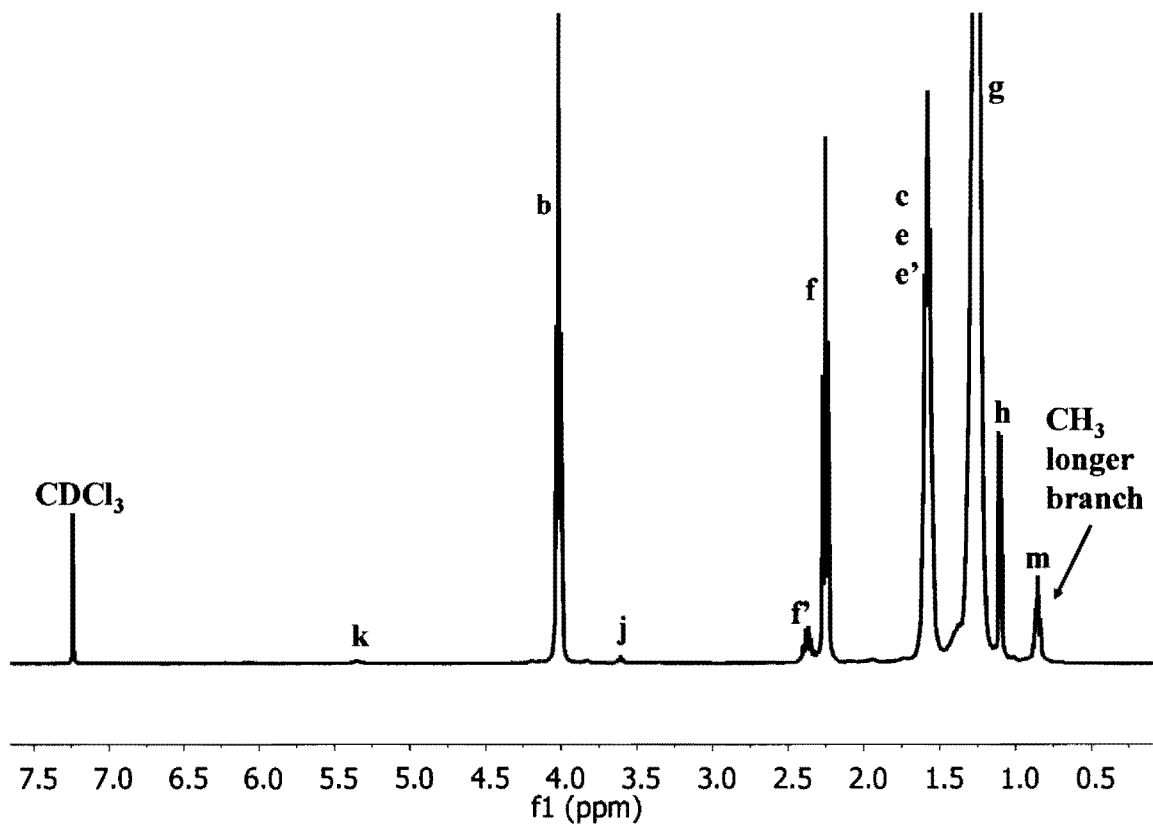


Figure S1. ^1H NMR spectrum of a typical polyester.

