Electronic Supplementary Information

Bio-based, Random Terpolymers with Defined Functionality Based on Poly(limonene carbonate-*ran*-menth-1-ene carbonate)

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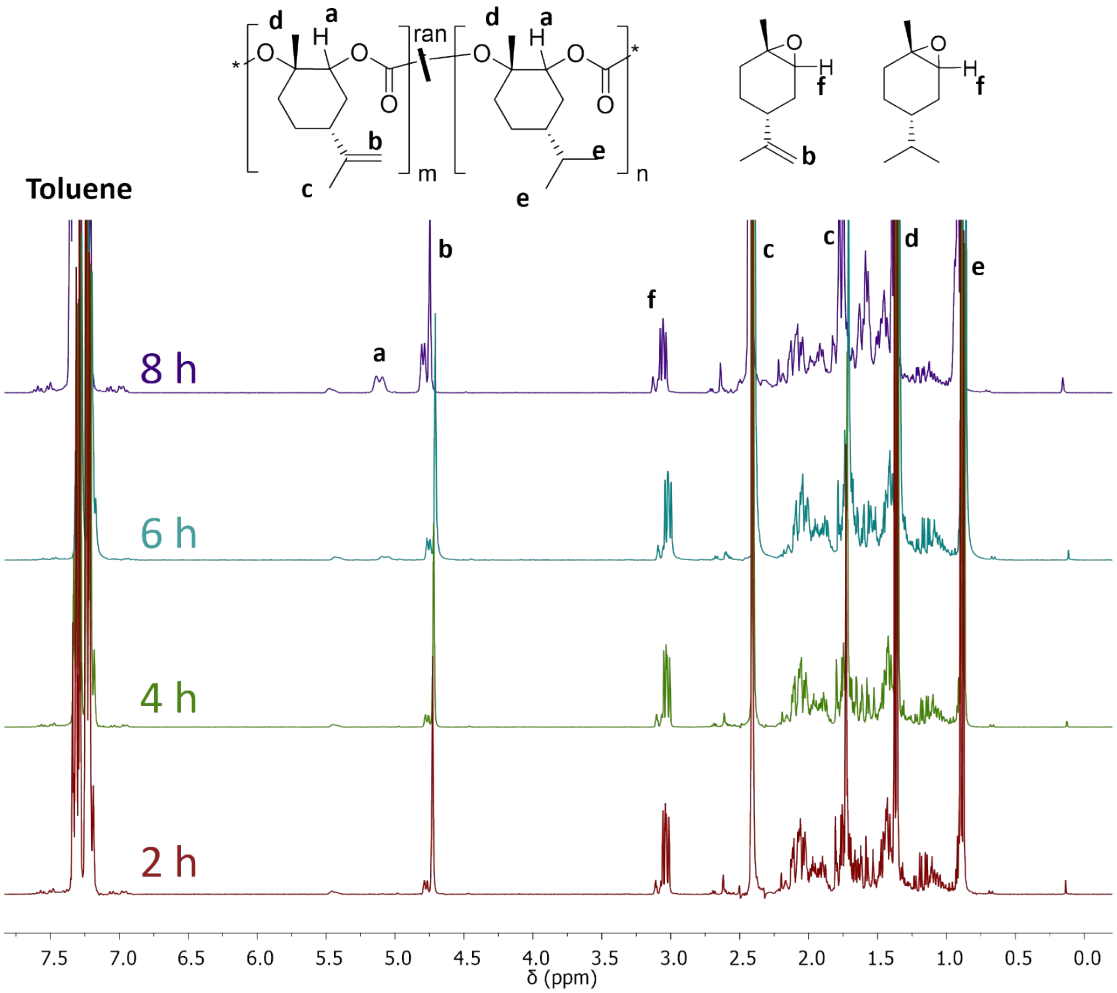

Fig. S1 ^{1}H NMR spectra for determining monomer conversion during terpolymerization of LimO, Men1O and CO_2 at various reaction times. The integral of the proton signal **f** at 3.0ppm is divided by the sum of the integrals of **f** and **a**. The result is then subtracted from 100%.

