

ARTICLE

Light-Mediated Curing of CO₂-Based Unsaturated Polyethercarbonates *via* Thiol-ene Click Chemistry

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Experimental

Materials

All reagents were purchased from commercial suppliers and used as received.

Double metal cyanide catalyst

The double metal cyanide (DMC) catalyst based on zinc hexacyanocobaltate was prepared according to the procedure of example 6 in patent WO-A 01/80994. A solution of zinc chloride (6.485 kg) in distilled water (23.9 kg) and tert-butanol (3.4 kg) was circulated at 50°C in a loop reactor. A solution of potassium hexacyanocobaltate (0.65 kg) in distilled water (8.0 kg) was metered into the reactor. Directly thereafter a mixture of tert-butanol (0.144 kg), polypropylene glycol 1000 (0.685 kg) and distilled water (6.5 kg) was metered in. The dispersion was circulated for 90 min. Part of the dispersion (58 kg) was filtered in a membrane filter press. A scrubbing solution (65 wt % tert-butanol, 33.7 wt% water, 1.3 wt% polypropyleneglycol 1000, 44 kg) was applied. After drying for 5.5 hours under reduced pressure the filter cake had a residual moisture content of around 3%.

NMR spectroscopy

A Bruker AV III (¹H, 500 MHz) and a Bruker AV II (¹H, 500 MHz) were used to record the ¹H NMR and ¹³C NMR spectra. Chemical shifts are referenced to tetramethylsilane (TMS). The deuterated solvents were used as obtained from suppliers.

Infrared spectroscopy

FT-IR spectra were recorded on a Bruker Alpha-P FT-IR Spectrometer (Bruker Optics) equipped with a diamond probe. All samples were scanned 24 times with a resolution of 4 cm⁻¹. The data were collected in the range of 4000 to 400 cm⁻¹ and evaluated by means of OPUS 7.0 (Bruker Optics) software. A background spectrum was recorded before every measurement.

Gel permeation chromatography

The number-average and weight-average molecular weight (M_n and M_w, respectively) of the unsaturated polyethercarbonates were determined by gel permeation chromatography (GPC). The procedure was in accordance with DIN 55672-1: "Gel permeation chromatography, Part 1 - Tetrahydrofuran as the eluting agent" (SECurity GPC System from PSS Polymer Service, flow rate 1.0 ml min⁻¹; columns: 2×PSS SDV linear M, 8×300 mm, 5 μm; RID detector). Polystyrene samples of known molecular weight were used for calibration, and the chromatogram was referenced against the absolute mass determined by mass spectroscopy. The polydispersity index (PDI) was calculated as the ratio of M_w to M_n.

Rheology

The rheological analysis of polymers was performed on a Parr Rheometer MCR501 equipped with an Omnicure Series 1000 UV source (Mercury lamp = 100 watt, Filter = 320-500 nm). A plate-plate measuring system (15 mm diameter) was used to measure the sol-gel points under constant strain (10%) and frequency (1 Hz).

Differential scanning calorimetry

The glass transition point (T_g) was determined by DSC. The phase behaviour was characterized by a Perkin-Elmer Pyris 6 differential scanning calorimeter. A sample of the polymer (about 10 mg) was placed into the sample holder, which was put into a flow of argon; the temperature was adjusted to 25°C. The sample was then heated to 100°C at 20°C·min⁻¹, kept at 100°C for 10 min, cooled to -80°C (-10°C·min⁻¹) and kept at that temperature for 10 min. The sample was heated three times to 100°C at a rate of 10°C·min⁻¹, kept at 100°C for 2 min, cooled to -80°C (-10°C·min⁻¹) and then kept at that temperature for 2 min. The glass transition temperature or the melting point is given as the inflection point of the heat flow curve in the third heating cycle.

Thermal gravimetric analysis

TGA traces were recorded on a Mettler Toledo Gas Controller GC20 with STRe System. A sample of the polymer (about 30 mg) was put into the sample holder, which was kept in a flow of argon; the temperature was adjusted to 25°C. The sample was then heated to 600°C at a rate of 10°C·min⁻¹.

