Homogeneously-acid catalyzed oligomerization of glycerol

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Contributions of partners:

University of Poitiers-IC2MP: in charge of the catalytic oligomerization of glycerol
University of Gent: analytical issues
SOLVAY: catalytic production of alkyl oligoglycerol and their analysis

Chemicals: Glycerol was purchased to Alfa Aesar and all triflates, triflimidates used in this work were kindly provided by SOLVAY.

Analysis:

GC-FID

For the determination of the polyglycerol profile, 5 mg sample was incubated with pyridine: HMDS: TFA (1:1:0.1; v:v:v) for 30 min at 60°C. After incubation the samples were analyzed by GC-FID equipment 6890N (Agilent Technologies, Diegem, Belgium). The capillary column was a DB-1HT nonpolar column (15 m x 0.25 mm x 0.1 μm) from Agilent Technologies (Diegem, Belgium). The (0.1 μL) was injected cold on column and the detector was operated at 340 °C. The oven was programmed as follows: 100°C for 1 min, which was raised to 290°C with a ramp at 10°C/min and then held for another 10 min. Helium was used both as a carrier gas (0.6 mL/min) and makeup gas (20 mL/min). Hydrogen and air flow rates were 40 mL/min and 400 mL/min, respectively.

GC-MS

Chromatographic analysis was performed on an Agilent 7890A GC equipped with a 5975C Mass Spectrometer (Agilent Technologies, Diegem, Belgium). The derivatized sample (1 μL) was introduced into the injector operating in the splitless mode at 250 °C and the separation was carried out on an Agilent HP-5 MS 30 m, 0.25 mm, 0.1 μm capillary column. The carrier gas was helium at a constant flow of 1 mL/min and the oven temperature was programmed as follows: 100°C for 1 min then a rate of 10°C/min till 310°C and hold for 10min. The MSD conditions were the following: capillary direct interface temperature, 250 °C; ionization energy, 70 eV and a full scan analysis was performed between m/z 50 and m/z 500.
**SFC-MS analysis**

SFC-MS analyses were performed using an Ultra Performance Convergence Chromatography ACUITY UPC2 apparatus from Waters equipped with a Single Quadrupole Detector 2 (SQD2) in ESI+ mode. Efficient separation of alkyalted polyglycerol was achieved with a UPC2 BEH column (3.0X100mm 1.7um i.d) using liquid CO$_2$ and MeOH as eluent (from 97% to 80% CO$_2$ in 20min) with a flow of 2.0ml/min and a back pressure of 2000psi. Prior injection, sample was diluted in isopropanol up to 2mg/L (based on the polyglycerol content) and filtered on PTFE filter syringe filter before analysis on SFCMS. Data treatments were applied to the raw chromatogram with in-build algorithm from MassLynx software (v4.1): COmponent Detection Algorithm (CODA) to reduce noise and a smooth of the signal.

**Nuclear magnetic resonance (NMR)**

NMR spectra were registered on a Bruker Avance III at 300 MHz. The quantitive NMR analysis was run with para-dichlorobenzene as reference and trifluoroacetate anhydrate to remove the hydroxyl peaks from NMR spectra.

**Experimental procedures:**

**Catalytic oligomerization of glycerol:** In a typical procedure, glycerol (3g, 32.57 mmol) was heated at 150°C in an open-air vessel in the presence 1.4 mol% of catalyst. When the reaction reached 80% conversion, the crude was diluted in 100 mL of ethanol and then passed through a plug of activated carbon to remove soluble black materials affording a slightly yellow colored solution containing the catalyst and polyglycerol with an average degree of oligomerization of 3.4.

**Catalytic etherification of (poly)glycerol with $n$-butanol in the presence of Bi(OTf)$_3$:** Glycerol was first oligomerized as described above. After purification over a plug of activated carbon, the resulting polyglycerol mixture containing Bi(OTf)$_3$ was heated at 150°C in the presence of 5 mmol of $n$-butanol. The reaction was heated for 24 h and the reaction progress was monitored by GC.

**Catalytic etherification of (poly)glycerol with $n$-dodecanol in the presence of Bi(OTf)$_3$ and Aquivion:** After oligomerization of glycerol in the presence of Bi(OTf)$_3$, polyglycerol (3.68 g), dodecanol (1.86 g, 0.01 mol) and Aquivion 98 powder from Solvay Co., Ltd (0.1eq based on the mole of dodecanol, acidity 0.98-1.06meq/g) as catalyst, were added into a 20 mL tube. The mixture was homogenized at 35 °C under vigorous shearing (13000 rpm, ultra-turax Fluko FA25), sealed with a cap. The reactions were then performed in an oil bath at 150 °C under vigorous stirring at nitrogen atmosphere or in static vacuum for 24 h. The reaction progress was monitored by GC.
**Fig. S1** Typical kinetic profiles obtained with Bronsted acid, here methanesulfonic acid (MSA) and dodecylbenzenesulfonic acid (DBSA)

**TFSI**

**Fig. S2** Typical distribution of G2 isomers obtained in the presence of a Bronsted acid, here bis(trifluoromethane)sulfonimide (TFSI)
Fig. S3 $^{13}$C NMR spectrum of recovered oligoglycerol in D$_2$O