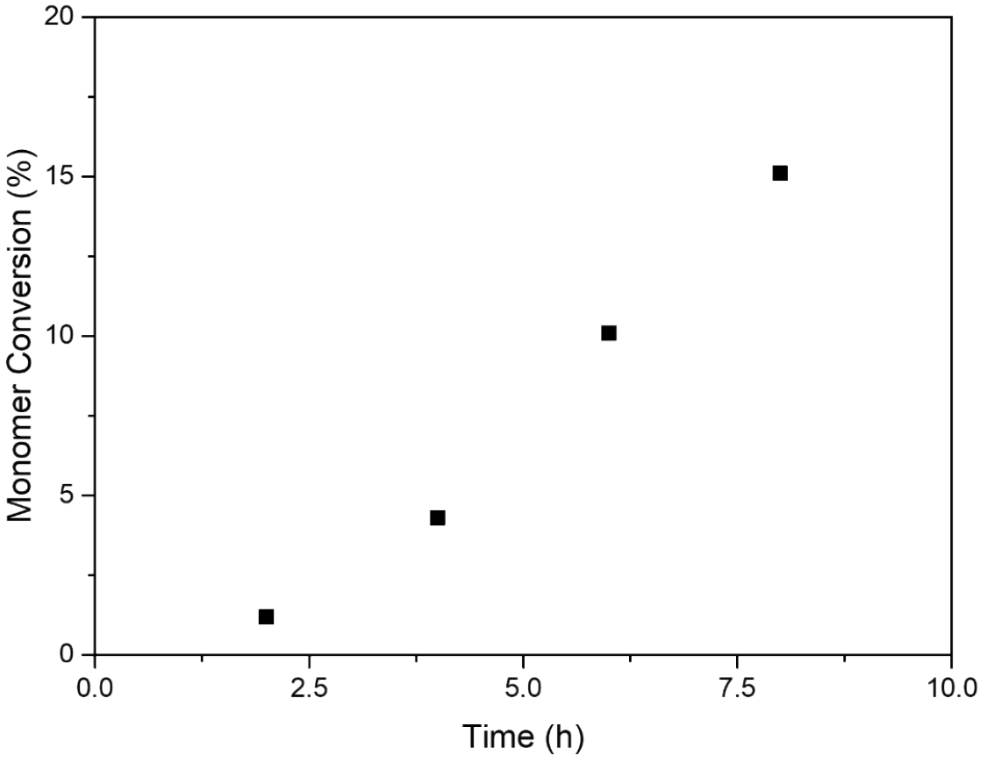

Fig. S2 Kinetics of the terpolymerization of LimO, Men1O and CO_2 with equimolar amounts of LimO and Men1O at room temperature. 10% conversion was reached after 6 h. A short lag time might occur due to CO_2 needing time to dissolve into the reaction mixture.