Procedure for the terpolymerization of CO₂ with propylene oxide and allylglycidylether (1a-c)

A high-pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω -dihydroxy polypropylene oxide (1000 g·mol⁻¹, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 130°C. The reactor was then pressurized with carbon dioxide to 15 bar. The pressure was kept at 15 bar by an incoming flow of CO₂. A mixture of allylglycidylether and propylene oxide (**1a** = 7/93 wt%; **1b** = 15/85 wt%; **1c** = 30/70 wt%) was added in three pulses of 2.0 g (1 mL·min⁻¹) each, and the mixture was stirred for 20 minutes after each pulse. The temperature was adjusted to 100°C. After the temperature and pressure were stable for at least five minutes, 54 g (1 mL·min⁻¹) of allylglycidylether and propylene oxide mixture (**1a** = 7/93 wt%; **1b** = 15/85 wt%; **1c** = 30/70 wt%) were added. After adding all the monomers, the mixture was stirred for another 60 min, cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator. The composition of the unsaturated polyethercarbonate obtained was analyzed.¹

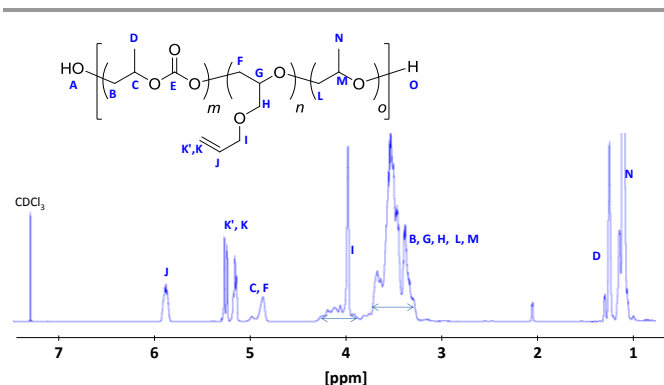


Figure S1. ¹H-NMR spectrum of polyethercarbonate **1c** after passing the sample through a thin-film evaporator and assignment of the signals. The spectrum is representative of the series of unsaturated polyethercarbonates.

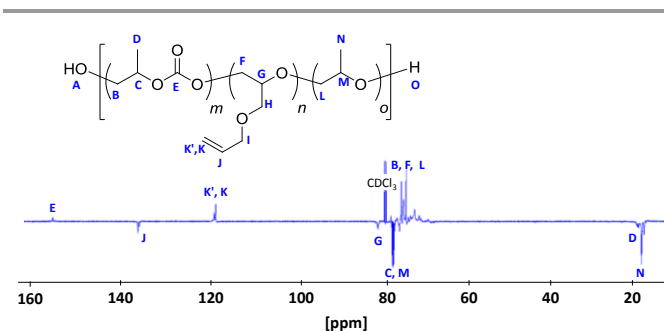


Figure S2. ¹³C-NMR spectrum of unsaturated polyethercarbonate **1c** and assignment of the signals

