Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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ARTICLE

Homogeneously-acid catalyzed oligomerization of glycerol

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Here we report the screening of various homogeneous acid catalysts in the oligomerization of glycerol at 150°C. Under optimized conditions, a mixture of oligoglycerol with an average degree of oligomerization of 3.4 was obtained at a glycerol conversion of 80%. At such conversion, the selectivity to oligoglycerols was higher than 90%. Oligoglycerols were then successfully alkylated opening an attractive route to valuable molecules (biosurfactants or hydrotropes).

Introduction

In recent years, use of glycerol as a renewable raw material for the chemical industry has received considerable attention.[1] This industrial and scientific fad for glycerol is mainly boosted by the growing worldwide production of biodiesel and more generally vegetable oils that generates a surplus of glycerol on the market. From the point of view of industry and sustainable chemistry, glycerol offers noticeable advantages such as (1) renewability, (2) biodegradability and safety and (3) low price, key points that should favour its industrial emergence.

To date, numerous studies have been devoted to the conversion of glycerol to acrolein, propylene glycol, glycerol carbonate, glycidol, among others.[2] Some of these processes have been already commercialized. Glycerol is a polar molecule and is thus also of particular interest for the design of renewably-sourced non-ionic and potentially safer surfactants or hydrotropes. Esterification of glycerol with fatty acids opens a straightforward access to industrially relevant and safe surfactants/hydrotropes.[1,2] However, one should mention that the instability of the ester moiety in the presence of water drastically restricts their industrial use in many applications. To widen the scope of these molecules in industry, much effort has been recently paid to the production of alkyl glyceryl ethers that are much more recalcitrant to hydrolysis, thus increasing their interest in various industrial fields such as formulation for paints or personal care, detergence, coating, fuel additives... Analysis of the current literature revealed that alkyl glyceryl ethers can be catalytically produced by telomerization of glycerol with diene,[3] reductive alkylation of fatty aldehydes or fatty acids with glycerol[4], addition of glycerol to olefins[5] or by a direct dehydrative etherification of glycerol with alkyl alcohols.[6] Although amphiphilic properties of these alkyl glyceryl ethers can be tailored by adjusting the length of the alkyl chain (C_4 to C_{18}), little attention has been given to the increase of the glyceryl polar chain despite it would also provide access to robust surfactants or hydrotropes with expected improved properties according to predictive calculations.

Catalytic oligomerization of glycerol is a difficult reaction mainly because of the difficulty to closely control the reaction selectivity. Oligomerization of glycerol can be heterogeneously or homogeneously-catalyzed either by bases[7] (NaOH, K_2CO_3, Cs-MCM41, metal oxides, etc…) or acids[8] (zeolite, cation exchange resins, etc…). Under basic conditions, high temperature are generally required (T > 220°C) leading to the competitive dehydration or dehydrogenation of (oligo)glycerol. On the other hand, under acid conditions, side dehydration of (oligo)glycerol to readily polymerizable substrates occurs which represent an important limitation of this route.

Solid acid catalysts such as zeolites are attractive materials for this reaction notably with respect to catalyst recycling and scale up. However, their deactivation in glycerol still represents an important shortcoming that need to be addressed.[9] In this manuscript, we screened various homogeneous acid catalysts with the aim of identifying a promising family that will be next used as a source of inspiration for the rational design of more appropriate solid acid catalyst (not included in this work). Recently, we have reported that metal triflates were capable of selectively etherifying glycerol with short chain alkyl alcohols such as *n*-butanol for instance.[6c] Notably, high yields to butylglycerylethers were obtained while the carbon mass balance of the reaction was nearly complete at total conversion supporting the high selectivity of these acid catalysts in such reaction.

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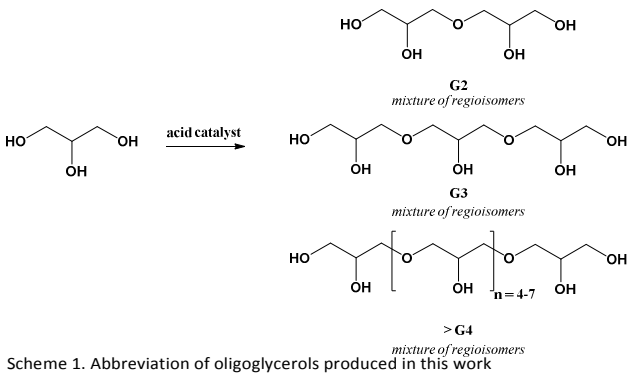
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Here we wish to report the screening of various homogeneous Lewis (triflates and triflimidates) and Bronsted acids in the oligomerization of glycerol. Activity and selectivity of catalysts, composition of the different oligoglycerol fractions and purification issues are addressed. Under optimized conditions, we found that an oligoglycerol fraction with a degree of oligomerization within the range of 2-7 can be selectively obtained at 80% conversion of glycerol. At such conversion rate, the selectivity to oligoglycerols was higher than 90% opening a straightforward route to renewably-sourced polyols that have a high potential of market in the field of surfactants or hydrotropes. Notably, produced oligoglycerols were subsequently alkylated with either *n*-butanol or *n*-dodecanol affording valuable alkyl oligoglycerol ethers with yields higher than 56%.

