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ARTICLE TYPE

Carbon dioxide as sustainable feedstock for polyurethane production

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Experimental Section

Materials

All chemicals were obtained from commercial suppliers and used as received, if not stated otherwise. Propylene oxide (99%) was obtained from Sigma-Aldrich.

Methods

The solubility of CO_2 was determined by a volumetric method. The polyol (50 cm^3) was placed into a high-pressure vessel (156.9 cm^3), stirred at 500 rpm and the entire vessel was heated to 90°C. A gas mouse (59.3 cm^3) was pressurized with CO_2 (5 bar) and equilibrated until the temperature was constant. Subsequently, the valve between the high-pressure vessel and gas mouse was opened, and the system was equilibrated until the temperature in both vessels was constant. Pressure and temperatures were recorded, the valve was closed, the gas mouse was again pressurized with CO_2 (several times to 5 bar, thereafter to 10, 15 and 20 bar, respectively), and the procedure repeated.

The composition of the reaction mixture during PO/CO_2 co-polymerization was followed with a Bruker MATRIX-MF spectrometer equipped with a high-pressure 3.17 mm attenuated total reflectance (ATR) IR fibre optical probe. The ATR IR fibre optical probe (90° diamond prism with 1 × 2 mm basal area and 1 mm height as ATR element, 2 × 45° reflection of the IR beam, IR beam coupled *via* fibre optics) was fitted into the reactor in such a way that the diamond at the end of the optical probe was immersed entirely into the reaction mixture. IR spectra (average of 100 scans) were recorded time-resolved in the region of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

The spectra were analysed with the software PEAXACT 3.0.7 using the Indirect Hard Modelling (IHM) method. From *in-situ* IR spectra of pure components, a hard model describing the spectrum of the mixture was built and calibrated with binary mixtures of known composition. Then, the hard model was fitted to time-resolved IR spectra recorded during the catalytic reaction. By this procedure, component weights were derived, which were converted to concentrations in mol% on basis of the calibration.[S1,2]

The composition of the reaction mixture was analysed by ^{1}H-NMR spectroscopy. The sample was dissolved in deuterated chloroform and measured on a Bruker spectrometer (AV400, 400 MHz). The relevant resonances in the ^{1}H-NMR spectra (based on TMS = 0 ppm) used for integration were: 1.11 – 1.17 (methyl group of the polyether moieties, area of the resonance corresponds to three H atoms), 1.25 – 1.32 (methyl group of the polycarbonate moieties, area of the resonance corresponds to three H atoms), 1.45 – 1.49 (methyl group of cPC, area of the resonance corresponds to three H atoms) and 2.95 – 2.99 (CH group of propylene oxide, area of the resonance corresponds to one H atom). Taking into account the intensities, the relative concentrations were calculated.

The number- and weight-average molecular weight (M_n and M_w, respectively) of the obtained polyethercarbonate polyols 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 PDI was calculated as the ratio of M_w to M_n.

Mass spectra were obtained on a Thermo Fischer LTQ Orbitrap XL spectrometer using methanol as solvent.

The phase behaviour was characterized by using a Perkin-Elmer Pyris 6 differential scanning calorimeter. A sample of the polymer (*ca*. 10 mg) was placed into the sample holder. The latter was placed into a flow of argon, and the temperature was adjusted to 25°C. Then, the sample was heated to 100°C at 20°C·min^{-1}, held at 100°C for 10 min, cooled to -80°C (-10°C·min^{-1}) and held there for 10 min. Then, 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 held at this 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.

The TGA traces were recorded on a Mettler Toledo Gas Controller GC20 with STRe System. A sample of the polymer (*ca*. 30 mg) was placed into the sample holder. The latter was placed into a flow of argon, and the temperature was adjusted to 25°C. Then, the sample was heated to 600°C at a rate of 10°C·min^{-1}. For reference, the TGA traces of polypropylene oxide (1000 g·mol^{-1}, F = 2) and polypropylene carbonate (fully alternating, Novomer) were recorded under the same conditions.

The scanning electron microscopy image was taken on a FEI/Philips XL30 ESEM at an acceleration voltage of 10 kV and a magnification of 28×.

