

# Unique base-initiated depolymerization of limonene-based polycarbonates

Chunliang Li,<sup>†,‡</sup> Rafaël J. Sablong,<sup>\*,§,†</sup> Rolf A.T.M. van Benthem<sup>†,⊥</sup> and Cor E. Koning<sup>†,⊥</sup>

<sup>†</sup>Laboratory of Physical Chemistry, Eindhoven University of Technology P.O. Box 513, 5600 MB Eindhoven, The Netherlands

<sup>‡</sup>Dutch Polymer Institute DPI, P.O. Box 902, 5600 AX Eindhoven, The Netherlands

<sup>§</sup>Polymer Technology Group Eindhoven B.V. (PTG/e B.V.) P.O. Box 6284, 5600 HG Eindhoven, The Netherlands

// DSM Coating Resins Ceintuurbaan 5, 8022 AW Zwolle, The Netherlands

⊥ DSM Ahead BV Urmonderbaan 22, 6167 RG Geleen, The Netherlands

## 1. General methods and considerations

All reactions involving air- or water-sensitive compounds were carried out under dry nitrogen using MBraun glove boxes or standard Schlenk line techniques. NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C in chloroform-d<sub>1</sub> and referenced versus the residual solvent shift.

Size Exclusion Chromatography (SEC) analyses were carried out at 40 °C using a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector, a Waters 2487 dual absorbance detector, and a PSS SDV 5 m guard column followed by two PSS SDV linearXL columns in series of 5 m (8 × 300). THF with 1% v/v acetic acid was used as eluent at a flow rate of 1.0 mL·min<sup>-1</sup>. The columns were calibrated using a series of polystyrene standards (Polymer Laboratories,  $M_p$  = 580 Da up to  $7.1 \times 10^6$  Da). Before analysis, the samples were filtered through a 0.2 µm PTFE filter (13 mm, PP housing, Alltech).

Fourier transform infrared spectroscopy (FTIR) was performed on a Varian FT-IR 3100 spectrophotometer equipped with a heat-controlled, single-reflection (ATR: attenuated total reflection) accessory unit (Golden Gate). All the IR measurements were performed in the reflection mode in a resolution of 4 cm<sup>-1</sup>.

## 2. Materials

Toluene, tetrahydrofuran (THF), dichloromethane (DCM) and diethyl ether were purchased from Biosolve and purified using an activated alumina purification system. *R*-Limonene dioxide (98 % purity, GC) was purchased from Rheinmetall Nitrochemie, distilled from calcium hydride (CaH<sub>2</sub>) and stored under nitrogen. *cis/trans-R*-Limonene 1,2-monoxide (98% purity) was purchased from Aldrich and distilled from CaH<sub>2</sub>. Carbon dioxide (99.999% purity) from Linde Gas was used without further purification. 1,2-Epoxy-1-methylcyclohexane (> 95% purity) was purchased from TCI Europe and distilled from CaH<sub>2</sub>. All the other chemicals were obtained from Aldrich and used as received. OH-terminated poly(limonene carbonate) (PLC), poly(limonene-8,9-oxide carbonate) (PLOC), poly(1-methylcyclohexene carbonate) (PMCHC) and *R*-limonene carbonate were synthesized according to published procedures.<sup>[1-5]</sup>

### 3. Experimental Section

**Base-initiated depolymerization of PLC.** In a nitrogen-filled glovebox, PLC (100 mg, 0.51 mmol carbonate repeat units) and TBD (0.02 mmol) were dissolved in 1 mL of toluene. The solution was transferred into a closed vial (10 mL) and placed in an oil bath heated to 110 °C. The reaction was monitored by  $^1\text{H}$  NMR. The yields were determined by comparison of the integrals of signals arising from the protons in  $^1\text{H}$  NMR spectra, including poly(limonene carbonate) ( $\delta$  5.0-5.1 ppm, 1H), *trans*-limonene oxide ( $\delta$  2.99 ppm, d, 1H) and *cis*-limonene oxide ( $\delta$  3.03 ppm, s, 1H).

