Electronic Supporting Information

Intensified *co*-oligomerization of propylene oxide and carbon dioxide in a continuous heat exchanger loop reactor at elevated pressures

Dr. Jens Langanke[a*] and Dr. Aurel Wolf[a]

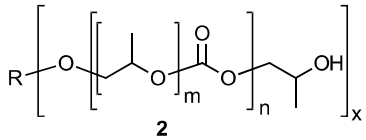
[a]Bayer Technology Services GmbH, Leverkusen, Germany

*corresponding author: jens.langanke@bayer.com

Analytics:

a) NMR

The reaction mixture was analysed by ^{1}H-NMR spectroscopy. The samples were dissolved in deuterated chloroform and measured on a *Bruker* spectrometer (DPX 400, 400 MHz). The relevant resonances in the ^{1}H-NMR spectra (based on TMS = 0 ppm) used for integration were: 1.08–1.18 (methyl group of (poly)ether moieties, area of the resonance corresponds to three H atoms), 1.27–1.34 (methyl group of carbonate moieties - *i.e.* CH_3 *vicinal* to the carbonate moiety *cf*. Fig. 1, area of the resonance corresponds to three H atoms), 1.49–1.51 (methyl group of **3**, area of the resonance corresponds to three H atoms), 2.41–2.01 (CH group of PO, area of the resonance corresponds to one H atom), 3.31–4.24 (CH group of the (poly)ether and carbonate moieties, area of the resonance corresponds to one H atom), 4.53–4.57 (CH group of **3**, area of the resonance corresponds to one H atom) and 4.82–5.08 (CH group of carbonate moieties, area of the resonance corresponds to one H atom). Taking the intensities into account, the relative concentrations as well as weight fractions were calculated.



2

Figure 1: General structure of polyether carbonate polyol (**2**) product

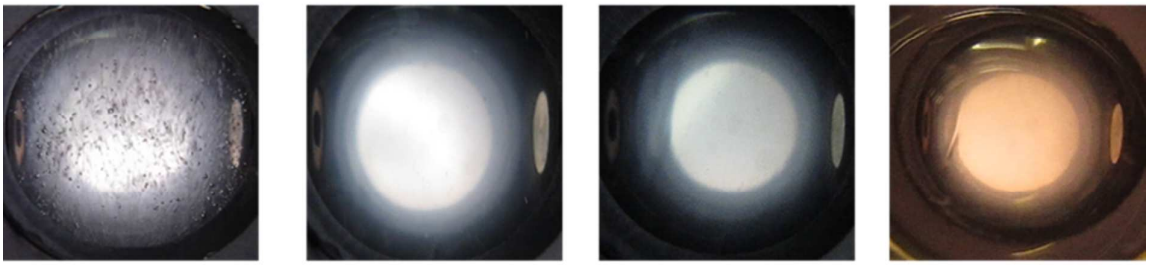
b) GPC

The number- (M_n) and weight-average molecular weight (M_w) of the obtained polyether carbonate polyols **2** were determined by gel permeation chromatography (GPC). The procedure was in accordance with ISO/DIN 55672-1 (*Gel permeation chromatography - Part 1: Tetrahydrofuran (THF) as elution solvent*) using THF as eluent (flow rate 1.0 mL · min^{-1}; columns: 2×PSS SDV linear M, 8×300 mm, 5 µm; RID detector). Standardized polystyrene (PS) samples of known MW were used for calibration, and the chromatogram was referenced against the absolute mass of these PS calibration polymers. The MWD was calculated from M_w/M_n ratio.

c) OH values

The OH value (OH#) of the pure product **2** after TFE work-up was determined according to ISO/DIN 53240-2 (*Determination of hydroxyl value - Part 2: Method with catalyst*) prior to application tests. The obtained OH#s in combination with results from NMR and GPC indicated the strict OH end group functionality of **2** – which is characteristic for DMC catalyzed alkoxylations in presence of R-OH starters.

Results and Discussion / Characterization of Flow Regimes:



65 bar 67 bar 76 bar 100 bar

Figure ESI.1: Phase behavior of the reaction mixture at 130 °C, τ = 30 min and ν = 20

(sight glass behind the heat exchanger).