

Zinc(II)-Triflate as Catalyst Precursor for Ring-Closing Depolymerization of End-of-Life Polytetrahydrofuran to Produce Tetrahydrofuran

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ABSTRACT: The recycling of polymers continues to be an important subject for a greener and sustainable society. Especially, the deconstruction of end-of-life polymers to monomers creates a feedstock for new high-quality polymeric materials and contributes to conserve resources and allow an efficient waste-managing system. In this study, zinc(II)-triflate as catalyst precursor has been examined in detail in the ring-closing depolymerization of end-of-life polytetrahydrofuran (PolyTHF) to generate tetrahydrofuran (THF). Noteworthy, the produced THF can be a suitable starting material for new polymeric materials. With the cheap and abundant $\text{Zn}(\text{OTf})_2$ (1.0 mol %) as precatalyst excellent yields (up to 95%) were feasible for the depolymerization of PolyTHF at 180°C within 30 min. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39791.

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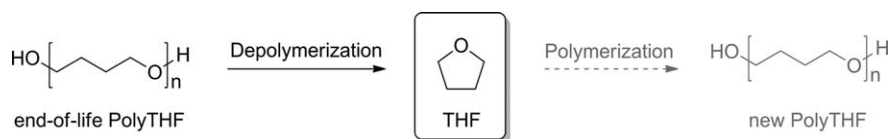
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INTRODUCTION

During the last decades, polymers rise to one of the most important materials for our society and allow the current level of living. The wide influence and the numerous purposes are a result of the straightforward large-scale production and the excellent adjustability of the polymer properties. In this regard, for the future an increasing demand is expected.^{1–5} Currently, the main source for polymers is the fossil fuel feedstock, which is steadily decreasing, hence for the near future new resources are needed.^{6–11} However, every year enormous amounts (multi-million ton scale) of end-of-life polymeric materials were generated and an efficient waste managing system is required. At present, the polymeric waste is stored at landfills, thermally recycled (thermal decomposition for energy purposes), or down-cycled to produce low-quality materials.^{12–16} Importantly, only a small part of the waste is recycled by depolymerization to obtain monomers or suitable synthons, which can be afterwards polymerized again to high-quality materials to close the cycle. Importantly, the end-of-life polymers can be partially a potential substitute for the fossil fuel feedstock as resource for polymers. To realize such recycling system several requirements have to be considered, for example, straightforwardness, low-energy, and cost-efficient. In this regard, catalysis can offer an option to accomplish these requests.^{17,18} Recently, we presented a low-temperature depolymerization of artificial polyethers [e.g.,

polytetrahydrofuran (PolyTHF), polyethylene oxide, and polypropylene oxide] to generate suitable chemicals (chloroesters) as possible starting materials for polymerization chemistry. In more detail, in the presence of catalytic amounts of simple zinc or iron salts polyethers were easily depolymerized with acid chlorides under noninert and solvent-free conditions.^{19–21} Importantly, stoichiometric amounts of acid chlorides were necessary to perform the cleavage of the carbon oxygen bonds, which creates additional synthetic steps and therefore further costs. In this regard, a depolymerization process without additional reagents will be more resourceful. Concerning this matter, polyethers can be easily accessed by ring-opening polymerization (ROP), for example, PolyTHF is easily produced from tetrahydrofuran (THF) in the presence of catalysts, and the question arise if it is possible to perform the reverse reaction means the ring-closing depolymerization, in more detail PolyTHF is converted to THF without the need of additional reagents (Scheme 1).^{22–29}

Interestingly, in the literature a small number of methodologies for the depolymerization of PolyTHF to produce THF have been reported. For realizing the ring-closing depolymerization of PolyTHF catalysis was necessary, for instance yttrium triflate, copper triflate, ytterbium triflate supported on silica-alumina, Kaolin, zeolite, aluminum silicate, sulfuric acid, or iron salts have been applied to generate THF.^{30–37} Based on the reported



Scheme 1. Depolymerization of end-of-life PolyTHF to produce THF.

procedures the selection of the catalyst is of significance to carry out the depolymerization with high productivity and reasonable costs. In this regard, the use of zinc salts can be of interest, due to abundance and low costs.^{38–40} Herein, we report on the value of an easy-to-adopt system composed of catalytic amounts of

zinc salts for the ring-closing depolymerization of PolyTHF to yield THF as valuable building block.

EXPERIMENTAL

General Procedure for the Depolymerization of PolyTHF

A flask was charged with PolyTHF ($M_n = 1000$, 5.0 g, Sigma Aldrich) and the corresponding zinc salt [$\text{Zn}(\text{OTf})_2$, 1.0 mol %, Sigma Aldrich] a Vigreux column (4.0 cm) and a fractional distillation head were connected. The mixture was stirred and heated to the corresponding temperature (oil or metal bath). The generated THF was continuously distilled off (head temperature: 55–60°C) and collected. After the reaction was completed, the yield was determined and the quality of THF was analyzed by ^1H NMR. bp 55–60°C; ^1H NMR (200 MHz, CDCl_3 , δ): 3.69 (m, 4H; CH_2), 1.79 (m, 4H; CH_2) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , δ): 67.9, 25.5 ppm.