**Preparation of acetate end-capped PLC.** Triethylamine (0.3 mL, 2 mmol) and hydroxyl-ended PLC (400 mg) were dissolved in 5 mL of anhydrous THF. Acetyl chloride (0.1 mL, 1.4 mmol) was added dropwise to the stirred THF solution at 0 °C. The THF solution of the copolymer was allowed to warm to ambient temperature overnight. The ammonium salt was removed by filtration through silica gel, and the filtrate was concentrated. The acetate end-capped PLC was precipitated in methanol, isolated by filtration, and dried under reduced pressure.

**Attempted depolymerization of acetate end-capped PLC.** Acetate end-capped PLC (carbonate repeating units = 0.51 mmol) and TBD (0.02 mmol) were dissolved in 1 mL of toluene in a nitrogen-filled glovebox and transferred into a closed vial (10 mL). The vial was heated to 110 °C. The reaction was monitored by  $^1\text{H}$  NMR.

### 4. NMR spectra of the initial polymers and depolymerization products

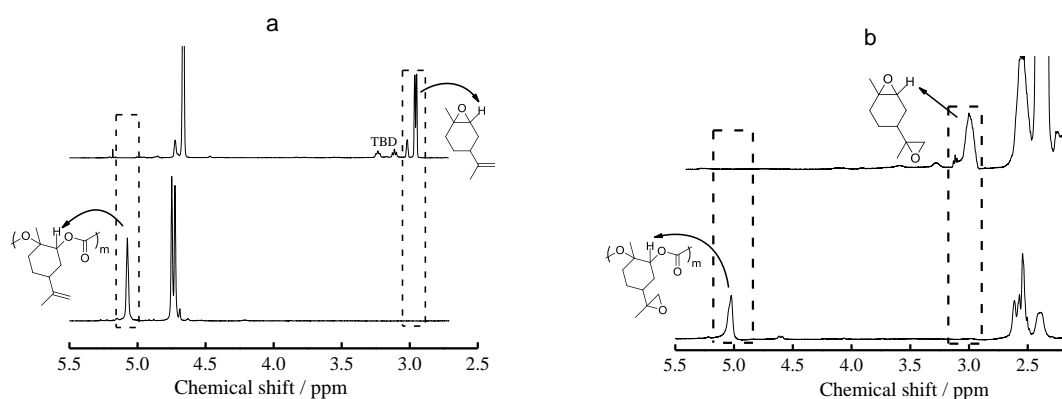


Figure S1.  $^1\text{H}$  NMR spectra of the depolymerization products and initial limonene-based polymers (a: poly(limonene carbonate) (PLC); b: poly(limonene-8,9-oxide carbonate) (PLOC)).

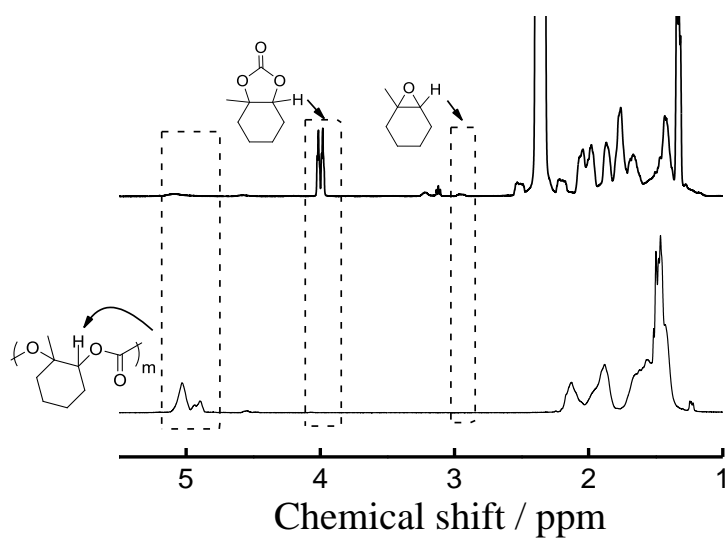


Figure S2.  $^1\text{H}$  NMR spectra of the depolymerization products and initial poly(1-methycyclohexene carbonate) (PMCHC).