Results and discussion

Inspired by our recent results, the activity and selectivity of various metal triflates and triflimidates in the oligomerization of glycerol was first evaluated. In a typical experiment, neat glycerol was heated at 150°C in an open flask under conventional heating and in the presence of 1.4 mol% of metal triflate or triflimidates. Conversion rate and reaction yields were determined by means of gas chromatography (GC) and HPLC analyses. For the sake of clarity, molecular structures and abbreviations of produced oligoglycerols are provided in Scheme 1.



Scheme 1. Abbreviation of oligoglycerols produced in this work

First, the temperature and time of the reaction were initially fixed at 150°C and 6 h, respectively, to select the most active catalyst. Results are summarized in table 1. From Table 1, it appears that $Al(TFSI)_3$ and $Ga(OTf)_3$ were the most active catalysts leading to a conversion of glycerol of 89% which corresponds to a Turn Over Frequency (TOF) of about 7.5 h^{-1} (entries 1, 2). In a first approximation, activity of tested metal triflates and triflimidates can be classified as follow: $Al(TFSI)_3$ ~ $Ga(OTf)_3$ > $Bi(OTf)_3$ > $Fe(TFSI)_3$ ~ $Al(OTf)_3$ ~ $Fe(OTf)_3$ > $Nd(OTf)_3$. Next, the evolution of the yield of G2, G3 and >G4 according to the glycerol conversion was checked. Note that more information on the chemical composition of the G2, G3 and >G4 fractions is given later in the manuscript. A selected representative kinetic profile is provided in Fig.1. As a general

Table 1. Oligomerization of glycerol in the presence of Lewis acids[a]

Entry	Catalyst	Conv. Glycerol (%)	Turn over frequency (h^{-1})[b]
1	$Al(TFSI)_3$	90	7.8
2	$Ga(OTf)_3$	88	7.3
3	$Bi(OTf)_3$	77	5.6
4	$Fe(TFSI)_3$	65	5.1
5	$Al(OTf)_3$	49	4.8
6	$Fe(OTf)_3$	36	3.7
7	$Nd(OTf)_3$	9	-

[a] 150°C, 6h, 1.4 mol% of Lewis catalyst; [b] collected at a glycerol conversion lower than 15%

trend, diglycerols were formed as a primary product. The yield of diglycerols reached a maximum of 32% at 50% conversion of glycerol and then decreased due to their subsequent etherification to triglycerols. Triglycerols appeared when the conversion of glycerol reached 20 %. Like diglycerols, the yield of triglycerols reached a maximum (16%) but at a higher conversion of glycerol (73%). Formation of oligoglycerols composed of more than 4 glyceryl units was observed only at 25% conversion of glycerol. As long as the reaction proceeded, the yield of >G4 gradually increased and reached 38% at a conversion of glycerol of 83%. It should be noted that no significant difference of selectivity was observed between all tested acid catalysts.

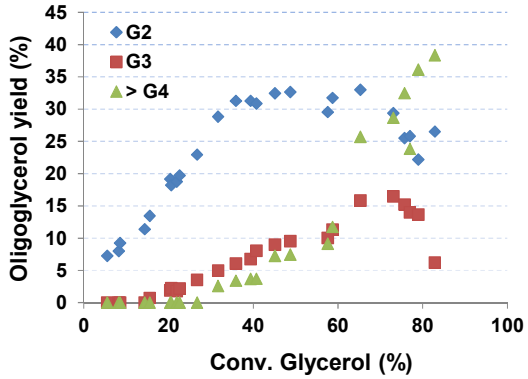


Fig. 1. Yields of oligoglycerols versus glycerol conversion (150°C, $Al(TFSI)_3$

The selectivity to oligoglycerols remained around 90% at 80% conversion of glycerol and then decreased rapidly down to 60% at a higher conversion rate (90%) due to the formation of side products presumably stemming from the acid-catalyzed degradation of oligoglycerols as corroborated by the formation of soluble and insoluble black materials at such high conversion. Although formation of oliglycerols with a degree of oligomerization higher than 4 may be possible at high conversion (>90%), no improvement of the formation of >G4 was observed by GC suggesting that oligoglycerols are mostly degraded at high conversion. The gas phase was also continuously analyzed by mass spectrometry in particular to check the possible formation of acrolein, a toxic chemicals known to be produced by intramolecular dehydration of glycerol under acid conditions.[10] Whatever the conversion, no acrolein was detected in the gas phase. Note that the

