Tetrahedron Letters 59 (2018) 832–835

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of glycol diesters through the depolymerization of polyethylene glycols with carboxylic acids using a proton-exchanged montmorillonite catalyst

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ARTICLE INFO

Article history:
Received 27 November 2017
Revised 13 January 2018
Accepted 19 January 2018
Available online 31 January 2018

Keywords:
Glycol diesters
Depolymerization
Solid acid catalyst
C–O bond cleavage
Polyethylene glycols

ABSTRACT

A convenient and sustainable method for the synthesis of glycol diesters was developed through the depolymerization of polyethylene glycols (PEGs) with carboxylic acids using proton-exchanged montmorillonite as an efficient solid acid catalyst. Several functionalized glycol diesters were obtained in good yields from PEGs and readily available carboxylic acids. Upon reaction completion, the catalyst could be easily separated by filtration and reused with its activity remaining unchanged.

Glycol diesters, which are highly useful as solvents and synthetic intermediates of functionalized materials,[1] are generally synthesized through the acylation of glycols with acyl chlorides or carboxylic anhydrides (Scheme 1a and b).[2] However, these conventional methods suffer from the formation of stoichiometric amounts of HCl or carboxylic acids as by-products. In addition, these acylating reagents are prepared through a stoichiometric reaction of carboxylic acids with $SOCl_2$ or dehydration reagents, which results in the concomitant formation of hazardous halogenated or organic waste. Since these methods are not suitable for sustainable green chemistry,[3] a simple and atom-economical method for synthesizing glycol diesters would be highly desirable. In this context, the acid-catalyzed condensation of glycols and carboxylic acids has received significant attention,[4] because carboxylic acids are readily available acylating reagents, and water is formed as the sole by-product in this case (Scheme 1c). Recently, our research group demonstrated the exploitation of unutilized PEG waste[5] as the oxyethylene units of glycol diesters through the depolymerization of PEGs with carboxylic anhydrides using proton-exchanged montmorillonite (H^+-mont) as a layered solid acid catalyst.[6] It is envisioned that the use of carboxylic acids for the depolymerization of PEGs would represent a more convenient and sustainable method for the synthesis of glycol diesters (Scheme 1d). In this study, the depolymerization of PEGs with carboxylic acids is investigated using solid acid catalysts, including various cation-exchanged montmorillonite catalysts.[7] The depolymerization of PEGs with carboxylic acids possessing various functional groups is also examined.

Previously, we reported that H^+-mont efficiently catalyzes the depolymerization of PEGs with a mixture of acetic anhydride/acetic acid (Ac_2O/AcOH) at 100 °C to give ethylene glycol diacetate (**3a**). However, the use of AcOH alone instead of Ac_2O/AcOH results in the formation of **3a** in an extremely low yield.[6] Accordingly, the depolymerization of tetraethylene glycol (**1a**) with AcOH (**2a**) to give **3a** was carried out at 160 °C in the presence of various solid acid catalysts, including cation-exchanged montmorillonites (M^{n+}-mont, M^{n+} denotes a metal species or proton).[8] Of the various M^{n+}-mont catalysts tested, H^+-mont exhibited the highest catalytic activity, affording **3a** in 55% yield after 2 h (Table 1, entry 1). The use of Al^{3+}- and Ti^{4+}-mont produced **3a** in 22% and 10% yield, respectively (Entries 4 and 5). On the other hand, other M^{n+}-monts, such as Cu^{2+}-, Ni^{2+}-, La^{3+}-, Zr^{4+}-, and Ce^{3+}-mont, did not promote the depolymerization of **1a** with **2a** (Entries 6–10). Commercially available solid acid catalysts, such as Amberlyst 36 and Nafion NR50, produced **3a** in 45% and 33% yield, respectively. Their turnover frequency (TOF) values were lower than that of H^+-mont (Entries 12 and 13).[9] The solid acid catalysts SiO_2-Al_2O_3, SO_4^{2-}/ZrO_2, and H^+-mordenite showed extremely low activities (Entries 14–16). These results suggest that H^+-mont acts as a highly active

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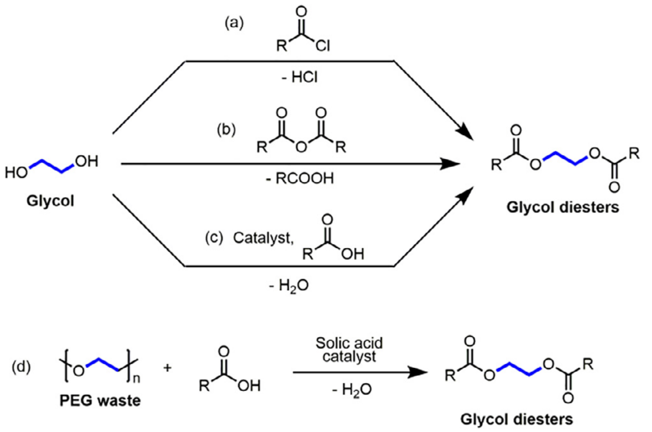
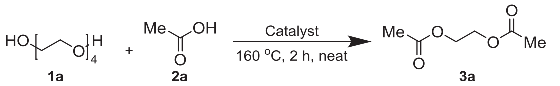
https://doi.org/10.1016/j.tetlet.2018.01.056



Scheme 1. Conventional synthesis of glycol diesters from glycol with (a) acyl chlorides, (b) acid anhydrides, and (c) carboxylic acids. (d) Synthesis of glycol diesters from carboxylic acids and PEG waste as the glycol unit.