## 5. SEC traces of the depolymerization products

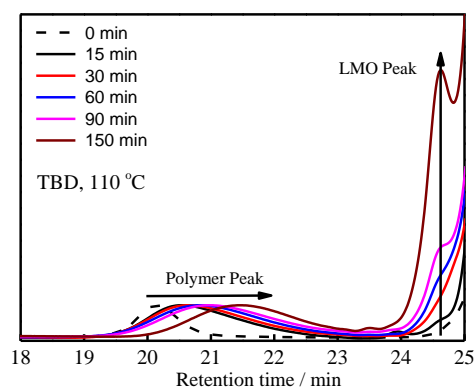


Figure S3. SEC traces of the reaction mixture at different times during the depolymerization of PLC.

## 6. FTIR analysis

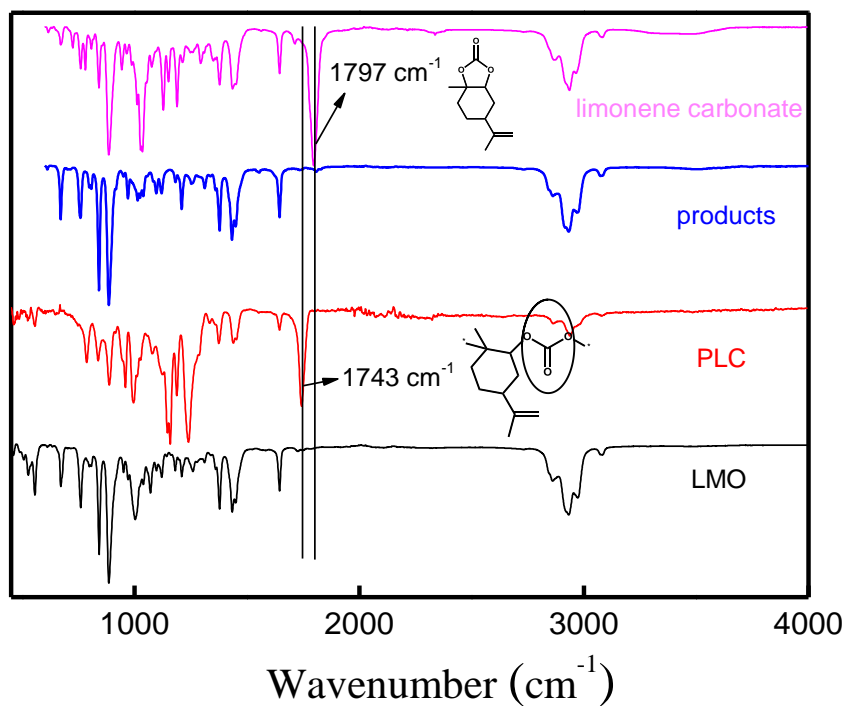


Figure S4. FT-IR spectra of initial poly(limonene carbonate) (PLC), limonene carbonate, limonene 1,2-monoxide (LMO) and the reaction products of PLC depolymerization.

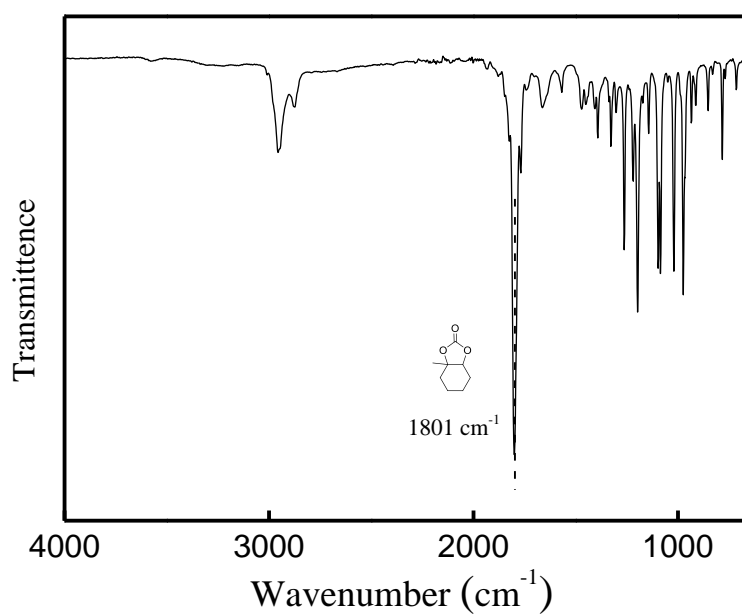


Figure S5. FT-IR spectrum of the depolymerization products of poly(1-methylcyclohexene carbonate) (PMCHC).