Table 2. Optimization of the reaction parameters

Entry	Catalyst loading (mol%)	Temperature (°C)	Time (h)	Conv. Glycerol (%)	G2 yield (%)	G3 yield (%)	> G4 yield (%)	Selectivity to oligloglycerols (%)[a]
1	1.4	150	4	58	31	11	10	90
2	1.4	150	5	79	22	16	36	94
3	1.4	130	24	57	33	12	10	96
4	1.4	100	24	<5	-	-	-	-
5	1.4	170	1	73	24	12	21	78
6	1.1	150	4	45	31	8	6	100
7	0.5	150	4	23	20	2	-	96
8	1.1	170	1	49	31	9	8	98
9	0.5	170	1	27	24	3	-	100

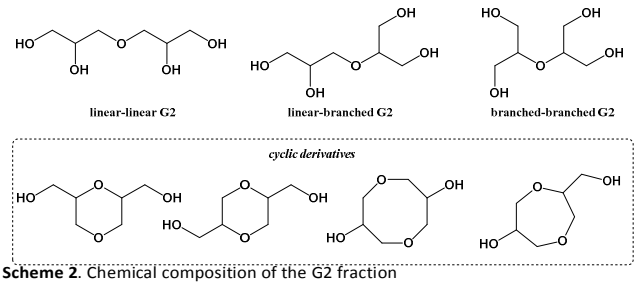
[a] The difference with 100% was due to the formation of unidentified side products stemming from the dehydration of glycerol and its oligomers to readily polymerizable chemicals

formation of acrolein cannot be totally ruled out due to its possible *in situ* polymerization. However, at a conversion of glycerol lower than 80%, this reaction was limited as supported by the selectivity to oligoglycerols reaching 90% (more details are provided later in the manuscript).

Having all these results in hand, we then screened different reaction parameters to find the proper balance between time of reaction, temperature and catalyst loading. In these experiments, $Al(TFSI)_3$ has been chosen as a catalyst. Results are summarized in Table 2. First, a different set of reaction temperature (100 to 170°C) was investigated. When the reaction temperature was decreased below 150°C, the reaction rate was dramatically decreased in accordance with the Arrhenius's law. For instance, whereas at 150°C 58% of conversion was achieved after 4 h of reaction (entry 1), 24 h were required to obtained similar conversion at 130°C (entry 3). A further drop of the temperature to 100°C however decreased the reaction rate to an unacceptable level (entry 4). Reversely, an increase of the reaction temperature had obviously a significant effect on the reaction rate since at 170°C, 70% of glycerol was converted within 1 h *vs* 5 h at 150°C (entries 2, 5). However, at 170°C, the selectivity to oligoglycerols determined at about 75% conversion was lower (78%) than at 150°C (>90%) and, in this case, an important formation of soluble and insoluble black materials was rapidly observed. Hence, 150°C was selected as an optimum temperature in the next experiments.

Like for the temperature, a drop of the catalyst loading from 1.4 mol% to 1.06 mol% and then 0.53 mol% decreased the formation rate of oligoglycerols but with no significant change of the reaction selectivity (entries 1, 6, 7). Similar results were also observed when the reaction was conducted at 170°C (entries 5, 8, 9).

Next, the regioselectivity of the reaction was investigated. Oligoglycerols (G2, G3 and G>4) are produced as a mixture of different regioisomers that can be linear or branched. In addition, the intramolecular cyclization of oligoglycerols affords dioxane-like chemicals. Production of such cyclized products needs to be limited since these chemicals are suspected to be toxic. Analysis of the G2 fraction was carried out by means of GC analyses. Chemical structures of the different regioisomers and cyclized products are provided in Scheme 2. Results were collected with $Al(TFSI)_3$. Similar profiles were obtained with other tested catalysts (see ESI).



