ELECTRONIC SUPPORTING INFORMATION

Homogeneously-acid catalyzed oligomerization of glycerol

N. Sayoud,^{*a*} K. De Oliveira Vigier,^{*a*} Tatiana Cucu,^{*b*} Bruno De Meulenaer,^{*b*} Zhaoyu Fan,^{*c*} Jonathan Lai,^{*c*} Jean-Marc Clacens,^{*c*} Armin Liebens^{*c*} and F. Jérôme^{*a**}

Contributions of parners :

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 μ m) from Agilent Technologies (Diegem, Belgium). The (0.1 μ L) 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 μ L) 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 μ m 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 alkylated polyglycerol was achieved with a UPC2 BEH column (3.0X100mm 1.7um i.d) using liquid CO₂ and MeOH as eluent (from 97% to 80% CO₂ 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 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)



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 D₂O