## 7. GC-MS analysis

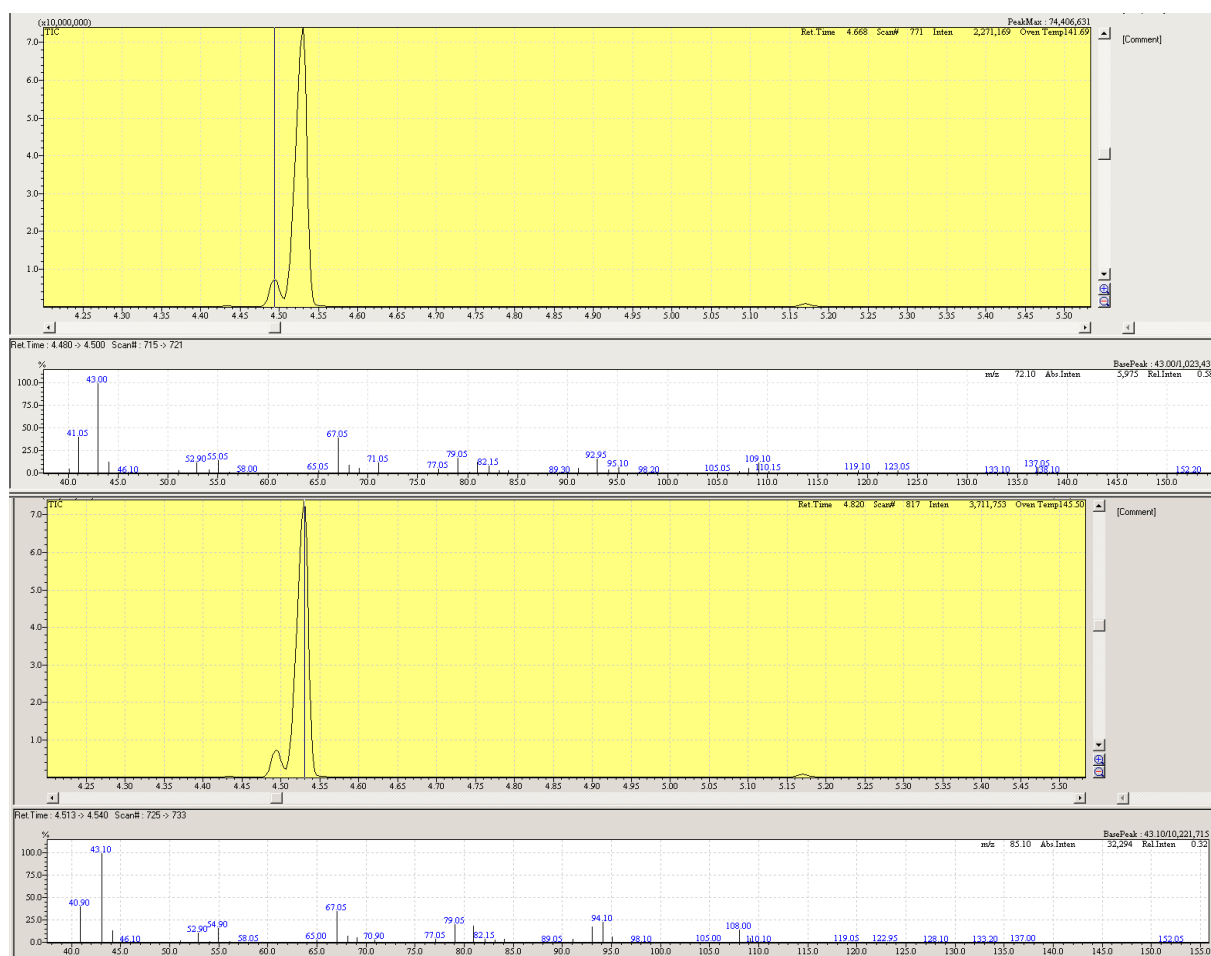


Figure S6. GC-MS analysis of the reaction products of PLC depolymerization.

## 8. References

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