Scheme 2. Chemical composition of the G2 fraction

First, the diglycerol fraction was analyzed more in details. To this end, we plotted the relative distribution of linear-linear (LL), linear-branched (LB), branched-branched (BB) G2 as well as cyclized products as a function of the glycerol conversion. As expected, linear-linear G2 were produced in the highest amount (60%) while branched-branched G2 were produced in the lowest amount (< 6%). Whereas the selectivity to linear-

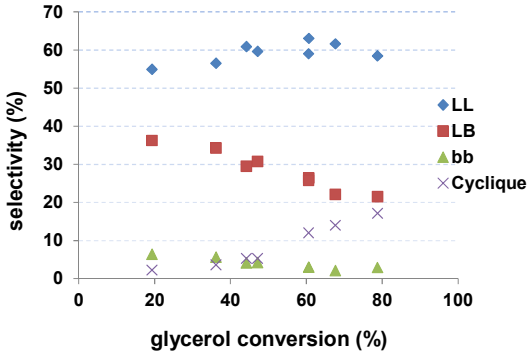
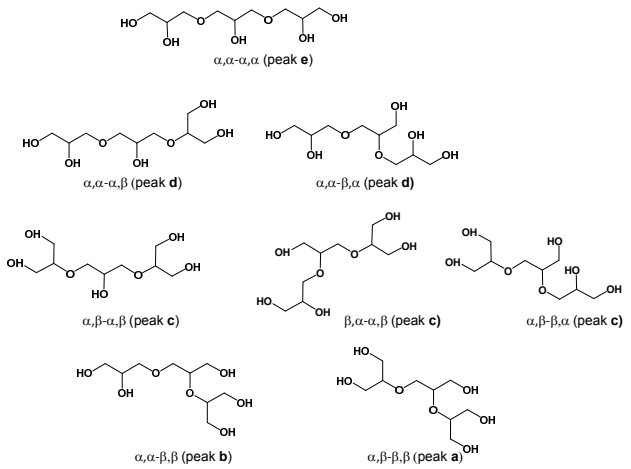


Fig.2. Composition of the G2 fraction as a function of the glycerol conversion

linear G2 remained constant whatever the conversion rate, the selectivity to linear-branched G2 decreased when the conversion of glycerol was increased. Similar tendency was observed with branched-branched G2 although in a lower extent. Concomitantly, an increase in the production of cyclized product was observed. Considering that the selectivity to linear-linear G2 remained unchanged, one may conclude that linear-branched G2 are more prone to intramolecular cyclization.

Analysis of the G3 fraction was much more complex. To get more insight on the G3 fraction, samples were first analyzed by GC-FID using a short DB-1HT column and a low flow of the carrier gas (0.6 ml/min). In agreement with a previous work of De Meulenaer,[11] the G3 fraction eluted in five distinctive peaks. These five peaks represent the linear isomers of triglycerol which are known to elute after the cyclic isomers due to their lower volatility (Fig. 3). Although eight linear isomers of triglycerols are expected to co-exist, a full separation of all compounds was not possible. Nevertheless, based on the elution order and previous works, a possible identification of the isomers could be made. For the sake of clarity, chemical structure and abbreviation of the eight linear regioisomers of G3 are provided in Scheme. 3. α and β represent the primary and secondary alcohol of the central glyceryl unit, respectively, through which the two other glyceryl units are bonded.



Scheme 3. Chemical structure and abbreviation of the G3 linear isomers

This way, peak **e** corresponds to the α,α-α,α isomer. The indication that this peak represents only one isomer is moreover supported by the fact that the shape of the peak is symmetric. Peak number **d** is probably represented by the α,α-β,α and α,α-α,β isomers again confirmed by the fact that the obtained peak was asymetric. Further, peak number **c** corresponds to the α,β-β,α and β,α-α,β and α,β-α,β linear isomers which is again confirmed by the broad asymetric shape. Peak **b** and **a** are symmetric peaks representing the α,α-β,β and α,β-β,β isomers respectively. This order of elution is moreover supported by the fact that the linear isomer α,α-α,α elutes later than the branched ones as they are less volatile compared to the more compact α,β-β,β isomer which elutes first. Each change of the α,α bond into α,β leads to a shift in volatility and retention time as shown in Fig. 3. Such elution order is also in perfect agreement with our previous work.[11]

Attempts to obtain a better elution of the G3 linear isomers were done this time using GC-MS with a 30 m column. Figure 4 shows the EIC of m/z 73, ion typical for silylation reactions ($Si+(CH_3)_3$). Confirmation of the peak identity by GC-MS was not possible because no characteristic ions could be detected for different isomers. Due to a longer column a better separation was obtained but still not optimal. From the chromatogram it is clear that peak **d** has a shoulder suggesting a co-elution of two isomers while peak **c** exhibits three shoulders indicating a co-elution of three isomers. Altogether, these results are in good agreement with the above described GC-FID analysis.