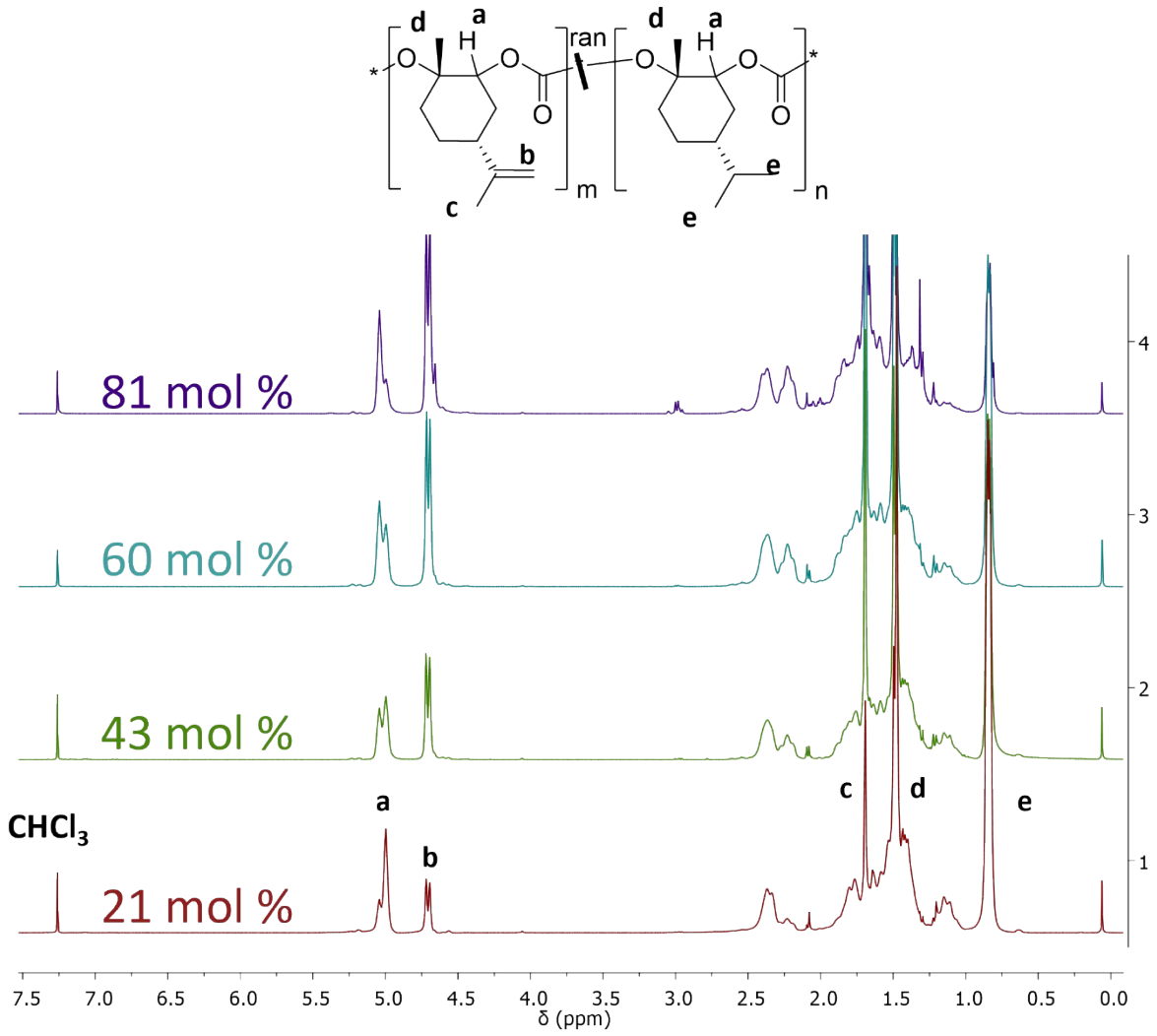

Fig. S3 ^{1}H NMR spectra of P(LimC-*ran*-Men1C) terpolymers with varying LimC content in $CDCl_3$.

