

Polymer formation from CO₂ – a Dream Production

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Introduction

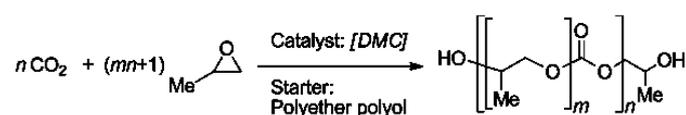
The utilisation of CO₂ as a feedstock for chemical syntheses has been envisioned by chemists for a long time. However, its chemical inertness and the high activation energy prohibited many straightforward routes to generate value-added products from CO₂ so far. Recent developments in high-performance catalysts have finally allowed the fine-tuning of process conditions under which CO₂ forms technically relevant co-polymers with epoxides. Monitoring the process allows to optimise the recipe in terms of feeding intervals, temperature profile etc. Due to the demanding process conditions – elevated pressure, gas-liquid regime – only an in situ technique can gather true information on the composition and behaviour of the reacting mixture.

How to force CO₂ into chemical reactions

From a thermodynamic and kinetic perspective, CO₂ is a rather challenging reactant due to its high inertness. Activating CO₂ for chemical reactions requires sophisticated catalysts that sufficiently weaken one of the C=O bonds. Thus, CO₂ and epoxides form copolymers with polyether and carbonate units in the presence of double metal cyanide (DMC) catalysts (Scheme 1).

An appropriate selection of the catalyst can steer the copolymerisation into the desired direction:

- Alternating polycarbonates (epoxide:CO₂ is 1:1)
- Polyethercarbonates (PEC; epoxide > CO₂)



Scheme 1: Formation of polyethercarbonate polyols from CO₂ and propylene oxide (PO)

In these reactions, a semi-batch recipe has proven suitable for controlling polymer growth and suppressing the formation of the main side product, cyclic propylene carbonate (cPC).

Reaction Setup

Technically relevant CO₂ chemistry typically requires elevated pressure, in order to increase availability of the reaction partners. Phase transition from gas into liquid and going beyond the critical point is fortunately achieved already under moderate conditions (triple point: 216 K, 5 bar; critical point: 304 K, 74 bar). Using small-scale pressurised reaction vessels already in chemical and process development stages is highly beneficial, since scale-up is significantly facilitated.

For the production of polyethercarbonates, 200 and 300 mL stainless steel autoclaves with magnetically coupled gas entrainment stirrers were used (Parr Instrument, Figure 1). Thanks to the automated liquid feed unit, very precise addition of liquid epoxides is ensured.

Process monitoring

An online MIR spectroscopic monitoring was established with the help of 1/8" fibre-optic diamond ATR probes (infrared fiber sensors, Aachen/Germany) connected to a Bruker MATRIX-MF process spectrometer. The probes were inserted into the pressurised reactor through standard tube fittings and immersed into the liquid phase. Vigorous stirring was required for

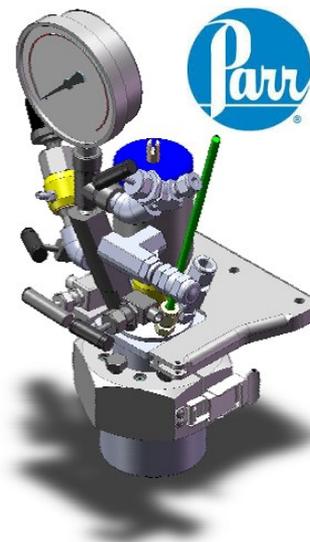


Fig. 1: Compact high-pressure reactor for CO₂ chemistry.

contacting gas and liquid phase, but did not negatively affect the wetting of the ATR element. The constant intensity of the CO₂ signal in the liquid showed that CO₂ supply from the gas phase was sufficiently fast.

Infrared spectra were collected during the reaction with a time resolution of 1 minute (100 co-added scans). A time series of spectra shows the profile of a typical experiment (Figure 2).

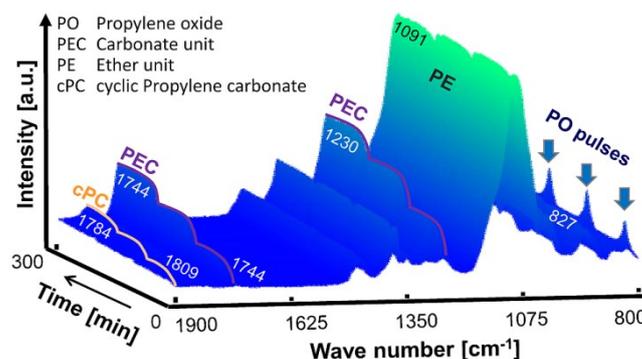


Fig. 2: Time series of MIR spectra from a typical experiment. Characteristic signals are indicated.

The protocol for studying the kinetics is as follows:

1. Charge an oligomeric starter polyether (PE) polyol and the catalyst into the reactor.
2. Pressurize with CO₂, pressure depending on desired carbonate fraction in the co-polymer.
3. Add the epoxide pulse-wise.
4. Repeat PO addition when a low PO concentration threshold is reached.

Following this protocol, adequate incorporation of roughly 20 wt-% CO₂ into the polymer was achieved at 15 bar (theoretical maximum 43 wt-%). The resulting polycarbonate/polyether ratio is the most relevant molecular parameter determining the material properties.

Modelling

The quantification of the four analytes required two independent analysis models. Propylene oxide (PO) and polyether units (PE) were quantified in the C–O region, which is dominated by PE signals (Figure 3). Cyclic carbonate (cPC) and carbonate units in the polymer (PEC) were discriminated in the C=O region between 1850 and 1700 cm⁻¹ by a Hard Model comprising two peaks for each component.