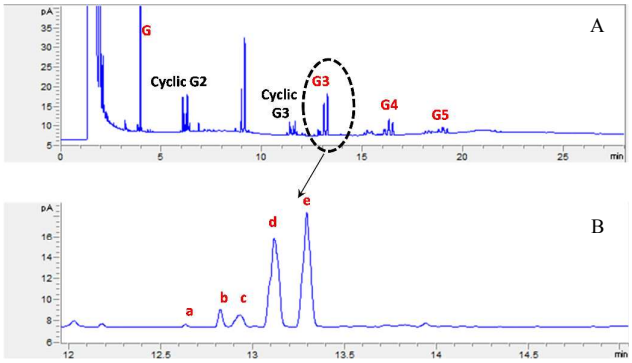


Fig 3. Typical chromatogram of the PG2 samples: A – full chromatogram, B – detailed chromatogram of the triglycerol fraction: **a** - β,β - β,β; **b** - α,β - β,β, **c** - β,α - β,α and β,α - α,β and α,β - α,β, **d** - α,α - β,α and α,α - α,β, **e** - α,α - α,α

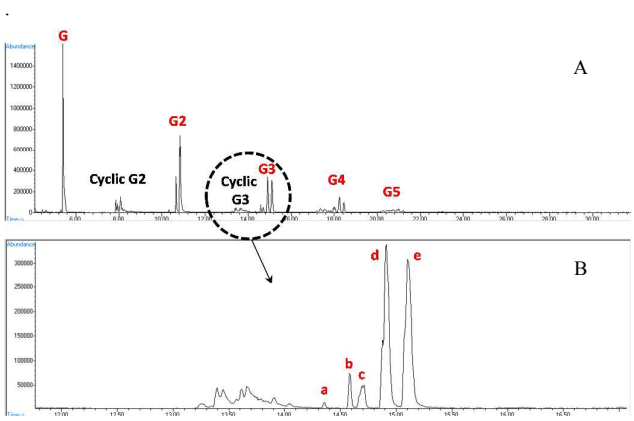
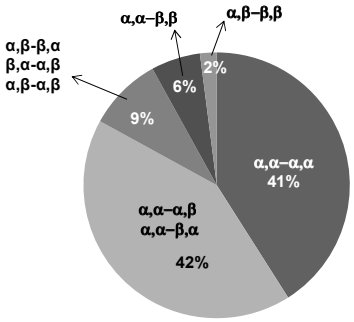


Fig 4. GC-MS chromatogram of the EIC of the m/z 73; A – full chromatogram, B – detailed chromatogram of the triglycerol fraction: **a** α,β-β,β; **b** α,α-β,β, **c** α,β-β,α and β,α-α,β and α,β-α,β, **d** α,α-β,α and α,α-α,β, **e** α,α- α,α

The relative distribution of the G3 isomers (does not include cyclized products that cannot be quantified with accuracy due to the overlapping of different peaks) did not significantly change with the reaction time or the glycerol conversion rate. As a general trend, α,α-α,α and α,α,α,β, α,α-β,α are



Scheme 4. Relative distribution of the G3 isomers (cyclized adducts were excluded)

predominantly produced followed by α,β-β,α, β,α-α,b, α,β-α,β and α,α-β,β and α,β-β,β. The scheme 4 represents the typical relative distribution between all G3 isomers produced during the catalytic reaction.

Analysis of the > G4 fraction was however too complex to be determined with accuracy. By means of GC analysis, it was difficult to determine the maximum degree of oligomerization of glycerol mainly due to an important decrease of the response coefficient when going from glycerol to oligoglycerols. Nevertheless, G5 was clearly observed (Fig. 3). Oligoglycerols can be more easily detected by size exclusion chromatography. However, here again, the overlapping of peaks due to the presence of different isomers (including cyclized products) makes the identification difficult. However, on the basis of the retention time, one may assume that the degree of oligomerization of glycerol remained lower than 7. This is also in accordance with MALDI-TOF analysis that did not reveal a significant production of high molecular weight oligoglycerol (> G7). Finally, LC/MS analysis also supported a maximum oligomerization degree of glycerol lower than 7.