Kinetic profiles

For recording the kinetics of the reaction, an autoclave (300 mL, Parr Instrument) equipped with a gas entrainment stirrer and an ATR IR fibre optical probe was charged with DMC catalyst (15.8 mg) and the starter polyether polyol (1000 g·mol^{-1}, F = 2, 39.98 g). The autoclave was closed, and the mixture was stirred at 1200 rpm and heated to 130°C. The autoclave was purged with argon and then pressurized with carbon dioxide to 15 bar. Thereafter, the pressure was maintained at 15 bar by feeding CO_2. Propylene oxide was added in three pulses of 4.0 g each, and the mixture was stirred for 30 minutes after each pulse. A sample of the liquid phase (8.95 g) was taken. Then, the temperature was adjusted to 100°C. The autoclave was pressurized to 50 bar by feeding CO_2. After the temperature and pressure had been stable for at least 5 minutes, the valve to the CO_2 supply was closed. Propylene oxide (9.6 g) was added *via* an HPLC pump (25 mL·min^{-1}). The mixture was stirred for 90 min during which IR spectra were recorded. Thereafter, a sample of the liquid phase (9.31 g) was taken, and the pressure was re-adjusted to 50 bar. Another two pulses of propylene oxide (9.52 g and 9.06 g) were added to the reaction mixture, and the same procedure was repeated as described above. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released and the liquid phase collected. The composition of the samples taken during the reaction and the final reaction mixture was analysed using ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC).

For preparing a reference sample at a lower pressure (15 bar), an autoclave (300 mL, Parr Instrument) equipped with a gas entrainment stirrer and an ATR IR fibre optical probe was charged with DMC catalyst (16.4 mg) and the starter polyether polyol (1000 g·mol^{-1}, F = 2, 40.1 g). The autoclave was closed, and the mixture was stirred at 1200 rpm and heated to 130°C. The autoclave was purged with argon and then pressurized with carbon dioxide to 15 bar. Thereafter, the pressure was maintained at 15 bar by feeding CO_2. Propylene oxide was added in three pulses of 4.0 g each, and the mixture was stirred for 30 minutes after each pulse. A sample of the liquid phase (9.2 g) was taken. Then, the temperature was adjusted to 100°C. After the temperature and pressure had been stable for at least 5 minutes, the valve to the CO_2 supply was closed. Propylene oxide (9.2 g) was added *via* an HPLC pump (25 mL·min^{-1}). The mixture was stirred for 90 min during which IR spectra were recorded. Thereafter, a sample of the liquid phase (9.2 g) was taken, and the pressure was re-adjusted to 15 bar. Another two pulses of propylene oxide (9.2 g each) were added to the reaction mixture, and the same procedure was repeated as described above. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released and the liquid phase collected. The composition of the samples taken during the reaction and the final reaction mixture was analysed using ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC).

Syntheses

A 1 L STR autoclave was used for synthesizing polyethercarbonate polyols from propylene oxide and carbon dioxide by PO/CO_2 copolymerization in the presence of an alcoholic starter (with conditions and relative quantities similar to the stated comparison sample preparation below). The starter together with the DMC-based zinc hexacyanocobaltate catalyst was placed into the vessel. The reaction was started by the addition of propylene oxide with a dosing pump, while the system was kept under constant CO_2 pressure (15-100 bar) and at constant temperature (90-140 °C). The resulting product mixture was analysed by ^{1}H-NMR spectroscopy as well as GPC chromatography.

For preparing the comparison sample with a CO_2-content of 7.1 wt.%, an autoclave (300 mL, Parr Instrument) equipped with a gas entrainment stirrer was charged with DMC catalyst (16.5 mg) and starter polyether polyol (1000 g·mol^{-1}, F = 2, 40.0 g). The autoclave was closed, and the mixture was stirred at 1200 rpm and heated to 130°C. The autoclave was purged with argon and then pressurized with carbon dioxide to 15 bar. Thereafter, the pressure was maintained at 15 bar by feeding carbon dioxide. Propylene oxide (12.1 g) was added in three pulses, and the mixture stirred for 30 minutes after each pulse. Then, the temperature was adjusted to 100°C. Propylene oxide was added (28.1 g) at a flow rate of 1 mL·min^{-1} *via* an HPLC pump. Thereafter, the mixture was stirred for 90 min. Subsequently, the reaction mixture was cooled to room temperature, the excess pressure released and the liquid phase collected. For removal of cPC, the reaction mixture was passed through a thin film evaporator heated to 120°C and set to a partial vacuum of 3 mbar.

