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Deborah Peruzzo, Mathieu Drelon, Clement Dumont, Andre Mortreux, Isabelle Suisse, et al.. Palladium catalyzed telomerization of bio-based polyols with atmospheric pressure bubbling butadiene. *Molecular Catalysis*, 2021, *Molecular Catalysis*, 502, pp.111369. 10.1016/j.mcat.2020.111369 . hal-04274756

HAL Id: hal-04274756

<https://hal.univ-lille.fr/hal-04274756>

Submitted on 8 Nov 2023

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Palladium catalyzed telomerization of bio-based polyols with atmospheric pressure bubbling butadiene.

Deborah Peruzzo,^a Mathieu Drelon,^a Clément Dumont,^b André Mortreux,^{†a} Isabelle Suisse,^a
Mathieu Sauthier^{a,*}

^a Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.

^b ICAM site de Lille, 6 rue Auber, 59016 Lille Cedex, France

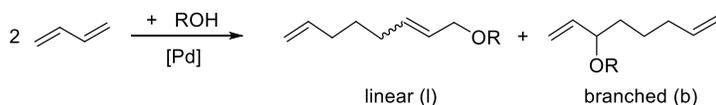
Abstract: The palladium catalyzed telomerization of butadiene with glycerol has been efficiently performed with bubbling butadiene at atmospheric pressure leading to high selectivities into monooctadienyl glycerylethers. The catalytic activity is found to be stable for a long period of time, up to 5 days, giving rise to turnover numbers as high as 1000. The reaction has been extended to isosorbide and solketal with always selective production of the monotelomers over long time.

Keywords: Telomerization, butadiene, glycerol, isosorbide, solketal

1. Introduction

The concept of green chemistry has a great impact on research developments as it takes into account the environmental and health impacts of chemicals production.[1-4] These green chemistry concepts foster research priorities such as reducing the consumption of non-renewable resources, using environmentally friendly solvents, decreasing wastes from the use of atom economical reactions for the synthesis of targeted products and using catalytic reactions that allow smooth conditions and high selectivities. As example, the palladium catalyzed telomerization of dienes with bio-based polyols is an efficient synthesis of ethers that fulfills these criteria. [5,6] The telomerization reaction corresponds to the metal catalyzed dimerization of dienes with addition of a nucleophile as water [7], alcohols [8,9] or amines [10,11] in most cases. In case of alcohols as nucleophiles, linear or branched octadienylethers are obtained (Scheme 1). This reaction has been largely investigated in literature [12-17] ever since its discovery back in the Sixties [18,19] and

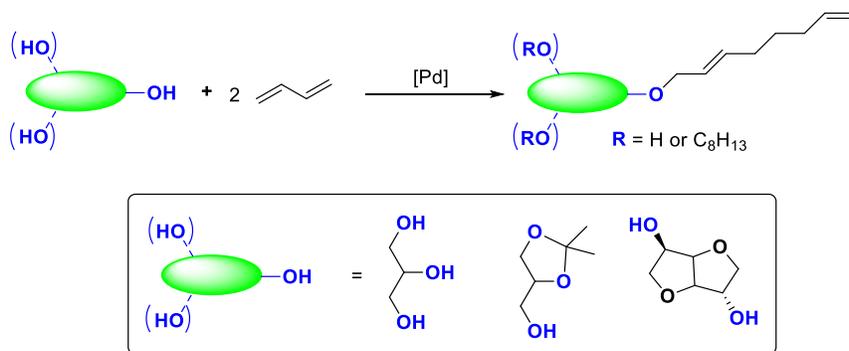
important improvements have been done in the last decades to generalize this reaction to polyhydroxylated derivatives. [20-24]



Scheme 1 : Telomerization of alcohols with butadiene

From polyols, mono to polyethers can be obtained and efforts have been mainly devoted to produce selectively monoethers, the objective being to produce compounds with amphiphilic structures. In view of sustainable chemistry, this catalytic transformation of polyols that are generally biobased is 100% atom-economical and no wastes are produced. Moreover, water could be used as solvent providing that hydrosoluble catalysts are employed.

In that frame, our group has proposed the efficient palladium catalyzed telomerization reaction of glycerol and isosorbide under biphasic media in a batch mode and under butadiene pressure. Depending on the choice of the organic co-solvent and nature of the catalyst employed to promote the reaction, mono- to fully substituted ethers could be obtained with high selectivities and yields (Scheme 2).



