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Synthesis of tetraline derivatives through depolymerization of polyethers with aromatic compounds using a heterogeneous titanium-exchanged montmorillonite catalyst†

Zen Maeno, Hiroyuki Torii, Shota Yamada, Takato Mitsudome, Tomoo Mizugaki and Koichiro Jitsukawa*

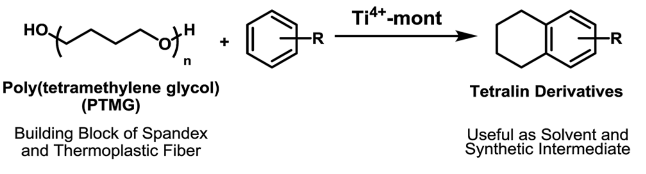
A novel depolymerization of poly(tetramethylene glycol) (PTMG) with benzene to tetralin using titanium-exchanged montmorillonite (Ti^{4+}-mont) as a solid acid catalyst is described. This catalyst is applicable to depolymerization of PTMG with some aromatic compounds. This is the first demonstration of the potential use of PTMG as a C4 synthon for organic synthesis.

Polymer waste is managed mainly through incineration or deposit in landfills.[1] However, these disposal techniques can cause environmental damage such as carbon dioxide emissions and soil pollution. Catalytic depolymerization is a more desirable management method because the waste polymers can be used to synthesize low-molecular-weight chemicals.[2] Using homogeneous catalysts, depolymerization reactions of polyethers, such as reductive cleavage to alkanes,[3a] acylative cleavage to esters,[3b–d] and cyclization to cyclic ethers,[3e,f] have been reported. However, these homogeneous catalyst systems often are limited by the separation of the products and the reuse of the catalyst. To carry out green sustainable chemistry, a heterogeneous catalyst system for the depolymerization of polyethers needs to be developed.

Montmorillonite ($(Na_{0.66}(OH)_4Si_8(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$, Na^+-mont) is a clay mineral consisting of negatively charged aluminosilicate layers and exchangeable Na cations in the interlayer spaces. Catalytically active cation species can be introduced into the interlayer by cation exchange.[4,5] The interlayer space of mont expands and intercalates various molecules, including organic polymers.[6] Based on these cation-exchange and intercalation abilities, an efficient method for the depolymerization of polyethers with acid chlorides to chloroalkyl esters using a proton-exchanged montmorillonite catalyst was developed.[7] Thus, cation-exchanged montmorillonites have the potential to act as effective heterogeneous catalysts for the depolymerization of other polyethers.

The aim of this work is the development of novel heterogeneously-catalyzed depolymerization of polyethers using montmorillonite catalyst. Herein, we achieved the depolymerization of poly(tetramethylene glycol) (PTMG) with benzene to tetralin using a titanium-exchanged montmorillonite catalyst (Ti^{4+}-mont) (Scheme 1). This catalytic system was applied to the depolymerization of PTMG with other aromatic compounds. This is the first report of the depolymerization of polyethers through the alkylation of aromatic compounds and of the use of PTMG as a C4 synthon.

The Ti^{4+}-mont was prepared according to a previously reported method (total amount of acid sites: 0.26 mmol g^{-1}).[5b] Depolymerization of PTMG ($M_n \approx 2000$) with benzene was investigated in the presence of various solid acid catalysts, including cation-exchanged montmorillonite (M^{n+}-mont, M^{n+} denotes metal species or proton). Among the M^{n+}-mont catalysts tested, Ti^{4+}-mont exhibited the greatest catalytic activity to afford tetralin in 86% yield (Table 1, entry 1). The Al^{3+}-, H^+-, and Cu^{2+}-mont also promoted the reaction, but yields were moderate to low (entries 3–5). The use of La^{3+}-mont or the parent Na^+-mont did not provide tetralin (entries 6 and 7). The commercially available solid acid catalyst, Nafion NR50, possessed extremely low catalytic activity (entry 8), and the solid acid catalysts, Amberlyst 36, SiO_2/Al_2O_3, SO_4^{2-}/ZrO_2, and H^+-mordenite, minimally promoted depolymerization to tetralin (entries 9–12). Typical homogeneous acids, *p*-TsOH monohydrate and trifluoroacetic acid, did not catalyze this depolymerization (entries



Scheme 1 Depolymerization of PTMG with aromatic compounds into tetralin derivatives.

Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. E-mail: jitkk@cheng.es.osaka-u.ac.jp; Fax: +81-6-6850-6261

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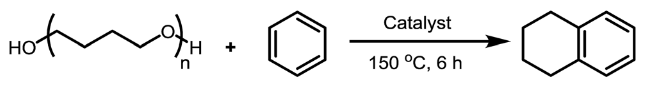
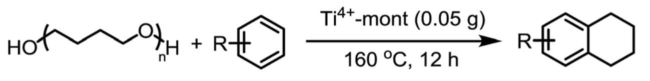
Table 1 Depolymerization of PTMG with benzene to tetralin using various acid catalysts[a]

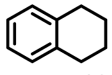
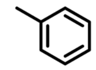
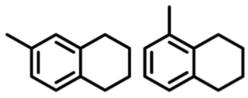
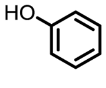
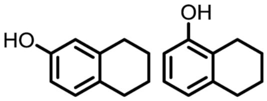
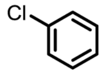
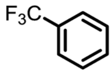
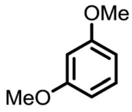
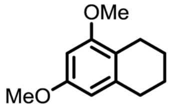


Entry	Catalyst	Yield[b]
1	Ti^{4+}-mont	86[c]
2	Ti^{4+}-mont (2nd reuse)	84[c]
3	Al^{3+}-mont	52
4	H^+-mont	47
5	Cu^{2+}-mont	10
6	La^{3+}-mont	0
7	Na^+-mont	0
8	Nafion NR50	3
9	Amberlyst 36	0
10	SiO_2/Al_2O_3	0
11	SO_4^{2-}/ZrO_2	0
12	H^+-mordenite	0
13	*p*-TsOH monohydrate[d]	0
14	CF_3COOH[d]	0

[a] Reaction conditions: Catalyst (0.2 g), PTMG (0.3 mmol per oxytetramethylene unit), benzene (8 mL). [b] Determined by GC using an internal standard technique and based on the amount of oxytetramethylene units in the used PTMG. [c] A trace amount of 1,2,3,4,5,6,7,8-octahydrophenanthrene was also generated. [d] 0.052 mmol.

Table 2 Scope of aromatic compounds in Ti^{4+}-mont catalyzed depolymerization of PTMG to tetralin derivatives[a]



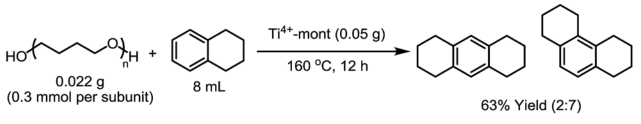
Entry	Aromatic compound	Tetralin derivatives[b]
1		 75% Yield
2		 65% Yield (3:2)
3	 	 68% Yield (1:1)
4[c]	 	N.D.[e]
5[c]	 	N.D.[e]
6[d]	 	 64% Yield

[a] Reaction conditions: Ti^{4+}-mont (0.05 g), PTMG (0.3 mmol per oxytetramethylene unit), aromatic compound (8 mL), 160 °C, 12 h. [b] Determined by GC using an internal standard technique. Based on the amount of oxyethylene units in PTMG. [c] 180 °C. [d] PTMG (0.9 mmol per oxytetramethylene unit), 1,3-dimethoxybenzene (9.0 mmol). [e] Not detected.