The conventional PU foams were prepared from a 80:20 mixture of 2,4- and 2,6-toluene diisocyanate (Desmodur® T 80) and a propylene oxide / ethylene oxide polyether triol with an average molecular weight of 3506 g · mol^{-1} (Arcol® 1108) following a standard foaming procedure [S^3]. The CO_2-based PU foams were prepared accordingly using a polyethercarbonate triol.

Supplementary data

With increasing CO_2 pressure during synthesis in the range of 15 - 90 bar, the CO_2 incorporation into the obtained polyethercarbonate polyols increased asymptotically to right above 22 wt.% (Fig. S 1).

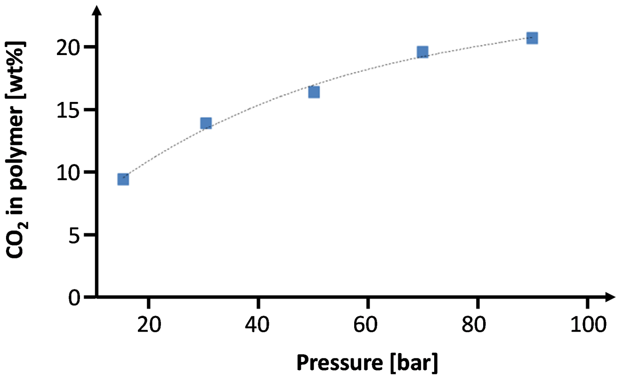

Fig. S 1 Incorporation of CO_2 into the polyethercarbonate polyol as a function of the CO_2 pressure applied during the synthesis (MW = 2000 g · mol^{-1}, reaction conditions see Syntheses)

The solubility of CO_2 in neat polyethercarbonate and polyether polyols shows a linear dependence on pressure (Fig. S 2).

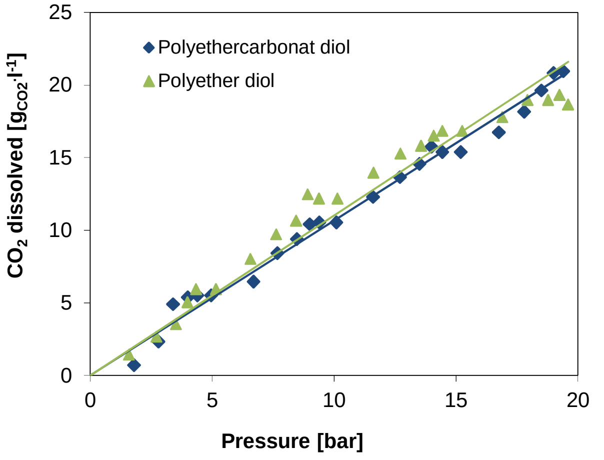

Fig. S 2 Solubility of CO_2 at 90°C in neat polyethercarbonate diol (4000 g/mol, 21.9 wt% CO_2, F = 2) in comparison to a corresponding polyether diol (polypropylene oxide, 1000 g·mol^{-1}, F = 2). Further detailed information on the phase equilibria and solubility of CO_2 and PO in polyethercarbonate polyols can be found in ref. [23].

To explore the parameter space, a pulse experiments was performed also at a lower pressure of 15 bar. Analysis of the composition of samples taken after each pulse confirms the stepwise formation of polyethercarbonate. The number of carbonate linkages increased from 3.0 mol-% for the parent polymer to 7.5, 11.3 and 13.8 % after the 1st, 2nd and 3rd pulse, respectively. The amount of cPC was very low and increased with the amount of carbonate linkages incorporated into the polymer chains (from 1.0 to 1.5, 2.0 and 2.2 mol-%, corresponding to an increase from 1.3 to 1.8, 2.6 and 3.2 wt-%, respectively, Fig. S 3).

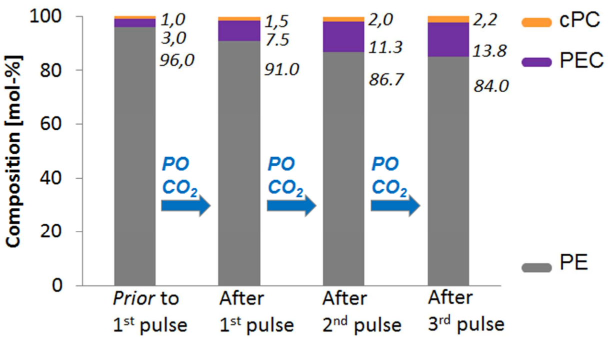

Fig. S 3 Analysis of the chemical composition of samples taken after the propylene oxide of a pulse had completely reacted.