Scheme 2 : Telomerization of butadiene with polyols

The use of a low pressure of butadiene is of interest as it allows the set-up of more simple glass reactors and thus avoids the need of specific and less widely accessible high-pressure reactors. However, very few examples of telomerization reaction at atmospheric pressure have been reported. We had proposed the telomerization of glycerol and isosorbide in aqueous medium under gaseous atmosphere of butadiene [25,26]. In that latter case, the reaction rate is lower than with batch conditions and butadiene pressure. This low catalytic activity was attributed to a difficult mass transfer of butadiene in the catalytic phase. We now propose the implementation of the palladium catalyzed telomerisation of glycerol, solketal and isosorbide in biphasic media under atmospheric butadiene pressure by bubbling the gas continuously in the liquid phase via a sintered glass thanks to a home-made designed glass reactor.

2. Experimental

2.1. Materials

Chemicals were purchased from Alfa Aesar, Tokyo Chemical Industry, Janssen Chimica, Sigma Aldrich, Linde (Butadiene) and Strem Chemicals. Isosorbide was generously given by Roquette Frères and used without further purification. The reactor used for the study is given in the SI.

2.2. Telomerization of butadiene with glycerol

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. The catalytic precursor [Pd(acac)₂] and the ligand (TPPTS = TriPhenylPhosphineTriSulfonate) were introduced in the glass reactor. Glycerol was mixed in another Schlenk tube together with methyl ethyl ketone (MEK), dodecane as internal standard (1 mL) and a solution of KOH 1 M. This solution was transferred into the reactor which was then heated at the desired temperature and magnetically stirred in a thermostated bath.

Butadiene at a flow of 2 mL/min was then bubbled in the liquid phase through a frit (see the S.I.). The pressure of butadiene was kept constant by means of a back-pressure regulator fitted at 1.05 bar. During the reaction, samples of the upper phase were taken at defined time slots and analyzed with GC.

During the whole reaction, a biphasic liquid / liquid system is observed. The hydrosoluble catalyst is located in the lower phase that contains glycerol and aqueous base (please see the SI). The upper

phase contains the organic solvent (MEK), the internal standard used for GC analysis (dodecane) and the products of reaction.

2.3. Analyses and quantification of the products

Conversions and yields were determined by gas chromatography using dodecane as internal standard.

The GC analyses were performed on a GC Shimadzu® 2010 equipped with a HT 5 column (30 m, 0.25 mm i.d., 0.25 µm thickness), equipped with a flame ionisation detector (FID).

Conditions: injector and detector = 280°C, gas = nitrogen at 0.64 mL/min, temperature = 150°C, ramp of 10 °C/min up to 270°C.

Telomers were observed as main products. In all analyzed samples, less than 2 % of butadiene dimers were observed.

3. Results and discussion

For this work, we decided to work at atmospheric pressure of butadiene by bubbling the gas into the liquid aqueous phase (See the SI for the reactor). Butadiene was delivered through a frit in order to increase the contact surface of the gas with the water/polyol solution that contains the catalyst. Moreover, thanks to this approach, aliquot samples of the reaction mixture could be taken and analyzed by GC at regular time intervals, allowing to follow the products distribution during the course of the reaction.

First experiments have been performed with glycerol. The polyol was dissolved in a basic aqueous phase and MEK as organic medium was added allowing the extraction of the telomers. The catalytic system was formed from a palladium precursor and the hydrosoluble TPPTS ligand. We initially used catalytic conditions similar to those described in batch mode : 10 mL MEK, 3.6 mL KOH 1 M, 0.03 g Pd(acac)₂ (0.098 mmol), 0.279 g TPPTS (0.475 mmol).[25] Butadiene at a flow of 2.2 mL/min was bubbled in the aqueous phase and the reaction was heated at 80°C.

Applied to glycerol with three OH functions, the formation of mono-, di- and tritelomers could be expected. As the butadiene is introduced continuously, we were interested in the production of telomers and their selectivity along time (Figure 1).

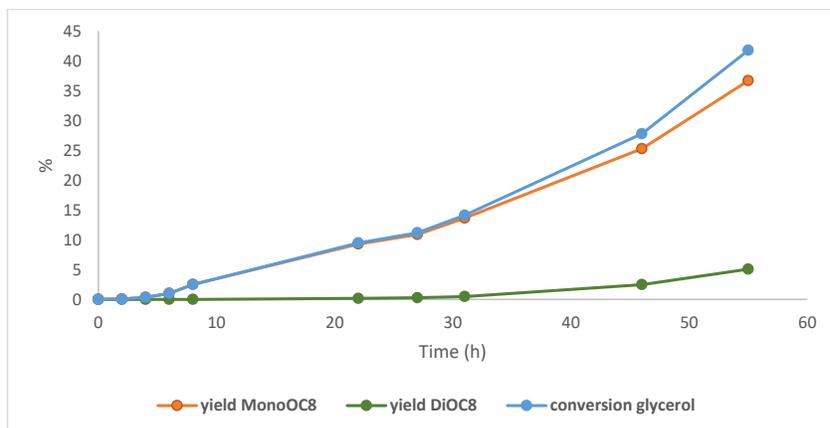


Figure 1 : Telomerization of butadiene with glycerol

Conditions : Glycerol = 15 g (0.163 mol) ; butadiene = 2.2 mL/min ; KOH 1 M = 3.6 mL ; MEK = 10 mL ; [Pd] = 0.06 mol% ; TPPTS/Pd = 5 ; T = 80°C.

