



Towards a process for the telomerization of butadiene with *N*-methylglucamine

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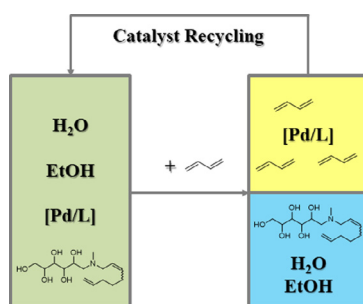
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HIGHLIGHTS

- One-step reaction to surfactants from bulk chemicals using homogeneous catalysis.
- Aqueous solvent systems ensure monophasic behavior during the reaction.
- New concept for recycling of the telomerization catalyst using the non-polar phase.

GRAPHICAL ABSTRACT



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ABSTRACT

The telomerization of 1,3-dienes with functionalized nucleophiles presents an atom efficient and selective synthesis of potential non-ionic surfactants. Crucial for application of these synthetic pathways is the effective recycling of the homogeneous palladium catalyst. In this work, we present the telomerization of 1,3-butadiene with the renewable aminopolyol *N*-methylglucamine to a non-ionic surfactant in an aqueous solvent system. In order to achieve phase separation, the addition of freshly added 1,3-butadiene instead of an additional solvent offers an elegant way of catalyst recycling. With this method, recycling of the catalyst is feasible; a total turnover number of 1456 was reached.

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1. Introduction

In the field of homogenous transition metal catalysis, the term *telomerization* refers to a dimerization of 1,3-dienes, while a nucleophile is added to the newly formed 2,7-octadienyl chain (Scheme 1). (Arno Behr et al., 2009a, 2009b)

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The versatility of this reaction results from the numerous combinations of different 1,3-dienes and nucleophiles. Aside from 1,3-butadiene, which is the most widely used diene for this reaction, other 1,3-dienes, like isoprene (Gordillo et al., 2009; Jackstell et al., 2007; Leca and Réau, 2006), piperylene (Neubert et al., 2016; Torrente-Murciano et al., 2010) and β -myrcene (Behr et al., 2010) have been applied successfully. The scope for employable nucleophiles includes different alcohols, amines, CO₂ and more. (Arno Behr et al., 2009a, 2009b) Polyvalent alcohols, e.g. glycerol, sugars and sugar alcohols, are promising substrates for

Nomenclature

List of symbols/abbreviations

Symbol/abbreviation meaning [given in [Unit]]

NMG	<i>N</i> -methylglucamine [–/–]
mol%	mole percent [[mol·mol ⁻¹ ·100]]
<i>n</i>	amount of substance [millimoles [mmol]]
<i>m</i>	mass [grams [g]]
<i>t</i>	time [hours [h]]

<i>T</i>	temperature [degrees celsius [°C]]
<i>p</i>	pressure [bars [bar]]
(<i>T</i>)TON	(total) turnover number [[mol·mol ⁻¹]/[–]]
ICP-OES	inductively coupled plasma optical emission spectroscopy [–/–]
<i>M/P</i>	metal/phosphorous-ratio [[mol·mol ⁻¹]/[–]]
TOF	Turnover frequency [[mol·mol ⁻¹ ·h ⁻¹]/[h ⁻¹]]

the synthesis of non-ionic surfactants, if they are alkylated in a selective manner (Bouquillon et al., 2010). Under these promising polyols, the renewable polyol amine *N*-methylglucamine (NMG), which is obtained by reductive amination of glucose (Scheme 2) (Foley et al., 2012; Hill and Rhode, 1999), occupies a special position, because of its secondary amino group.

The secondary amino group is much more active in the telomerization than the primary or secondary alcohol groups, which makes it possible to selectively alkylate this position only (Grotevendt et al., 2007). Recently, we demonstrated this in the telomerization of β -myrcene with *N*-methylglucamine, leading to surface active products (Faßbach et al., 2017). However, this method suffers from two major drawbacks. Firstly, the asymmetric substitution of the 1,3-diene unit at position 2 leads to a variety of different product isomers, whereas 1,3-butadiene leads almost exclusively to a linear, non-substituted 2,7-octadienyl chain (Scheme 3).

Secondly, the high polarity gap between water-soluble *N*-methylglucamine (1 g L⁻¹) and insoluble β -myrcene (<30 mg L⁻¹) (I. Fichan et al., 1999) can only be effectively overcome by using amphiphilic ligands. On the downside, that means that an efficient catalyst recycling by phase separation is intrinsically difficult.

The main target of this work is the conceptualization of a process to carry out the telomerization of 1,3-dienes with *N*-methylglucamine. For this, two main goals were set that have been taken into account at each level of the process development. Firstly, reaction conditions have to be found that allow for an efficient conversion. This includes the choice of a catalyst, a solvent system, as well as the reaction time and temperature. All these factors have to be evaluated with regards to a catalyst recycling concept that enables the reuse of the homogeneous precious metal catalyst. In the presented case, this is achieved with a rather unusual immobilization of the catalyst in the non-polar phase (Scheme 4).

2. Materials and methods

2.1. Batch experiments

Initial screening experiments were performed in a 25 mL custom-made stainless steel autoclave (Behr et al., 2008). The catalyst was weighed directly into the reactor pot. The *N*-methylglucamine was added as a saturated stock solution (1 g NMG in 1 g H₂O), the additional solvent was added afterwards. The reactor was closed and 1,3-butadiene was added volumetrically via a pressure-resistant tube. To determine the accurate mass of the added 1,3-butadiene, the reactor was weighed before and after addition. The reactor was placed in a heated aluminum block at 80 °C. The reaction was magnetically stirred at 500 rpm.

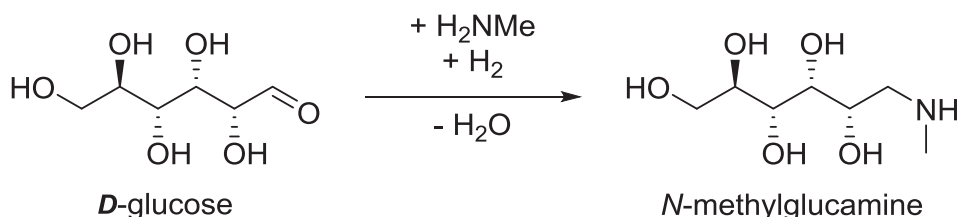
2.2. Recycling experiments

The recycling experiments were carried out using a glass reactor in a fixed setup (see Supporting Information, Fig. S4 and S5). The aqueous solution of *N*-methylglucamine was prepared in the desired concentration and put in the reactor with a long syringe through the ball valve. The catalyst (Pd(acac)₂ and triphenylphosphine) was dissolved in ethanol and added to the aqueous solution. The reactor setup was closed and 1,3-butadiene was added via a pressure resistant tube. The amount of butadiene was determined volumetrically. The glass reactor was heated in an oil bath and magnetically stirred at 500 rpm.

After the reaction was finished, the reactor was cooled down using an ice-bath to add fresh 1,3-butadiene for extracting the catalyst. After five minutes of stirring, the reactor was heated up to 50 °C for optimal phase separation. The product phase was removed using a PTFE capillary. Finally, a new stock solution containing water, ethanol and *N*-methylglucamine was added through the same capillary using argon pressure.



Scheme 1. Telomerization of 1,3-butadiene with an amine.



Scheme 2. Synthesis of *N*-methylglucamine from glucose.

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