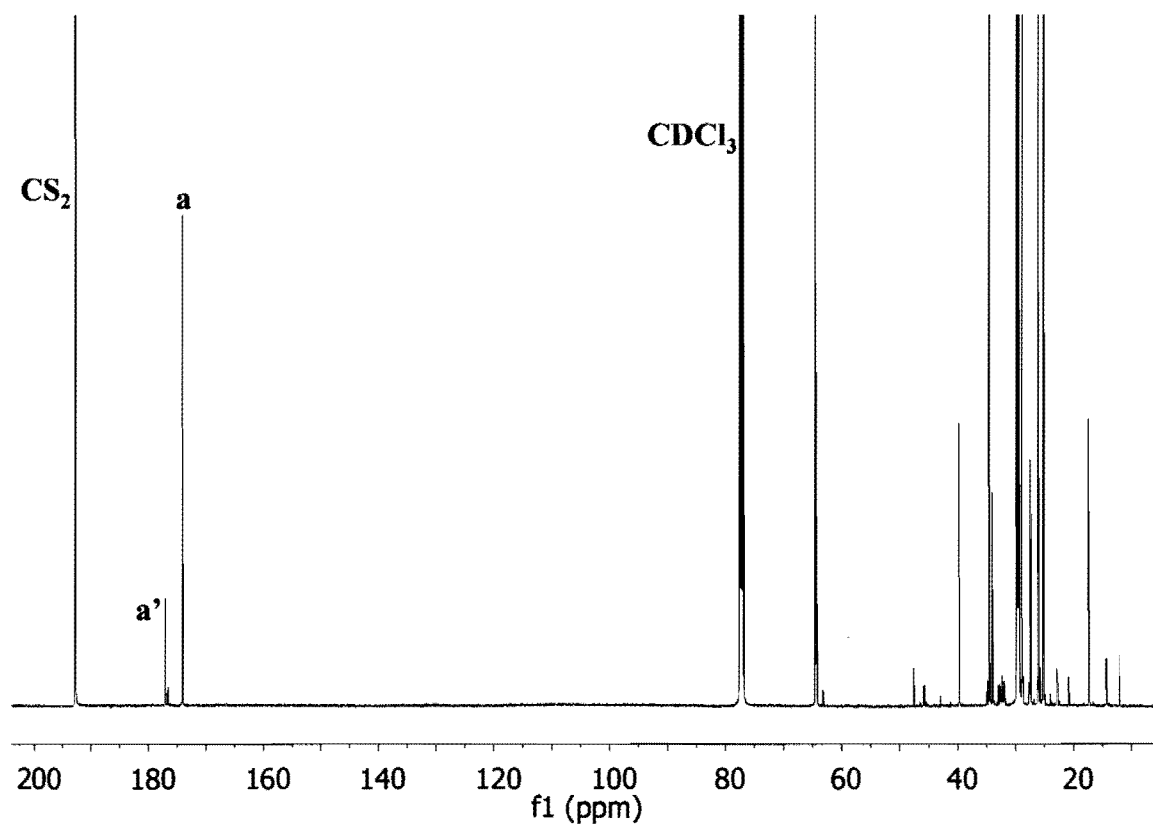


Figure S2. ^{13}C NMR spectrum of a typical polyester.