During the first 8 hours, the conversion of glycerol and production of ethers remained extremely low. In these reaction conditions, this rather long induction period could correspond to the time necessary to generate Pd(0) catalytic species by *in situ* reduction of the metallic precursor by the phosphine. As the reaction began, the production of monotelomers was constant during the first 30 hours. Consistent with the low glycerol conversion and the efficient extraction of the ethers from the catalytic phase to the organic one, the selectivity in monotelomers was very high within this time period with no ditelomer formed. Surprisingly, longer reaction times led to increasing reaction rates and thus higher products formation along with lower selectivity in monotelomers. 37 % yield of monotelomers (12 g) and 5 % yield of of ditelomers (2.5 g) are obtained (overall 42% glycerol conversion) after 55 h of reaction. The increase of reaction rates that follows the conversion of glycerol appears as related to the composition of the reaction crude that changes with the formation of the ethers. In the case of a butadiene mass transfer limitation, one can expect that the increase of the activity is due to the amphiphilic character of the glycerol monotelomers which contributes

to increase the solubility of butadiene in the water/glycerol catalytic phase. In order to better assess mass transfer limitations and delineate the origin of the rate increase in the course of the reaction, we further studied the impact of other reaction parameters on the formation of glycerol telomers. The effect of catalyst loading was first studied and catalytic reactions conducted with respectively 0.03, 0.06 and 0.12 mol % of palladium-based catalyst were setup using the same reactor and reaction conditions as in the first experiment (Figure 2).

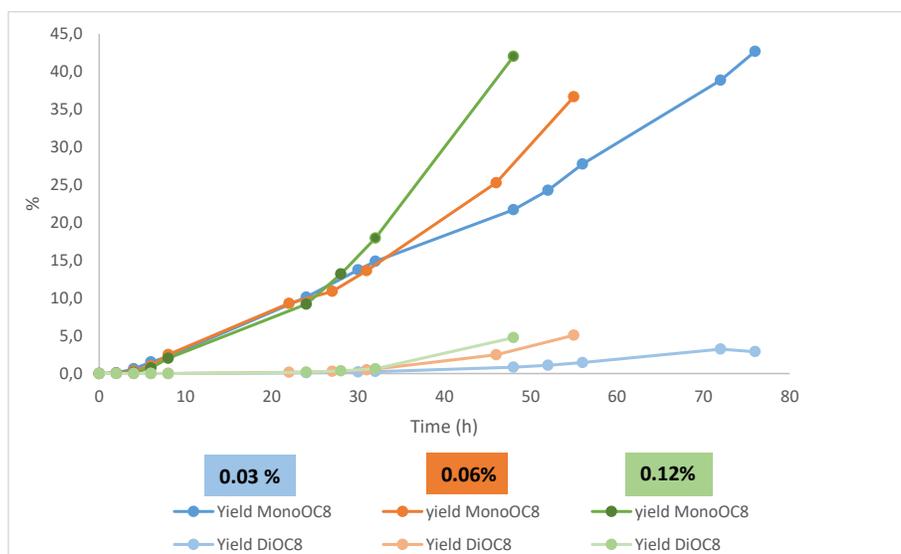


Figure 2: Variation of the catalyst amount during the telomerization of butadiene with glycerol. Conditions : Glycerol = 0.163 mol ; butadiene flow rate = 2.2 mL/min ; [Pd] = X mol% ; KOH 1 M = 3.6 mL ; MEK = 10 mL ; TPPTS/Pd = 5 ; T = 80°C.

The activation time and, very unexpectedly, the reaction rates were very similar whatever the catalyst loading. The telomerization reactions under butadiene pressure are commonly under chemical control and the reaction rates are classically related to the catalyst loadings in homogeneous or biphasic conditions. The independency of reaction rates with catalyst loadings is characteristic of a mass transfer controlling the reaction rate. In the present case, the rate of solubilization of butadiene in the polyol/water phase limits the overall process. Interestingly, after 30 hours of reaction, the three curves clearly diverge and show different reaction rates that follow the expected trend (higher rates for higher catalyst concentrations). As the monotelomers are

produced, these amphiphilic compounds are partitioned between the catalytic aqueous phase and the organic one, thus allowing a better butadiene solubilization into the catalytic phase and favoring the production of the monotelomers together with the subsequent formation of ditelomers. In that case, the butadiene solubilization is no longer a limiting process and the reaction rate is chemically controlled. The reaction rate is increasing with higher catalyst loadings.