Table I. Depolymerization of PolyTHF

Entry ^a	Precatalyst (mol %) ^b	Run ^c	T (°C)	t (min)	Yield (%) ^d
1	Zn(OTf) ₂ (2.5)	1	180	30	67
2	Zn(OTf) ₂ (2.5)	1	180	60	79
3	Zn(OTf) ₂ (2.5)	2	180	30	73
4	Zn(OTf) ₂ (2.5)	2	180	60	84
5	-	1	180	60	<1
6	ZnCl ₂ (2.5)	1	180	60	<1
7	ZnCl ₂ (2.5)	2	200	60	16
8	Zn(OAc) ₂ (2.5)	1	180	60	<1
9	Zn(OAc) ₂ (2.5)	2	200	60	<1
10	Zn(acac) ₂ H ₂ O (2.5)	1	180	60	<1
11	Zn(acac) ₂ H ₂ O (2.5)	2	200	60	<1
12	ZnO (2.5)	1	180	60	<1
13	ZnO (2.5)	2	200	60	<1
14	ZnSO ₄ (2.5)	1	180	30	<1
15	ZnSO ₄ (2.5)	1	180	60	<1
16	Zn(OTf) ₂ (2.5)	1	160	30	35
17	Zn(OTf) ₂ (2.5)	1	160	60	56
18	Zn(OTf) ₂ (2.5)	1	140	60	2
19	Zn(OTf) ₂ (1.0)	1	180	30	90
20	TfOH (1.0)	1	180	30	97
21 ^e	Zn(OTf) ₂ (1.0)	1	180	30	83
22 ^f	Zn(OTf) ₂ (1.0)	1	180	30	91
23 ^g	Zn(OTf) ₂ (1.0)	1	180	30	49

^aReaction conditions: PolyTHF ($M_n = 1000$, 5 g, 69 mmol), zinc-salt (1.0–2.5 mol % per subunit).

^bCatalyst loading corresponds to the polymer subunit.

^cFor the 2. run a fresh portion of the polymer was added to the residue of the 1. run.

^dIsolated yield. The quality of the product was checked by ^1H NMR.

^ePolyTHF ($M_n = 2000$, stabilized with BHT).

^fPolyTHF ($M_n = 650$, stabilized with BHT).

^gPolyTHF end-capped with acetyl (synthesized from PolyTHF $M_n = 1000$).

RESULTS AND DISCUSSION

Initially, the ring-closing depolymerization of PolyTHF in the presence of different zinc salts have been investigated (Table I). In more detail, a flask was charged with PolyTHF ($M_n = 1000$, stabilized with BHT = 2,6-di-*tert*-butyl-4-methylphenol) and the corresponding zinc salt connected with a Vigreux column (4.0 cm) and a fractional distillation head. The mixture was stirred and heated to 180°C (oil or metal bath temperature, internal temperature: ~152°C). The generated THF was continuously distilled off (head temperature: 55–60°C) and collected. After 30 min, the yield of THF was determined and the quality was analyzed by ^1H NMR. Applying Zn(OTf)₂ as precatalyst after 30 min a yield of THF of 67% was obtained, while after 1 h 79% was realized (Table I, entries 1 and 2). Noteworthy, no inert atmosphere or any solvent were necessary to perform the

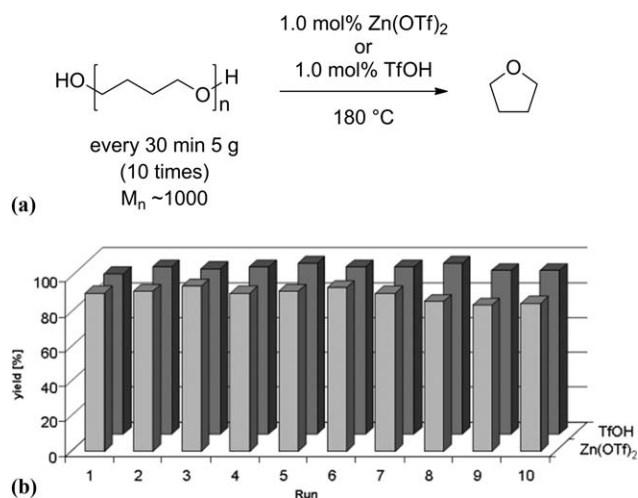
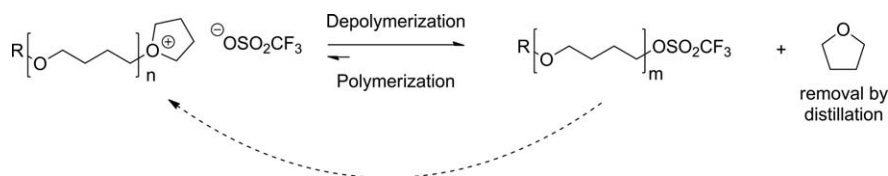


Figure 1. Depolymerization of PolyTHF.