Table 1
Depolymerization of tetraethylene glycol with acetic acid using various acid catalysts.



Entry	Catalyst	Yield [%][a]	TOF [h^{-1}][b]
1	H^+-mont	55	15.2
2	H^+-mont (24 h)	89	–
3	H^+-mont (24 h, 2nd reuse)	90	–
4	Al^{3+}-mont	22	7.0
5	Ti^{4+}-mont	10	8.7
6	Cu^{2+}-mont	4	–
7	Ni^{2+}-mont	<1	–
8	La^{3+}-mont	<1	–
9	Zr^{4+}-mont	<1	–
10	Ce^{3+}-mont	<1	–
11	Na^+-mont	<1	–
12	Amberlyst 36	45	2.0
13	Nafion NR50	33	10.0
14	SiO_2/Al_2O_3	<1	–
15	SO_4^{2-}/ZrO_2	<1	–
16	H^+-mordenite	3	–

Reagents and conditions: catalyst (0.05 g), **1a** (0.1165 g, 2.4 mmol per oxyethylene subunit), AcOH (**2a**) (2.75 mL).

[a] Determined by GC using an internal standard. Based on the total amount of the oxyethylene unit of **1a**.

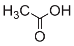
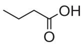
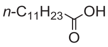
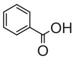
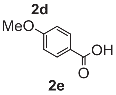
[b] TOF = (molar amount of **3a** produced)/(mol H^+ h).

solid acid catalyst for the depolymerization **1a** with **2a**. Furthermore, when the reaction time was increased to 24 h, H^+-mont gave **3a** in 89% yield (Entry 2). After the reaction, H^+-mont was separable by filtration, and the recovered catalyst was reusable without a significant loss in activity (Entry 3).[10]

The depolymerization of low-molecular-weight PEG (**1b**, Mn ≈ 400, Mn denotes the number-average molecular weight) with various carboxylic acids was carried out using H^+-mont (Table 2). Butyric acid (**2b**) reacted with **1b** to give ethylene glycol dibutyrate **3b** in 81% yield (Entry 2). The reaction of **1b** with a fatty acid, lauric acid (**2c**), proceeded to afford ethylene glycol dilaurate (**3c**) in an isolated 87% yield (Entry 3). Saturated carboxylic acids are suitable for this reaction. However, the reaction of **1a** with carboxylic acids containing an olefin moiety, such as cinnamic acid and 2,3-diphenylacrylic acid, did not give the desired product and yielded unknown viscous products. Aromatic carboxylic acids, such as benzoic acid (**2d**), *p*-methoxybenzoic acid (**2e**), and 1-naphthoic acid (**2f**), were successfully used for the synthesis of the corresponding monomer glycol diesters (**3d**, **3e**, and **3f**) from **1b** (Entries 4–6). Carboxylic acids containing a nitrogen atom, such as *N*-phthaloylglycine (**2g**), were also used for the depolymerization of **1b**, resulting in 1,2-bis(*N*-phthaloylglycyl)ethane (**3g**) in 54% yield (Entry 7). The use of succinic acid (**2h**), which is a dicarboxylic acid, for the depolymerization of **1b** afforded the corresponding glycol diesters containing two terminal carboxylic acid groups (**3h**) in 79% yield (Entry 8). Although **3 h** is a potentially suitable compound for polyester synthesis,[1e,1g] poly(ethylene glycol succinate) was not formed in this reaction. When formic acid (**2i**) was used as a carboxylic acid source, glycol diformate (**3i**) was obtained in only 24% yield (Entry 9). The low yield of **3i** might be due to the instability of the desired product. From a synthetic organic chemistry standpoint, depolymerization using chloroacetic acid is of great interest, as shown in Scheme 2. The reaction of chloroacetic acid (**2j**) with **1b** gave 1,2-bis(chloroacetoxy)ethane (**3j**) in 71% yield. Compound **3j** is the starting compound for ethylene glycol bis(azidoacetate) **4**, which is useful as a plasticizer and cross-linker,[1 h,1i] as well as for the biodegradable surfactant **5**.[1f] Various functionalized glycol diesters were synthesized through the depolymerization of PEGs with the corresponding carboxylic acids using H^+-mont as the catalyst.

The catalytic depolymerization of several PEGs with **2a** was also investigated using H^+-mont. The reaction of low-molecular-weight PEG (**1b**, Mn ≈ 400) with **2a** afforded **3a** in 85% yield (Table 3, entry 1), while in the case of middle-molecular-weight PEGs (**1c**, Mn ≈ 1000) the yield was 69% at 230 °C (Entry 2). The reaction of high-

Table 2
Depolymerization of polyethylene glycol (Mn ≈ 400, **1b**) with various carboxylic acids using H^+-mont.

Entry	Carboxylic acid **2**	**2** [equiv.]	H^+-mont [g]	Temp. [°C]	Time [h]	Product **3**	Yield [%]
1	 **2a**	10	0.4	160	24	**3a**	85[a]
2	 **2b**	10	0.05	160	3	**3b**	81[a]
3	 **2c**	5	0.4	160	11	**3c**	87[b]
4	 **2d**	10	0.4	180	24	**3d**	81[c]
5	 **2e**	10	0.05	185	48	**3e**	74[c]

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