We anticipate then that reducing the amount of co-solvent, an important parameter to obtain a high monotelomers selectivity, would allow to observe this acceleration effect more rapidly, while maintaining the telomers in the catalytic aqueous phase. Starting from 10 mL, the volume of MEK was decreased to 5 mL and 1 mL (Figure 3).

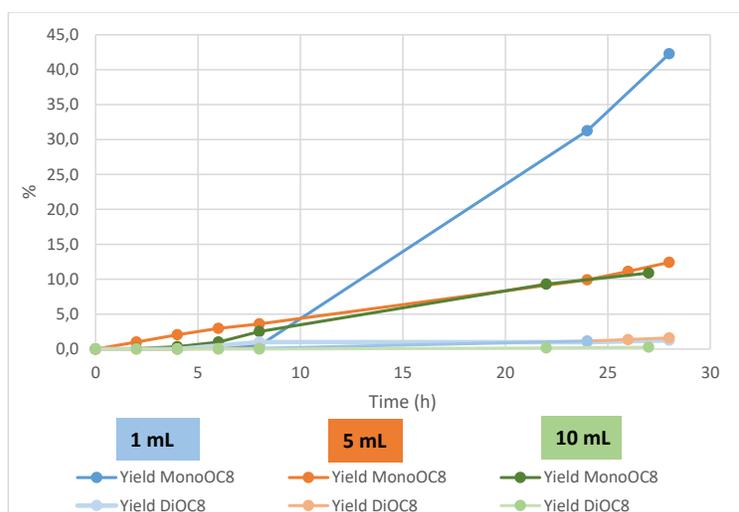


Figure 3: Variation of the MEK volume during telomerization of butadiene with glycerol.

Conditions : Glycerol = 0.163 mol ; butadiene flow rate= 2.2 mL/min ; KOH 1 M = 3.6 mL ; [Pd(acac)₂] = 0.06 mol% ; TPPTS/Pd = 5 ; T = 80°C.

Whereas using 5 and 10 mL of MEK, the average reaction rates appear to be very similar until 25 h, a spectacular activating effect is observed using a lower amount of co-solvent, giving a strong increase of the reaction rate after 8 h. Using a low amount of organic phase, the amphiphilic monotelomers concentration at the interface of this biphasic system is a key parameter favoring an

increase of the butadiene solubilization earlier in respect to the reaction time. A precise analysis of the composition of the reaction mixture was performed at 28 h (Table 1).

Table 1: Effect of MEK volume during glycerol telomerization with butadiene.^a

Entry	MEK (mL)	Glycerol Conversion (%)	Monotelomers Yields (%)	Mono (l/b) ^b	Mono/Di (%/%)
1	10	11	11	79/21	98/2
2	5	14	12	73/27	89/11
3	1	43	42	72/28	95/5

^a Reaction conditions : Glycerol = 15 g (0.163 mol); Pd(acac)₂ = 0.03 g (0.098 mmol); TPPTS/Pd = 5; KOH 1 M = 3.6 mL; T = 80 °C, t = 28 h; Butadiene flow rate = 2.2 mL/min.

^b Measured at t = 10 h.

Monotelomers were major products and the ratios between linear/branched structures were similar in all cases. The reaction with 1 mL of MEK is therefore remarkable since it combines a very high selectivity into monotelomers (95%) and a satisfying conversion of 43% for a reaction using butadiene at atmospheric pressure.

The optimization experiments clearly show that the catalytic system used in this study is rather slow but elsewhere stable for several days and thus suitable for glycerol ethers. The atmospheric pressure reactor used in this study is particularly handy for semi-continuous experiments under constant atmospheric butadiene pressure and would thus allow a selective and continuous production of ethers along with catalytic phase recycling. An experiment was thus performed starting from the reaction conditions used in Figure 1 with 10 mL of MEK in order to facilitate the extraction procedure. This amount of solvent is particularly suitable to perform the extraction of the products formed during the reaction: the phases are rapidly and well separated, the viscosity is low and thus facilitates the solvent extraction with a simple syringe equipped with a fine needle. The telomers containing the organic phase were removed and a new organic phase of MEK containing glycerol was introduced after 24 h of reaction. The amount of added glycerol corresponds to the amount of converted glycerol (determined by GC analysis of the extracted organic phase). This protocol was further iterated several times and the reaction lasted 110 h (Figure 4).