Scheme 2. Potential depolymerization mechanism of PolyTHF to produce THF.

reaction. Interestingly, after the evolution of THF (1 h), to the zinc containing residue was added a fresh portion of PolyTHF ($M_n = 1000$) and the mixture was heated again to 180°C . A yield of 73% was observed after 30 min revealing the possibility of reuse the catalyst material (Table I, entries 3 and 4). In the absence of any zinc salt no product formation was observed, which proves the need for zinc salt addition (Table I, entry 5). Noteworthy, in the presence of other zinc precursors, for example, $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{acac})_2$, H_2O , ZnSO_4 , or ZnO , no THF formation was achieved. However, only with catalytic amounts of ZnCl_2 a moderate yield of 16% was observed at 200°C (Table I, entry 8). In addition, the reaction temperature was decreased to 160 and 140°C for the $\text{Zn}(\text{OTf})_2$ based reaction, showing a decrease of reactivity (Table I, entries 17 and 18). Interestingly, the decrease of the catalyst loading to 1.0 mol % resulted in an increase of the yield to 90% after 30 min, which corresponds to a turnover frequency of 180 h^{-1} (Table I, entry 19). For various reported methodologies the application of triflate based salts has been shown. To investigate the influence of the anion catalytic amounts of trifluoromethanesulfonic acid (TfOH) were applied (Table I, entry 20). Interestingly, in the presence of 1.0 mol % TfOH PolyTHF was depolymerized in an excellent yield of 97% to THF.^{41–48} Based on this finding the applied $\text{Zn}(\text{OTf})_2$ can be probably an easy to handle solid and low toxic source for TfOH. In addition, comparable cost arise from $\text{Zn}(\text{OTf})_2$ (Sigma Aldrich 10 g = $\sim 63.80\text{ €}$, 31.90 € per triflate group) vs. TfOH (Sigma Aldrich 10 g = $\sim 37.80\text{ €}$). Hence, $\text{Zn}(\text{OTf})_2$ was used for further experiments. Moreover, PolyTHF with different molecular weights and PolyTHF end-capped with acetyl groups were successfully depolymerized with $\text{Zn}(\text{OTf})_2$ (Table I, entries 21–23).

After having set up a suitable system with 1.0 mol % $\text{Zn}(\text{OTf})_2$ at 180°C (Table I, entry 17) the reuse of the catalyst was studied (Figure 1). In more detail, every 30 min a fresh portion of PolyTHF ($M_n = 1000$) was added to the system. For the runs 1–7 yields of THF in the range of 90–95% were observed, while depletion was noticed for runs 8–10 with yields in the range of 84–86% were noticed. Overall, an average yield of 90% was feasible, which corresponds to a turnover number of 900 and a turnover frequency of 180 h^{-1} . In addition, the reaction solution was investigated by GC-MS methods after 10 min revealing the formation of PolyTHF with lower molecular weights and an accumulation of the stabilization reagent BHT. Noteworthy, the current system exhibits an excellent recyclability in comparison to the recently reported FeCl_3 system, because after ninth run a yield of 84% [$\text{Zn}(\text{OTf})_2$] vs. 13% (FeCl_3) was observed.³⁷ Interestingly, a comparable performance was observed for catalytic amounts of TfOH, indicating once more the potential formation of TfOH with the $\text{Zn}(\text{OTf})_2$ system (Figure 1). Moreover,

the system ($\text{Zn}(\text{OTf})_2$, 180°C) was applied to other polyethers such as polyethylene oxide and polypropylene oxide. However, no product formation was detected.

With respect to the reaction mechanism, we propose a mechanism that is in accordance to the mechanism reported for the ROP of THF with catalytic amounts of trifluoromethanesulfonic acid or derivatives (Scheme 2). For instance, Pruckmayr et al. and Matyjaszewski et al. investigated the polymerization reaction in detail and suggested a cationic polymerization process with tetrahydrofuranium ions as crucial intermediates.^{41–48} Moreover, equilibria between polymerization and depolymerization were discussed. Based on that, the removal of THF by distillation should shift the equilibria to the depolymerization pathway.

CONCLUSIONS

In summary, we have set up an efficient method for the ring-closing depolymerization of PolyTHF to generate THF in high quality. As excellent precatalyst or source for trifluoromethanesulfonic acid $\text{Zn}(\text{OTf})_2$ was found, which converted PolyTHF to THF at 180°C within 30 min with 90% yield at low catalyst loadings. Moreover, it was possible to reuse the catalyst up to 10 times with only small lose of productivity.

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