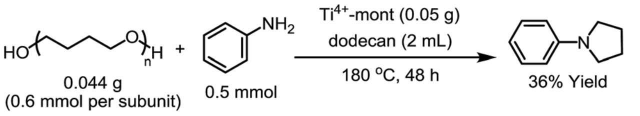
13 and 14). These results indicate that Ti^{4+}-mont acted as a highly active solid acid catalyst, different from other acid catalysts for the depolymerization of PTMG with benzene. After the reaction, Ti^{4+}-mont could be separated by filtration and reused without loss of activity during reuse experiments (Table 1, entry 2).

The Ti^{4+}-mont-catalyzed depolymerizations of PTMG with various aromatic compounds also were investigated. Toluene reacted with PTMG to form a mixture of 5- and 6-methyltetralin in 65% total yield (3 : 2 ratio of regioisomers) (Table 2, entry 2). The depolymerization of PTMG with phenol also occurred, giving the corresponding tetralins in 68% yield (1 : 1 ratio of regioisomers) (entry 3). However, an aromatic compound containing an electron-withdrawing Cl or CF_3 group gave no tetralin derivative, even at increased temperatures (entries 4 and 5). Reaction of 1,3-dimethoxybenzene provided 5,7-dimethoxy-1,2,3,4-tetrahydronaphthalene in 64% yield (entry 6).‡ Using tetralin as a reactant, 1,2,3,4,5,6,7,8-octahydroanthracene and -octahydrophenanthrene were obtained in a 2 : 7 ratio (Scheme 2), indicating that successive alkylation occurred during reaction of PTMG with benzene. In this case, a trace amount of 1,2,3,4,5,6,7,8-octahydrophenanthrene also was generated (Table 1, entry 1). Interestingly, use of aniline resulted in a 36% yield of *N*-phenylpyrrolidine (Scheme 3).[8] The low yield might be due to deactivation of the acid site of Ti^{4+}-mont by the *N*-phenylpyrrolidine generated.

The addition of 2,6-lutidine to the Ti^{4+}-mont-catalyzed depolymerization of PTMG with benzene suppressed the reaction, suggesting that the Brønsted acid site within the interlayer space of Ti^{4+}-mont is the active species.[9] The access of PTMG into the interlayer space of Ti^{4+}-mont was confirmed by XRD measurements, which showed that treatment with PTMG expanded the interlayer distance of Ti^{4+}-mont from 2.8 Å to 4.5 Å [Fig. S1(a) and (b)†]. After depolymerization, the layered structure of Ti^{4+}-mont was maintained and the interlayer distance decreased to the initial distance [Fig. S1(c)†]. Thus, the reaction might proceed through a Friedel–Crafts-type alkylation, where the C–O bond of PTMG is activated on the Brønsted acid site to generate the PTMG fragment containing a carbocation, which attacks the aromatic compound to form the alkylated aromatic compound. Subsequently, intramolecular alkylation of the alkylated aromatic compound occurs on the acid sites to afford the corresponding tetralin.



Scheme 2 Ti^{4+}-mont-catalyzed depolymerization of PTMG with tetralin.



Scheme 3 Ti^{4+}-mont-catalyzed depolymerization of PTMG with aniline.

Conclusions

In conclusion, heterogeneously-catalyzed depolymerization of PTMG with aromatic compounds to produce tetralin derivatives was newly developed using Ti^{4+}-mont as an effective solid acid catalyst. The Ti^{4+}-mont could be separated by filtration and reused while maintaining its efficiency. The present catalytic system demonstrates the potential of PTMG as a C4 synthon for the synthesis of cyclic compounds, which can promote the effective utilization of waste polymers.

Acknowledgements

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Notes and references

‡ Unfortunately, the reactions of other methoxy-substituted aromatic derivatives, such as anisole and 1,4-dimethoxybenzene, afforded the trace amount of desired product. In these cases, hydrolysis of methoxy moieties occurred during the reaction even although the details were unknown. At lower reaction temperature (130 °C), the reaction of PTMG and anisole afforded 5- and 6-methoxy-1,2,3,4-tetrahydronaphthalene (25% yield, 2 : 3 ratio of regioisomers), but complicated side products, including hydrolysis product, were still observed.

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