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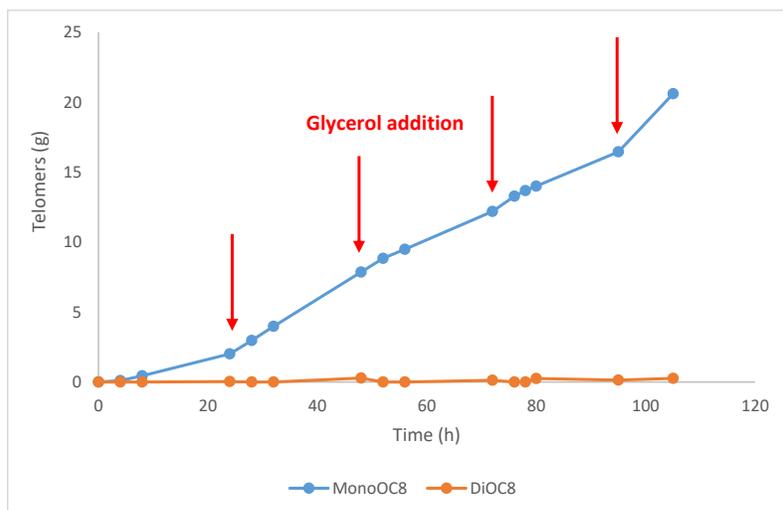


Figure 4 : Telomerization reaction of glycerol. The red arrows indicate the organic phase removal and addition of new reactants (fresh glycerol and organic solvent)

Initial conditions : Glycerol = 0.163 mol; butadiene flow rate = 2.2 mL/min ; KOH 1 M = 3.6 mL ; MEK = 10 mL ; [Pd(acac)₂] = 0.06 mol% ; TPPTS/Pd = 5; T = 80°C.

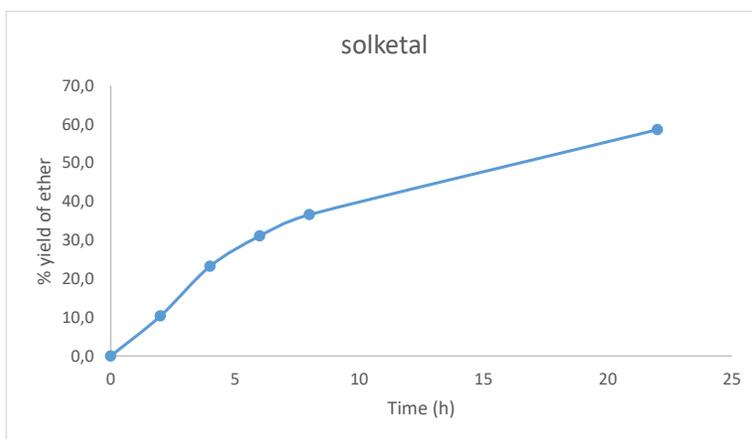
The amount of added glycerol corresponds to the amount of converted glycerol (determined by GC analysis of the extracted organic phases).

The first 24 h of reaction showed the lowest catalytic activity which is explained by the long activation time. The results obtained after 4 recycling steps (Figure 4) evidence a faster and stable productivity of ethers over 110 h of reaction. As expected from the optimization results, the reaction proved to be very selective with 99% of monotelomers and allowed the synthesis of up to 20 g of product (TON=1000) simply recovered after MEK evaporation. The results obtained from this experiment showed that a reaction performed under atmospheric pressure and continuous flow of butadiene with a simple glassware equipment is beneficial for the production of high quantity of pure glycerol monotelomers.

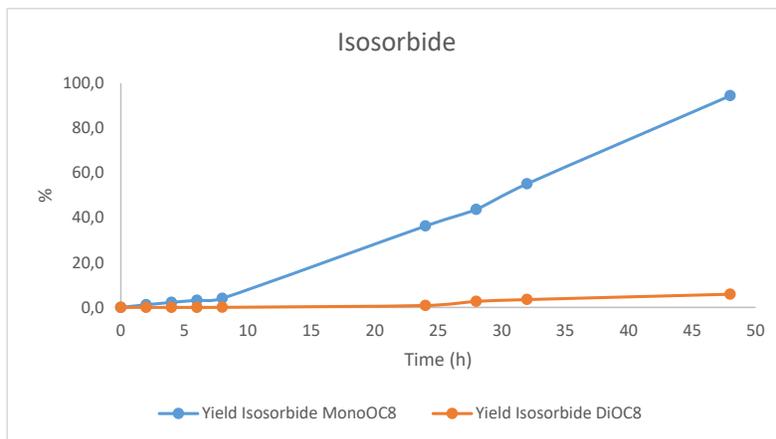
The experimental implementation was extended to solketal and isosorbide (Figure 5). The aim of this approach was to evaluate the impact of the polyol hydrophilicity on the reaction rates. Solketal is a monoalcohol obtained from the acetalization of glycerol with acetone [27]. In contrast to