In order to optimise model performance, temperature-specific regressions were applied. In the prediction step, these models use the measured temperature for selecting the correct regression model.

Analysis

The analysis models were applied to the spectra measured online in the liquid phase. Each PO pulse is accompanied by a steep decrease of the other component concentrations due to the dilution.

The resulting PO concentration profile was of excellent quality, and validation with a 1st order kinetic approach was feasible (Figure 3). Accordingly, the build-up of PEC carbonate units and the less pronounced build-up of PE units – resulting in an increased carbonate/ether ratio in the polymer – were observable. The generation of the by-product (cPC) remained at an acceptably low level.

The growth of the polymer was tracked offline by gel permeation chromatography (GPC, Figure 4).

By correlating the molecular weight distribution and other physico-chemical properties with the synthesis protocol, a fine-tuning of the polymer performance with regard to durability and flexibility was feasible.

Application performed at CAT Catalytic Center (RWTH Aachen University) in the *Dream Production* R+D project funded by the German authorities (BMBF).

Further reading

J. Langanke, K. Böhm, T.E. Müller et al., Green Chemistry 2014.

DOI: [10.1039/c3gc41788c](https://doi.org/10.1039/c3gc41788c).

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About the Dream Production project:

Together with academic partners – among them CAT Catalytic Center, supported by S-PACT – Bayer MaterialScience has launched two R&D projects aiming at the incorporation of CO₂ into materials production. A major success of the Dream Production project has been the presented **co-polymerisation of CO₂ and epoxides**. Currently, Bayer is preparing the **implementation of the technology in production**.

The Dream Polymers project continues the success story. Another polymer precursor is produced from **CO₂ as a raw material**, adding up to 40 percent fossil resources saved in this polymer's production.

Only Parr's High Pressure reactor technology as well as S-PACT supported inline mid-infrared (MIR) spectroscopy have allowed to identify the most promising chemical concepts for the presented achievements.

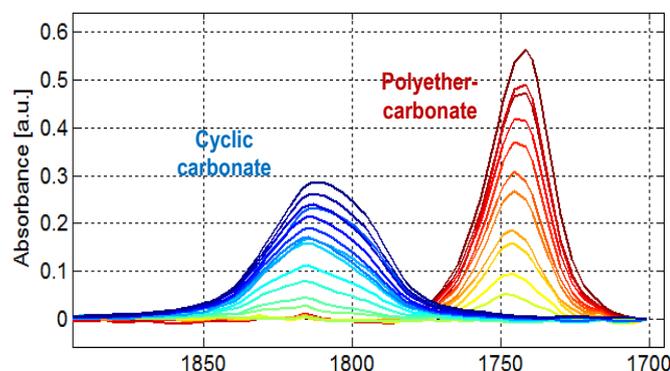
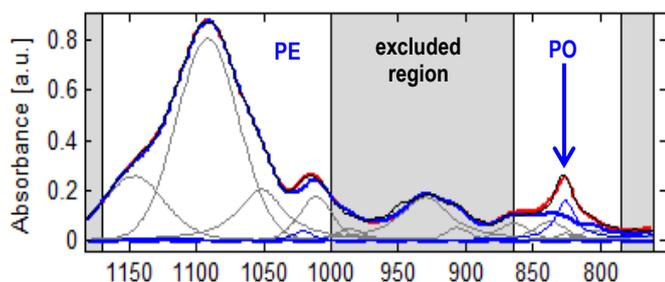


Fig. 3: Left: Mixture Hard Model (red) for PE (bold blue, with constituent peaks) and PO (light blue). Right: Spectra of PEC and cPC in PPG 1000.

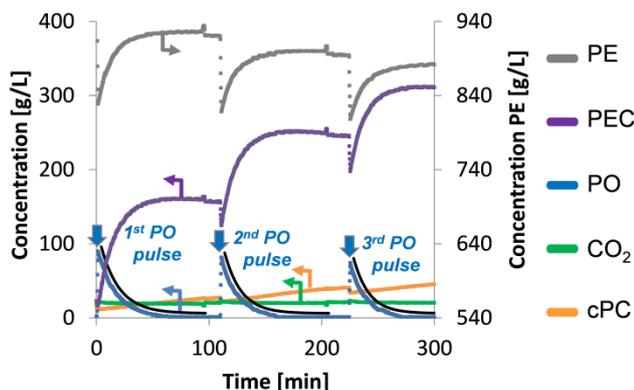


Fig. 4: Predicted concentration profiles (see legend) and 1st order kinetic simulation of PO (black, shifted for clarity).

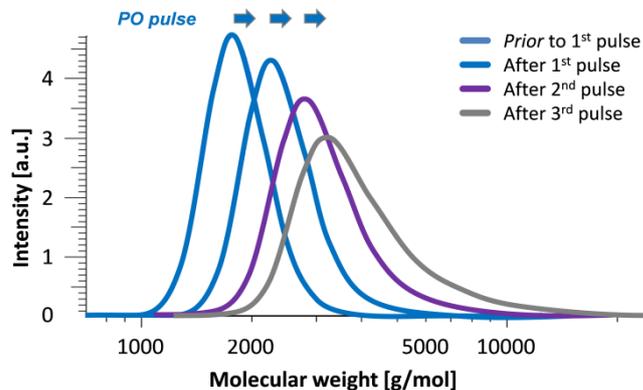


Fig. 5: Molecular weight distribution of the PO-based poly-ethercarbonate, determined by GPC.