Purification of the oligoglycerol fractions has been then undertaken. As previously pointed out by B. M. Weckhuysen and co-workers,[12] we observed that at a low conversion the reaction media is nearly colourless but turned to dark brown at a conversion close to 80%. This change of colour was attributed to the formation of side products notably stemming from the dehydration of glycerol and oligoglycerols to readily polymerizable chemicals (exact elucidation of the chemical composition of the black materials was not trivial). Although the amount of these chemicals is low (see below), their presence coloured the reaction media at an unacceptable level for direct use in cosmetic and/or formulation for instance.[12] Hence, at the end of the reaction (80% conversion of glycerol), the recovered solution of oligoglycerols was diluted in ethanol and then passed through a plug of activated carbon leading to the removal of the coloured dark brown products. After removal of ethanol under vacuum, a light yellowish liquid was obtained. Using this procedure, more than 95 wt% of oligoglycerols were recovered further confirming the high selectivity of the reaction at 80% conversion of glycerol (*i.e.* 5 wt% of impurities was retained by the activated carbon). At a higher conversion rate (95%), the amount of unidentified side products was increased which was highlighted above by a drop of the oligoglycerol selectivity. In agreement, at a conversion of 95%, only 69 wt% of oligoglycerols were recovered supporting, in this case, a significant degradation of oligoglycerols to unidentified products that were retained by the activated carbon.

After purification over charcoal, the light yellowish liquid was analyzed by ^{1}H, ^{13}C NMR and FT-IR. FT/IR did not reveal the presence of C=C or C=O bonds (resulting from the intramolecular dehydration of oligoglycerol). However, by ^{13}C NMR, a very small peak located at 177 ppm was observed which may be attributed to the presence of a partly dehydrated product presumably responsible for the light yellowish coloration (Fig. S3). From ^{13}C NMR, one can also see that, after filtration over charcoal, triflic/triflate species were still present (quadruplet centred at 120 ppm) which will be useful for subsequent etherification of oligoglycerols with alkyl chain (see below). On the basis of the peak intensity, the amount of impurities responsible for the slightly coloration of oligoglycerols appears to be quite low. The presence of impurities, even in a small amount, has a dramatic impact on the coloration of oligoglycerols that may hampers their commercial use in some applications. Post-bleaching treatments often represent a key and critical aspect of the process. Industrially, hydrogenation reaction was also proposed for the bleaching.

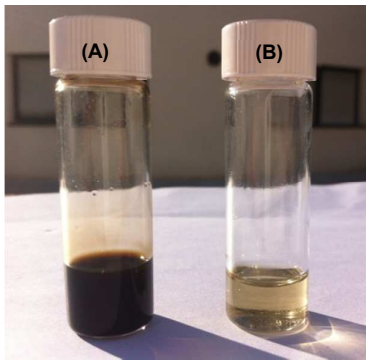


Fig. 5 Picture of oligoglycerol recovered at 80% conversion in the presence of $Al(TFSI)_3$ at 150°C (A) before filtration over charcoal and (B) after filtration over charcoal

In the presence of water, metal triflates or triflimidates are known to be capable of releasing triflic and triflimidic acid, respectively. In a previous article, we have shown that this phenomenon can also occur in glycerol.[6c] In order to get more insight on the nature of the true catalytic species involved in this reaction, similar experiments were conducted using Bronsted acid. In this part, the optimized conditions as defined with $Al(TFSI)_3$ *i.e.* 1.4 mol% of catalyst, 150°C were applied. Otherwise noted, all reactions were stopped after 4 h of heating. Results are presented in Table 3. Bronsted acids also catalyzed the oligomerization of glycerol and can be classified as follow HTFSI > H_2SO_4 > TfOH > MSA ~ DBSA. One may notice that the TOF of Bronsted acid followed their acid strengths. Contrary to what was previously observed by us in the case of the catalytic etherification of glycerol with *n*-butanol,[6c] no significant difference of TOF and selectivity was observed

between all tested Lewis and Bronsted acids in neat glycerol. A maximum yield of G2 and G3 was always obtained at 50% and 70% conversion of glycerol, respectively while the production of oligoglycerol with more than four glyceryl units is dominant at high conversion. Examples of kinetic profiles are provided in the ESI. Altogether, these results suggest that Bronsted acids are the real catalytic species in such reaction. To further support this hypothesis, the catalytic reaction was conducted in the presence of a catalytic amount of 1,5-di-tertiobutylpyridine. This sterically hindered pyridine derivative has been reported to be capable of trapping released Bronsted acid. Notably, due to the presence of two sterically hindered tertiobutyl groups, this pyridine derivative is not capable of coordinating bulky Lewis acids such as metal triflates or triflimidates but can react with released triflic or triflimidic acid.[13] Interestingly, addition of 1.4 mol% of 1,5-di-tertiobutylpyridine at the beginning of the reaction, either with $Al(TFSI)_3$ or $Bi(OTf)_3$, completely inhibited the reaction showing that HTFSI and TfOH does have a major role in the reaction mechanism.