The molecular weight (M_n) of the polymer chains increased stepwise with each pulse from 1362 for the parent polymer to 1526, 1686 and 1885 g·mol^{-1} after the 1st, 2nd and 3rd pulse, respectively (Fig. S 4). It is particularly noteworthy here that the molecular weight distribution remained very narrow, which is reflected in less than 10% increase in the polydispersity index from 1.05 for the parent polymer to 1.04, 1.06 and 1.10 after the 1st, 2nd and 3rd pulse, respectively.

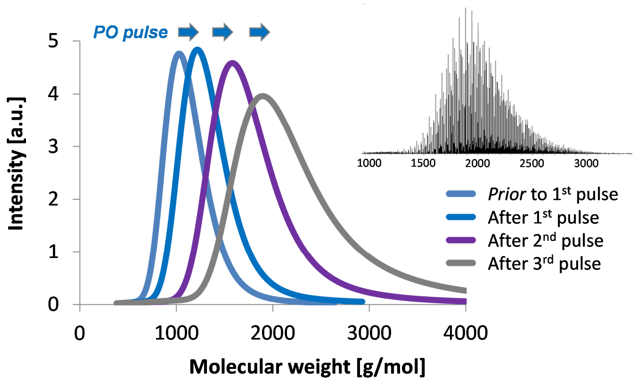

Fig. S 4 Analysis of the molecular weight distributions (GPC) of samples taken after the propylene oxide of a pulse had completely reacted.

MALDI-TOF analysis of a sample taken after the third pulse confirms the narrow molecular weight distribution of the resulting polyethercarbonate (Fig. S 5).

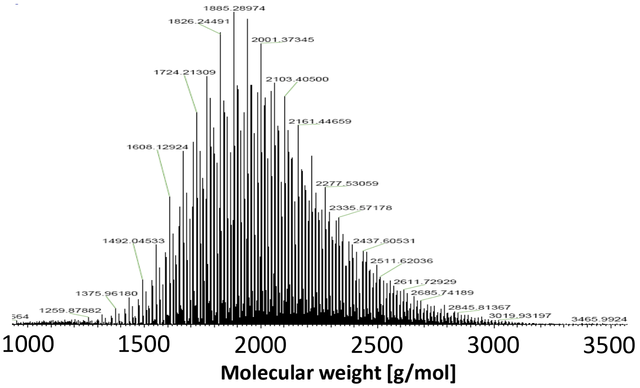

Fig. S 5 MALDI-TOF analysis of a sample taken after the 3rd pulse.

For physicochemical analysis a sample was prepared under the same conditions as used for recording the kinetics of the reaction in the pulse experiment, except that the pressure in the reactor was maintained constant at 15 bar by feeding carbon dioxide and propylene oxide was added at a constant flow rate. The cPC formed as by-product (2.2 wt.%) was removed by thin film evaporation. For the resulting polyethercarbonate diol with CO_2-content of 7.1 wt.% and a molecular weight M_n of $3155\ g{\cdot}mol^{-1}$, a glass transition temperature of -60.4°C was recorded (Fig. S 6).

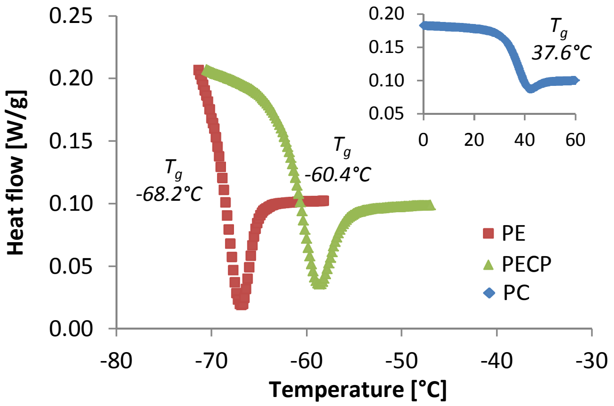

Fig. S 6 Glass transition temperature (T_g) of a polyethercarbonate polyol (PECP) with 7.1 wt.% CO_2 in comparison to polypropylene glycol as typical polyether (PE) and alternating polypropylene carbonate (PC).

Notes and references

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