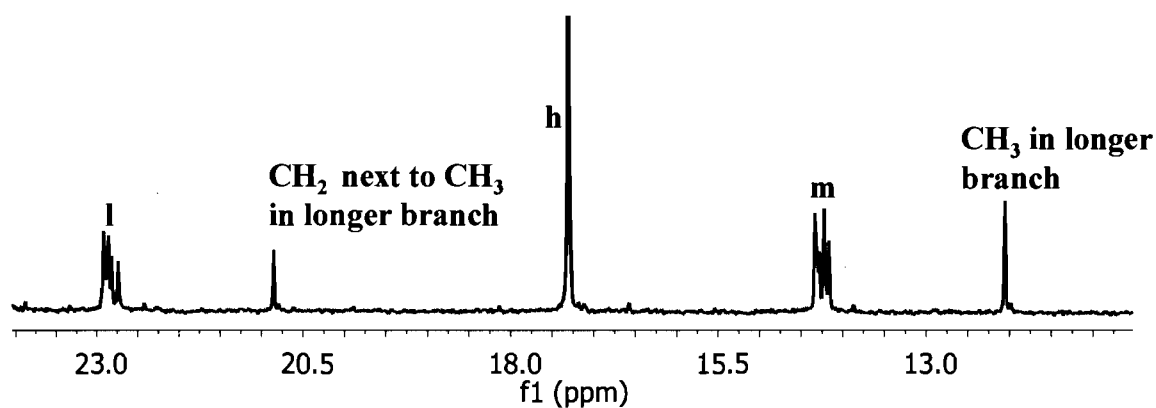
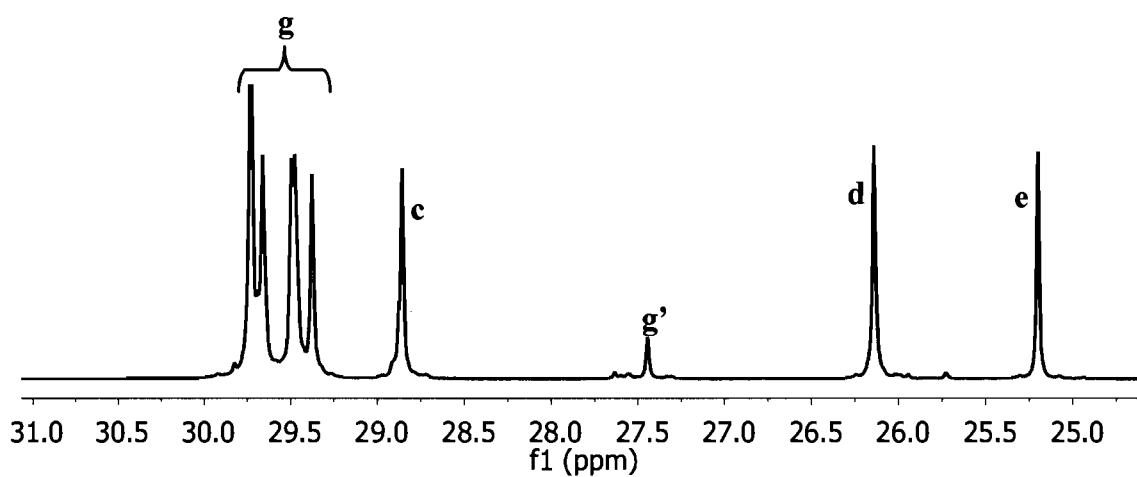
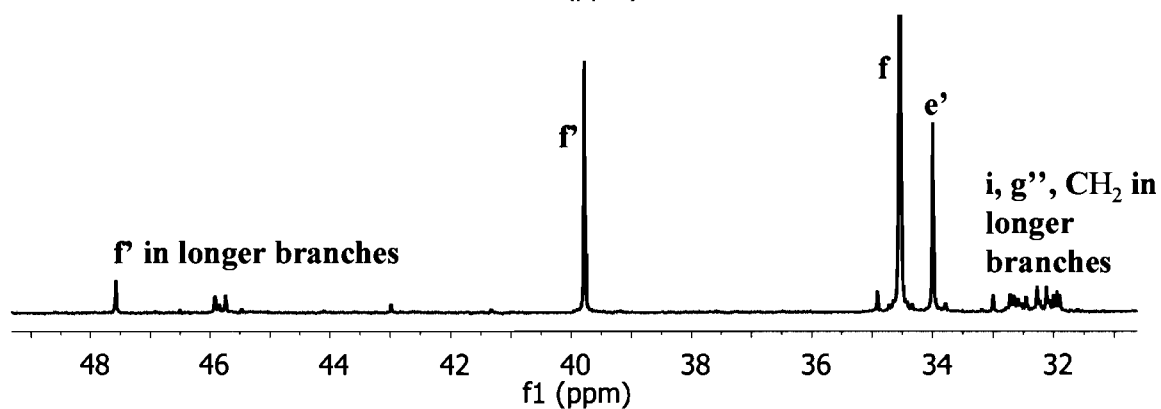
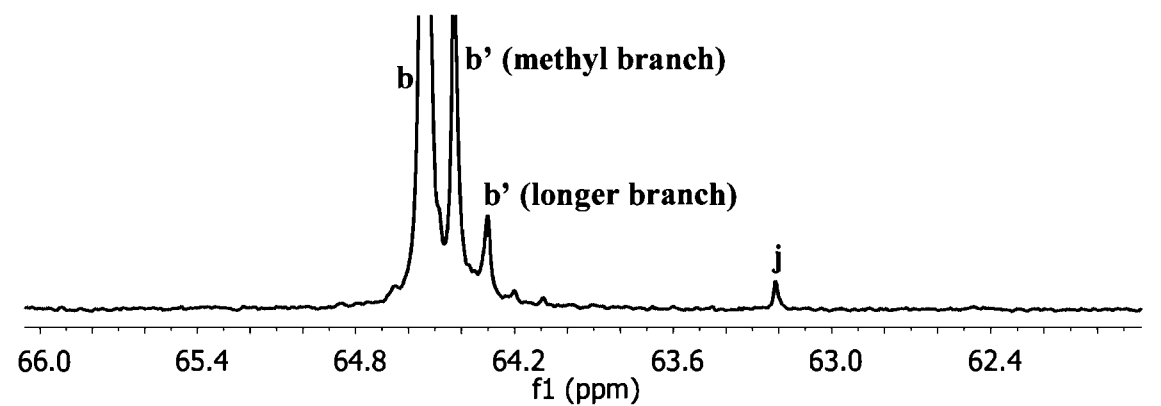


Figure S3. Details of ^{13}C NMR spectrum of a typical polyester.