This result is of significant importance and allows previous results to be partly rationalized. In particular, in the previously reported catalytic etherification of glycerol with *n*-butanol, a synergistic effect was evidenced between Lewis and released Bronsted acids.[6c] In neat glycerol, our results suggest that Bronsted acids are the true catalytic species and no synergistic effect with Lewis acid was evidenced in this case. This difference of behaviour is actually also highlighted by a difference of selectivity. Whereas glycerol was successfully oligomerized at 150°C in the presence of $Bi(OTf)_3$, the oligomerization of glycerol remained negligible (<5%) when the same catalyst (at same temperature) was used in the etherification of glycerol with *n*-butanol (glycerol/*n*-butanol ratio 4/1).[6c] This difference of selectivity further supports that the reaction mechanism is different in both cases.

Table 3. Oligomerization of glycerol in the presence of Bronsted acids[a]

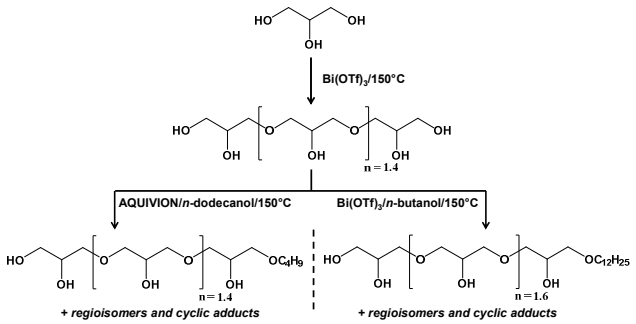
Entry	Catalyst	Conv. Glycerol (%)	Turn over frequency (h^{-1})[b]
1	HTFSI	74	10.2
2	H_2SO_4	69	8,7
3	TfOH	41	5.2
4	MSA	34	5.3
5	DBSA	31	3.6

[a] 150°C, 4h, 1.4 mol% of Lewis catalyst; [b] collected at a glycerol conversion lower than 15%

Having all these results in hand, we then attempted the direct production of oligoglycerol ethers by consecutive catalytic oligomerization of glycerol followed by its catalytic etherification with either *n*-butanol (application as hydrotropes) or *n*-dodecanol (application as surfactants). Previously, we have shown that $Bi(OTf)_3$ was capable of selectively catalyzing the etherification of glycerol with short chain alkyl alcohols.[6c] For this reason, $Bi(OTf)_3$ was selected here as an acid catalyst for the production of alkyl oligoglycerol ethers instead of $Al(TFSI)_3$ which was found less efficient in such etherification reaction. In a typical procedure, glycerol was first heated in the presence of 1.4 mol% of $Bi(OTf)_3$ at 150°C for 24 h affording oligoglycerol with 87% yield (the 13% remaining being mostly free glycerol). The solution of oligoglycerols was then passed through a plug of activated carbon to remove trace of soluble black materials prior reacting with 0.3 eq of *n*-butanol. Note that acid species were not retained by activated carbon and thus can be reused for the alkylation of oligoglycerols (Fig. S3). In the case of *n*-dodecanol, the experimental procedure was adapted. Indeed, due to the lipophilicity of *n*-dodecanol, the reaction media was biphasic which induced mass transfer problems (with $Bi(OTf)_3$, dodecyl oligoglyceryl ethers were only produced in a trace amount). Hence, from *n*-dodecanol, glycerol was first oligomerized in the presence of $Bi(OTf)_3$, filtered over a plug of active carbon and then, inspired by previous work, Aquivion (solid acid catalyst, 0.1 eq H^+) was added.[6d] The choice for Aquivion was motivated by its amphiphilic properties allowing a better interaction between the oligoglycerol and the *n*-dodecanol phases.

Because of the statistic production of a wide range of isomers, oligomers and alkylation degree, analysis of the reaction media is not trivial. Inspired by our previous work on glycerol etherification with fatty chains,[6d] alkyl oligoglycerol ethers were analyzed by means of SFC-MS, ^{1}H NMR and GC (Table 4).