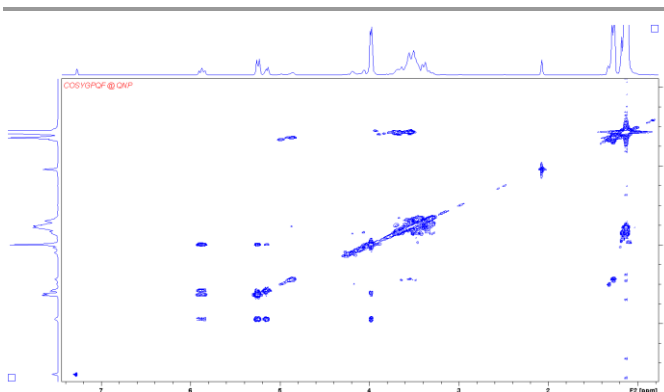


Figure S3. ¹H-¹H COSY NMR spectrum of unsaturated polyethercarbonate **1c**

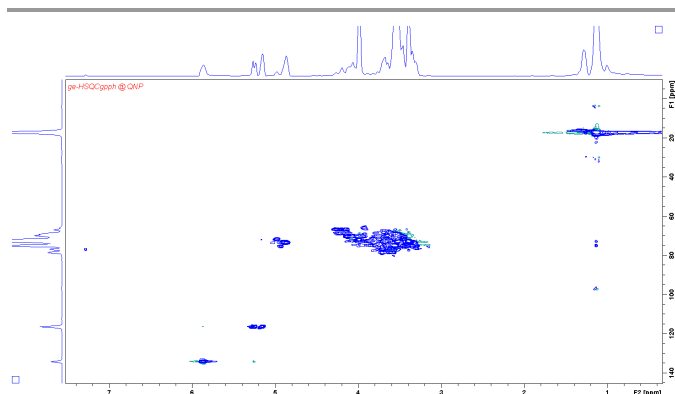


Figure S4. HSQC NMR spectrum of unsaturated polyethercarbonate **1c**

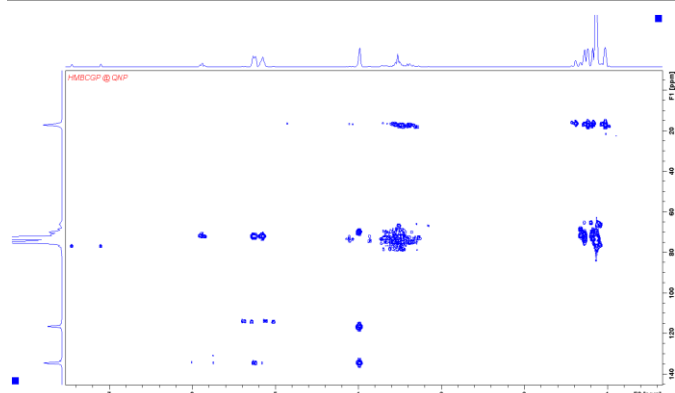


Figure S5. HMBC NMR spectrum of unsaturated polyethercarbonate **1c**

Procedure for curing the mixture of unsaturated polyethercarbonate and polymercaptane

A mixture of unsaturated polyethercarbonate (3.0 g) and pentaerythritol tetrakis(3-mercaptopropionate) (PTM, 1 mol thiol groups per allyl group) was prepared on an aluminium plate. Bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (0.01 wt%) was added to the mixture, which was mixed thoroughly. The polymer mixture (0.4 g) was placed on the rheometer plate and irradiated with UV light ($I_{UV} = 22.5 \text{ W/cm}^2$) for 120 s, if not stated otherwise.

Procedure for the copolymerization of CO_2 with allylglycidylether

A high-pressure reactor (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16 mg) and α,ω -dihydroxy polypropylene oxide (1000 $\text{g}\cdot\text{mol}^{-1}$, 20.0 g). The reactor was closed, the mixture stirred at 800 rpm, purged with argon and heated to 130°C. The reactor was then pressurized with carbon dioxide to 15 bar. The pressure was kept at 15 bar by an incoming flow of CO_2 . Allylglycidylether was added in three pulses of 2.0 g (1 $\text{mL}\cdot\text{min}^{-1}$) each, and the mixture was stirred for 20 minutes after each pulse. The

temperature was adjusted to 100°C. After the temperature and pressure were stable for at least five minutes, allylglycidylether (14 g, 1 $\text{mL}\cdot\text{min}^{-1}$) was added into the reactor. After completion of allylglycidylether addition, the mixture was stirred for another 60 min, cooled to room temperature, the excess pressure released, the liquid phase collected and the volatiles removed in a thin film evaporator.

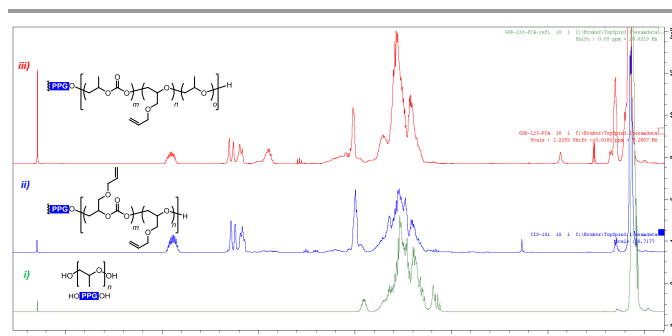


Figure S6. Comparative analysis of the ^1H -NMR spectra of α,ω -dihydroxy polypropylene oxide (i, green, bottom), a copolymer of AGE and CO_2 (**1d**, ii, blue, middle), and a terpolymer of PO, AGE and CO_2 (**1c**, iii, red, top).

References

1. E. Lindner, M. Henes, W. Wielandt, K. Eichele, M. Steimann, G. A. Luinstra and H.-H. Goertz, *J. Organomet. Chem.*, 2003, **681**, 12-23.