glycerol, solketal is less polar with two hydroxyl groups masked by the acetal function. With this alcohol, the ligand TPPTS, insoluble in apolar solvent, can be advantageously replaced by the most commonly used TPP (triphenylphosphine). Moreover, no extracting co-solvent is necessary as only monotelomers are obtained. Isosorbide is a diol with two secondary hydroxyl groups industrially produced from the double dehydration of D-sorbitol [28]. Isosorbide has been successfully used as telogen in the telomerization reaction thus leading selectively to any of the two possible monoethers depending on the chosen experimental conditions [26]. In that latter case, the addition of toluene as organic co-solvent, was performed in order to extract the monotelomers from the catalytic phase.

In line with the experiments that involved glycerol as reactant, the evolution of the mass of telomers during the reaction course are described in Figure 5.



Experimental conditions: solketal = 15 g (113 mmol), KOH 1 M = 3.6 mL, dodecane = 1 mL, butadiene flow rate = 2.2 mL/min, [Pd(acac)₂] = 0.06 mol% ; PPh₃/Pd = 5, 80°C.



Experimental conditions: isosorbide = 13.14 g (90 mmol), [Pd(acac)₂] = 0.06 mol% ; TPPTS/Pd = 5, toluene = 10 mL, KOH 1 M = 3.6 mL, dodecane = 1 mL, 80°C, butadiene flow rate = 2.2 mL/min

Figure 5 : Telomerization reaction with solketal and isosorbide with continuous butadiene flow.

The reaction with solketal didn't show any induction period and was clearly much faster than with glycerol. The absence of activation time is coherent with most of catalytic reactions performed under butadiene pressure with the TPP ligand in homogeneous conditions or the TPPTS ligand in biphasic conditions [5],[6]. The different nature of the ligands used thus doesn't explain this difference of reactivity. In all cases, long activation times have been observed under low butadiene pressure and it is thus striking that in a lipophilic alcohol such as solketal that easily solubilizes butadiene, no activation time is observed under atmospheric pressure. This indicates that not only the alcohol nor the phosphine are involved in the key catalyst activation (palladium reduction), butadiene is also involved and one can expect that this is related to a higher stabilization of transient palladium(0) species by the diene. The higher solubility of butadiene in solketal additionally explains the higher reaction rate obtained with this alcohol in comparison to glycerol. In the case of isosorbide, which necessitates the use of the Pd/TPPTS catalytic system and the addition of a co-solvent (toluene), an induction time is observed. Nevertheless, as the reaction began, the observed rate is higher than with glycerol probably because of the lesser hydrophilic character of

isosorbide in comparison to glycerol. After 22 h of reaction, the conversion of isosorbide is complete and isosorbide monoethers are obtained with a 94 % yield (22 g of product).

4. Conclusion

Telomerization of various bio-based alcohols as glycerol, isosorbide and solketal with butadiene at atmospheric pressure has been successfully performed with a non-pressurized glassware reactor that allows bubbling of butadiene in the catalytic phase. Very high selectivities toward monotelomers could be achieved with glycerol by using water/MEK biphasic media and the Pd/TPPTS catalytic system. The reaction necessitates a long activation time and the study of the reaction parameters clearly shows a low mass transfer-controlled reaction rate. The rate is more particularly limited by the low solubility and slow solubilization of butadiene in the catalytic phase. The less hydrophilic solketal as better butadiene solvent than water is rapidly converted without any initial activation time while isosorbide reacted more slowly after an activation period. In the case of glycerol, the formation of monotelomers that favors the solubilization of butadiene in the aqueous catalytic phase increases the rate of glycerol etherification in the course of the reaction. Monotelomers can be synthesized selectively albeit with a low reaction rate thanks to the removal of the MEK/monotelomers phase after 24 h of reaction. This could be repeated in this study four times every 24 hours using the same catalytic mixture. We believe that this system can be easily setup and up-scaled, the excess of unreacted butadiene being recycled or looped back to the reactor.

Acknowledgements

This work (M. Drelon's fellowship) was financially support by the State as part of the "Programme d'Investissement d'Avenir" under reference ANR 15-CE07-0018-01 H2CAT. We acknowledge the Ministère de l'Enseignement supérieur, de la Recherche et de l'Innovation, the Institut Universitaire de France and the CNRS for their financial support. We also would like to thank Céline Delabre for her technical support (GC analysis of the crudes) and Maïa Matsakis for the construction of the glass reactor.