Table 4. Analysis of oligoglycerol and alkyl oligoglycerol by SFC-MS and NMR



Sample	OD[a]	Alkyl alcohol conv. (%)[b]	Yield monoalkyl oligoglycerol (%)	Yield dialkyl oligoglycerol (%)
Oligoglycerol	3.4	-	-	-
Butyl oligoglycerol	3.4	66	62	-
Dodecyl oligoglycerol	3.6	76	56	8

[a] oligomerization degree; [b] determined by NMR

First, SFC-MS analyses revealed that the oligomerization degree of oligoglycerol produced in the first step was about 3.4 in the presence of $Bi(OTf)_3$ which is consistent with our above described results collected by SEC. Next, produced butyl oligoglycerol were analysed by ^{1}H NMR (in DMSO-d_6) and GC. During the alkylation reaction, the yield of monobutyl oligoglycerol ethers reached 62% further supporting that acid species are still active after the oligomerization of glycerol and

filtration over active carbon. By means of GC analyses, the conversion of *n*-butanol was found to be 66%. In addition, presence of dibutyl ether was not detected. These results indicate that the selectivity of the reaction to monobutyl oligoglycerol was 94% at 66% conversion.

From *n*-dodecanol, the yield of monododecyl oligoglycerol ethers was in a similar range and reached 56%. However, the selectivity of the reaction to mono- and dibutyl oligoglycerol was lower than in the case of *n*-butanol (84% *vs* 94%) which is due to the concomitant production of didodecyl ethers (16%) presumably due to (i) the higher conversion rate of *n*-dodecanol than that of *n*-butanol (76% *vs* 66%) and (ii) mass transfer problem enhancing the dimerization of *n*-dodecanol.

Note that for both alkyl alcohols, the selectivity to alkyl oligoglycerol was also supported by SFC-MS analyses. In addition, SFC-MS revealed that the oligomerization degree (OD) of oligoglycerol remained unchanged before (OD=3.4) and after (OD=3.6) the alkylation reaction.

From this study, one may conclude that, at 70-80% conversion of alkyl alcohol, monoalkyl oligoglycerol (at least 56% yield) with a degree of oligomerization of 3.5 can be produced, thus opening an interesting route to bio-based non-ionic surfactants or hydrotropes.

Conclusions

We found here that metal triflates and triflimidates were particularly efficient in the oligomerization of glycerol. Under optimized conditions (150°C, 6h, 1.4 mol%), oligoglycerol swith an average degree of oligomerization of 3.4 were obtained at 80% conversion of glycerol. Notably, at such conversion rate, the selectivity to oligoglycerols was higher than 90%. Recovered oligoglycerols were then successfully alkylated either with *n*-butanol or *n*-dodecanol affording the valuable alkyl oligoglycerol ethers with a yield higher than 56%. Mechanism investigations revealed that Bronsted acid, released by glycerolysis of metal triflates or triflimidates, are actually the true catalytic species. By combining results from this study and those collected in previous articles, it clearly appears that water-tolerant solid acid catalysts bearing strong Bronsted acid sites should be an ideal candidate for the oligomerization of glycerol at relatively low temperature (<150°C), a pre-requisite to avoid the side production of acrolein and other undesirable products. More generally, it is our opinion that this work opens an interesting bio-based route to analogous of oligoethylene glycol that are widely used in the production of non-ionic surfactants.

Acknowledgements

Authors are grateful to the CNRS, the University of Poitiers and SOLVAY for financial support. Nassim Sayoud also thanks the University of Poitiers and the European Council (Erasmus Mundus program) for the funding of his PhD grant.

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Journal Name

ARTICLE

Graphical abstract

Homogeneously-acid catalyzed oligomerization of glycerol

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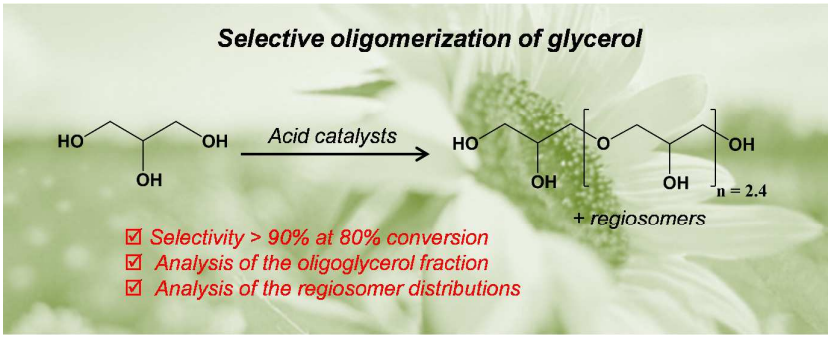

Here, we report the oligomerization of glycerol in the presence of various Bronsted and Lewis acid catalysts. Under optimized conditions, oligoglycerols with an average degree of oligomerization of 3.4 were selectively obtained at 80% conversion of glycerol opening a promising route to biosurfactants