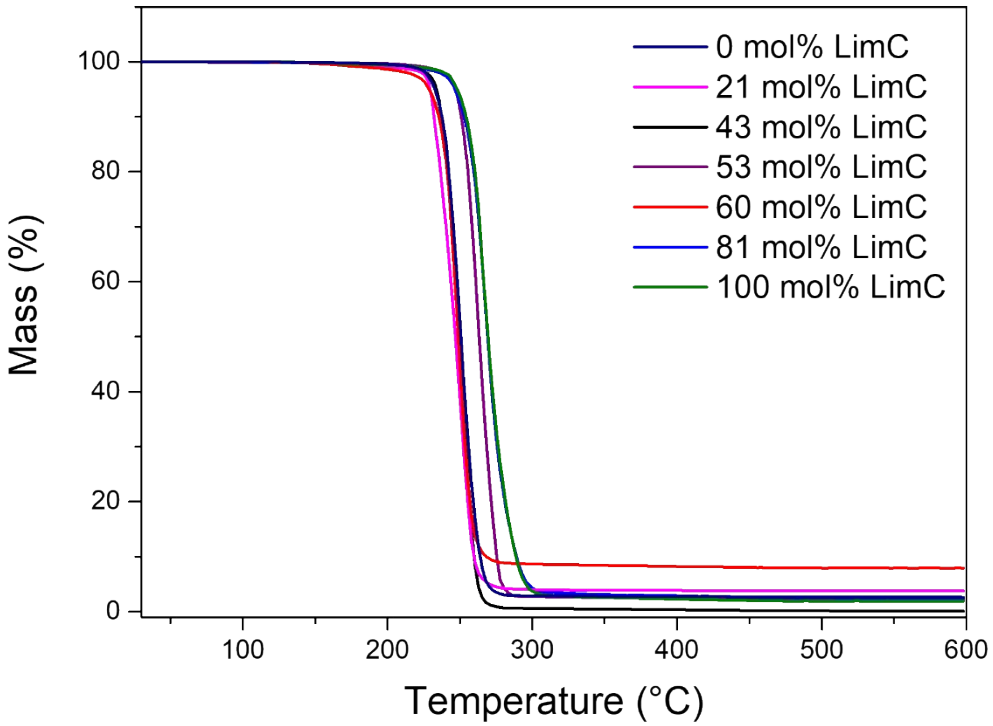

Fig. S4. Thermogravimetric analysis (TGA) of P(LimC-*ran*-Men1C) terpolymers with varying LimC content (N_2, heating rate 10 K min^{-1}).

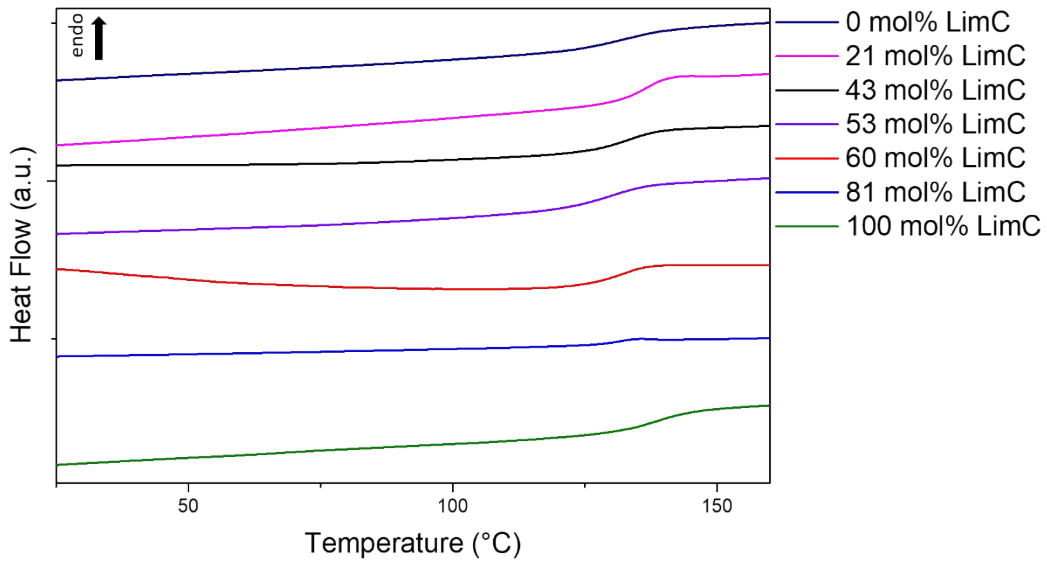

Fig. S5 Differential scanning calorimetry (DSC) analysis of P(LimC-*ran*-Men1C) terpolymers with varying LimC content (heating rate 40 K min^{-1}, second heating traces). The DSC traces were shifted vertically for means of clarity.

Non-linear least square (NLLS) method

The copolymer equation of Mayo and Lewis, that gives the composition of a copolymer formed in dependence of the monomer concentrations in the feed, can be written as follows with $f = \frac{m_1}{m_2}$ and $F = \frac{[M_1]}{[M_2]}$. [M_1] and [M_2] are the monomer concentrations in solution and m_1/m_2 is the molar ratio of the monomer units in the copolymer:

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (1)$$

With $f_2 = (1 - f_1)$:

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2 f_1(1 - f_1) + r_2(1 - f_1)^2} \quad (2)$$

This is then used to fit the plotted values of f_1 and F_1. The reactivity ratios, r, were then taken from the fitting results.