References

- [1] Anastas, P. T.; Zimmerman, J. B., Design through the 12 principles of green engineering, *Env. Sci. Technol.* 37 (2003) 95A–101A.
DOI: 10.1021/es032373g
- [2] Zimmerman, J. B.; Anastas, P. T.; Erythropel, H. C. ; Leitner, W., Designing for a green chemistry future, *Science* 367 (2020) 397–400.
DOI: 10.1126/science.aay3060.
- [3] Sheldon R. A., The road to biorenewables : carbohydrates to commodity chemicals, *ACS Sustainable Chem. Eng.* 6 (2018), 4464–4480.
DOI : 10.1021/acssuschemeng.8b00376.
- [4] Hülsey M. J. ; Yang H.; Yan N., Sustainable routes for the synthesis of renewable heteroatom-containing chemicals *ACS Sustainable Chem. Eng.* 6 (2018) 5694–5707.
DOI : 10.1021/acssuschemeng.8b00612
- [5] Behr, A.; Becker, M.; Beckmann, T.; Johnen L.; Leschinski, J.; Reyer, S., Telomerization: Advances and Applications of a Versatile Reaction, *Angew. Chem. Int. Ed.* 48 (2009) 48, 3598–3614.
DOI: 10.1002/anie.200804599
- [6] Faßbach, T. A.; Vorholt, A. J.; Leitner W., The Telomerization of 1,3-Dienes – A Reaction Grows Up, *ChemCatChem* 2019, 11, 1153–1166.
DOI:10.1002/cctc.201801821.
- [7] Yoshimura N., Ed. Wiley VCH, Multiphase homogeneous catalysis (2005) 221–224.
DOI : 10.1002/9783527619597
- [8] Klinkenberg, J. L.; Lawry, K. P., Sterically encumbered and poorly electron-donating oxaphosphaadamantane ligands for the Pd-Catalyzed telomerization of butadiene with methanol, *Org. Process. Res. Dev.* 23 (2019) 1654–1658.
DOI : 10.1021/acs.oprd.9b00018
- [9] Jackstell, R.; Frisch, A.; Beller, M.; Röttger, D.; Malaun, M.; Bildstein, B. Efficient telomerization of 1,3-butadiene with alcohols in the presence of in situ generated palladium(0) carbene complexes, *J. Mol. Catal. A: Chem.* 185 (2002) 105–112.
DOI : 10.1016/S1381-1169(02)00068-7

[10] Grotevendt, A. ; Bartolome, M. ; Nielsen, D. J. ; Spannenberg, A. ; Jackstell, R. ; Cavell, K. J. ; Oro, L. A., Beller, M. Efficient catalyst for telomerisation of butadiene with amines, *Tetrahedron Lett.* 48 (2007) 9203–9207.

DOI : 10.1016/j.tetlet.2007.10.076

[11] Suslov, D. S.; Bykov, M. V.; Belova, M. V.; Abramov, P. A.; Tkach, V. S., Palladium(II)-acetylacetonate complexes containing phosphine and diphosphine ligands and their catalytic activities in telomerisation of 1,3-dienes with diethylamine, *J. Organomet. Chem.* 752 (2014) 37–43.

DOI : 10.1016/j.jorganchem.2013.11.017

[12] Benvenuti, F.; Carlini, C.; Lami, M.; Marchionna, M. ; Patrini, R. ; Raspolli Galetti, A. M. ; Sbrana, G. Telomerization of 1,3-butadiene with alcohols catalyzed by homogeneous palladium(0) complexes in the presence of mono- and diphosphine ligands, *J. Mol. Catal. Chem. A*, 144 (1999) 27–40.

DOI : 10.1016/S1381-1169(98)00349-5

[13] Jackstell, R.; Gómez Andreu, M.; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller M., A highly efficient catalyst for the telomerization of 1,3-dienes with alcohols: first synthesis of a monocarbene-palladium(0)-olefin complex, *Ang. Chem., Int. Ed.* 41 (2002) 986–989.

DOI : 10.1002/1521-3773(20020315)41:6<986::AID-ANIE986>3.0.CO;2-M

[14] Clement, N. D.; Routaboul, L.; Grotevendt, A.; Jackstell, R. ; Beller, M., Development of palladium-carbene catalysts for telomerization and dimerization of 1,3-dienes: from basic research to industrial applications, *Chem. Eur. J.* 14 (2008) 7408–7420.

DOI : 10.1002/chem.200800858

[15] Faßbach, T. A.; Kirchmann, R.; Behr, A.; Romanski, S.; Leinweber, D.; Vorholt, A. J. , Telomerization of 1,3-butadiene with highly substituted alcohols using Pd/NHC-catalysts - Structure-reactivity-relationship of the O-nucleophile, *J. Mol. Catal.* 423 (2016) 526–532.