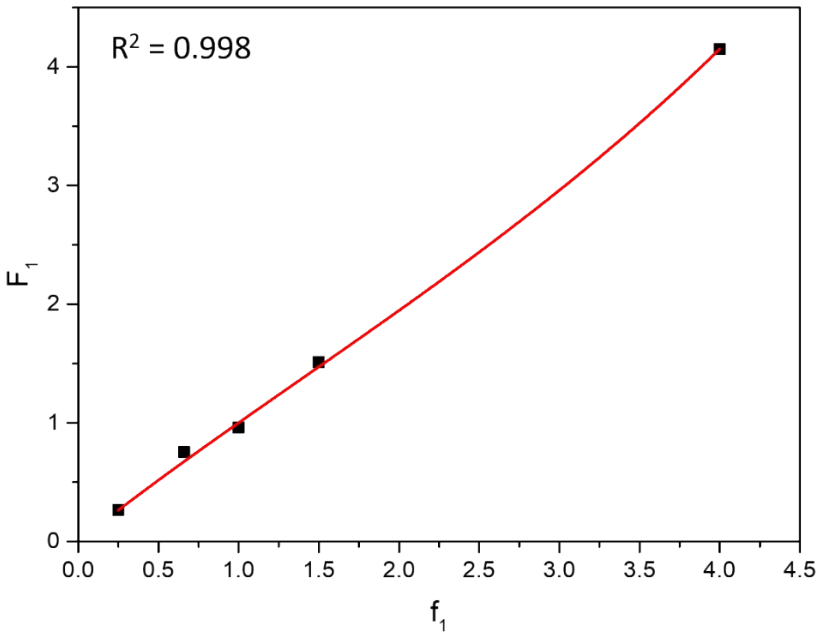

Fig. S6 NLLS plot for the terpolymerization of LimO (M_1) and Men1O (M_2) with CO_2.

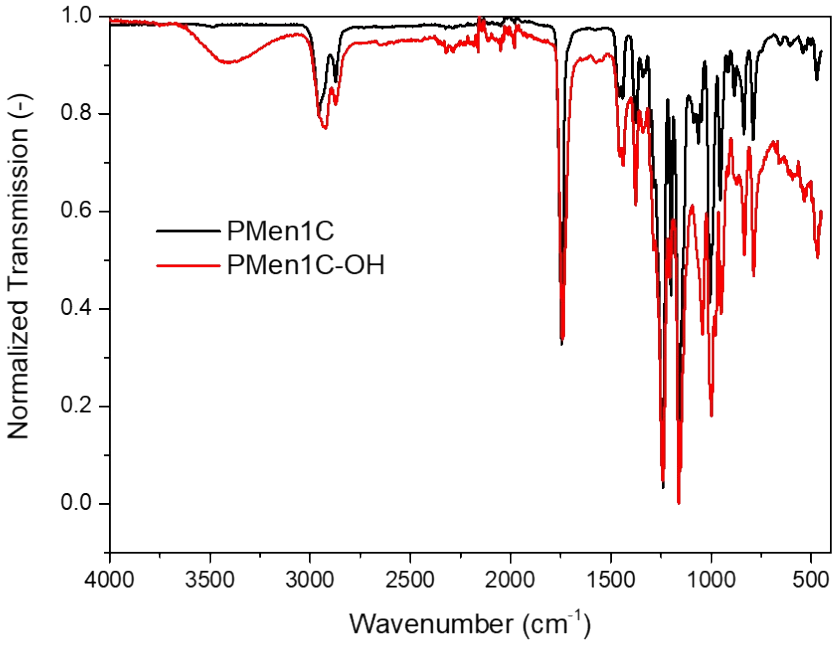

Fig. S7. ATR FT-IR spectra of PMen1C compared to 100% OH-functionalized PMen1C-OH. The O-H stretching vibration is clearly visible at 3400 cm^{-1}.