DOI : 10.1016/j.molcata.2016.05.002

[16] Briggs, J. R.; Hagen, H.; Julka, S.; Patton, J. T., Palladium-catalyzed 1,3-butadiene telomerization with methanol. Improved catalyst performance using bis-*o*-methoxy substituted triarylphosphines, *J. Organomet. Chem.* 696 (2011) 1677–1686.

DOI : 10.1016/j.jorganchem.2011.02.007

[17] Herrmann, N.; Vogelsang, D.; Behr, A.; Seidensticker, T., Homogeneously Catalyzed 1,3-Diene Functionalization - A Success Story from Laboratory to Miniplant Scale, *ChemCatChem* 10 (2018) 5342–5365.

DOI : 10.1002/cctc.201801362

[18] Smutny, E. J., Oligomerization and dimerization of butadiene under homogeneous catalysis. Reaction with nucleophiles and the synthesis of 1,3,7-octatriene, *J. Am. Chem. Soc.*, 89 (1967) 6793–6794.

DOI : 10.1021/ja01001a089

[19] Takahashi, S.; Shibano, T.; Hagihara, N., The dimerization of butadiene by palladium complex catalysts, *Tetrahedron Lett.* 26 (1967), 2451–2453.

DOI : 10.1016/S0040-4039(00)90830-X

[20] Faßbach T. A., Behr A., Vorholt A. J. (2017) Telomerisation of Renewables. In: *Homogeneous Catalysis with Renewables. Catalysis by Metal Complexes*, vol 39. Springer, Cham, 81–91.

DOI : 10.1007/978-3-319-54161-7_5

[21] Bouquillon, S.; Muzart, J.; Pinel, C.; Rataboul F., Palladium-catalyzed telomerization of butadiene with polyols: from mono to polysaccharides, In: Rauter A., Vogel P., Queneau Y. (eds) *Carbohydrates in Sustainable Development II. Topics in Current Chemistry* (2010) vol 295. Springer, Berlin, Heidelberg

DOI : 10.1007/128_2010_53

[22] Bruijninx P.C.A., Jastrzebski R., Hausoul P.J.C., Gebbink R.J.M.K., Weckhuysen B.M. Pd-Catalyzed Telomerization of 1,3-Dienes with Multifunctional Renewable Substrates: Versatile Routes for the Valorization of Biomass-Derived Platform Molecules. In: Meier M., Weckhuysen B., Bruijninx P. (eds) *Organometallics and Renewables*. (2012) *Topics in Organometallic Chemistry*, vol 39. Springer, Berlin, Heidelberg.

DOI : 10.1007/978-3-642-28288-1_2

[23] Drelon, M.; Merel, D. S.; Mortreux, A.; Suisse, I.; Sauthier, M., Towards Selective Syntheses of Octadienylethers from the Butadiene Palladium-catalyzed Telomerization with Polyols in Aqueous Biphasic Medium, *ChemCatChem* 11 (2019) 1742–1746.

DOI : 10.1002/cctc.201802068

[24] Hausoul, P.J.C.; Bruijninx, P.C.A.; Weckhuysen, B.M.; Gebbink, R.J.M.K., Pd/TOMPP-catalyzed telomerization of 1,3-butadiene: from biomass-based substrates to new mechanistic insights, *Pure and Applied Chemistry* 84 (2012), 1713–1727.

DOI : 10.1351/PAC-CON-11-12-06

[25] Bigot, S.; Lai, J.; Suisse, I.; Sauthier, M.; Mortreux, A.; Castanet, Y., Telomerisation of 1,3-butadiene with glycerol under aqueous biphasic conditions: Influence of the reaction conditions on the products distribution, *Applied Catalysis A: General* 382 (2010) 181–189.

DOI : 10.1016/j.apcata.2010.04.039

[26] Lai, J.; Bigot, S.; Sauthier, M.; Molinier, V.; Suisse, I.; Castanet, Y.; Aubry, J.-M.; Mortreux A., Telomerisation of 1,3-butadiene with 1,4:3,6-dianhydrohexitols: an atom-economic and selective synthesis of amphiphilic monoethers from agro-based diols, *ChemSusChem* 4 (2011) 1104–1111.

DOI : 10.1002/cssc.201100135

[27] Da Silva, C. X. A.; Goncalves, V. L. C.; Mota, C. J. A.; Water-tolerant zeolite catalyst for the acetalisation of glycerol, *Green Chem.* 11 (2009) 38-41.

DOI: 10.1039/B813564A

[28] Dussenne, C.; Delaunay, T.; Wiatz, V.; Wyart, H.; Suisse I.; Sauthier M., Synthesis of isosorbide: an overview of challenging reactions, *Green Chem.* 19 (2017) 5332–5344.

DOI : 10.1039/c7gc01912b