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Low-Temperature Iron-Catalyzed Depolymerization of Polyethers

Stephan Enthaler* and Maik Weidauer[a]

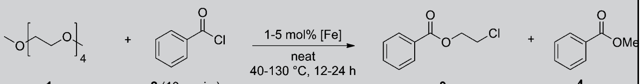
Dedicated to Professor Matthias Beller on the occasion of his 50th birthday.

Nowadays synthetic polymers (or: plastics) play a fundamental, ubiquitous role in everyday life.[1] In view of the steadily increasing demand for polymeric materials (growing rate ca. 9% p.a.), rising amounts of plastic waste represents the downside of this success.[2] Many polymers are based on monomers produced from fossil fuels, which are gradually decreasing, and their degradation is simply a matter of time.[3] Moreover, waste polymers are commonly thermally decomposed for energy production (thermal recycling) or converted to low-quality materials (downcycling).[4] Only a small fraction of the polymer waste is submitted to degradation and conversion into new and high-quality materials.[5] Accordingly, the recycling of polymers continues to be a significant and topical subject in chemistry.[6]

In this context low-temperature depolymerization methods are an interesting approach towards using plastic waste as a source of raw materials. Specifically, the polymer is converted to functional synthons or monomers, which can reprocessed as starting materials in polymerization chemistry.[7] Interesting polymeric materials for this method are polyethers (e.g., polytetrahydrofuran, polyethylene glycol, polyethylene oxide, polypropylene oxide), which are omnipresent in modern life. To realize a low-temperature approach the application of catalysts can be useful.[8,9] In the presence of suitable transition metals the ether functionality can be activated by coordination to the metal centre and following this event an attack with nucleophiles (e.g., acid chlorides) is feasible (Figure 1).[10,11] By continuous diminution of the polymer by this procedure an increasing amount of the corresponding chloroester will be obtained as well-defined molecule. Chloroesters can be easily transformed into other compounds (e.g., vinyl esters, halohydrins, vinyl chloride) that can be applied as monomers in polymerization processes.[12] Moreover, the selection of the catalyst is of great importance because modern research focuses on the substitution of expensive and toxic transition metals. Indeed, during the last years the chemistry of cheap, abundant, and low-toxicity "bio"metals as catalyst core (e.g., iron) has been rediscovered and numerous exciting reactions have been reported.[13,14] In this regard, we describe the first iron-catalyzed depolymerization method, applying widely available iron salts to obtain suitable products (chloroesters) appropriate for follow-up chemistry (Figure 1).[15]

Initial studies on the influence of the reaction conditions were carried out with tetraethylene glycol dimethyl ether (**1**) as the model substrate for polyethers and benzoyl chloride as nucleophile (Table 1). Firstly, different iron salts were examined as catalyst precursor under non-inert conditions (entries 1–6). In all cases full conversions of **1** were observed and no significant difference was noticed for Fe^{II} or Fe^{III} salts. An excellent yield for the desired chloroester was obtained with $FeCl_2{\cdot}4H_2O$ as precatalyst at 130 °C, while in the absence of an iron source no product was detected (entries 1 and 2). Moreover, when the catalyst loading was reduced to 1.0 mol% there was only a slight reduction of the activity in comparison to 5.0 mol% (entries 7 and 8). In addition, the influence of the reaction temperature was studied (entries 10–13). Decreasing the temperature to 100 °C resulted in an excellent yield, while at 60 °C a lower yield was noticed accompanied by the detection of various intermediates. Notably, at 40 °C the reaction was hampered (entry 13). Remarkably, the iron-based catalyst showed an excellent performance at low temperature (< 100 °C), while a recently reported zinc-based protocol required a reaction temperature of 130 °C.[10b]

Table 1. Iron-catalyzed depolymerization of tetraethylene glycol dimethyl ether (**1**).



1 | 2 (10 equiv.) | 3 | 4

Entry[a]	Iron source	Amount [mol%]	T [°C]	Conv. (**1**) [%]	Yield (**3**)[b] [%]
1	–	–	130	< 1	< 1
2	$FeCl_2{\cdot}4H_2O$	5	130	> 99	87
3	$FeCl_3$	5	130	> 99	81
4	$FeBr_3$	5	130	> 99	69
5	$Fe(ClO_4)_2{\cdot}H_2O$	5	130	> 99	71
6	$Fe(ClO_4)_3{\cdot}4H_2O$	5	130	> 99	73
7	$FeCl_2{\cdot}4H_2O$	2.5	130	> 99	82
8	$FeCl_2{\cdot}4H_2O$	1.0	130	> 99	68
9[c]	$FeCl_2{\cdot}4H_2O$	5	130	> 99	84
10	$FeCl_2{\cdot}4H_2O$	5	100	> 99	86
11	$FeCl_2{\cdot}4H_2O$	5	80	> 99	69
12	$FeCl_2{\cdot}4H_2O$	5	60	> 99	25
13	$FeCl_2{\cdot}4H_2O$	5	40	< 1	< 1

[a] Reaction conditions: **1** (0.72 mmol), iron source (1.0–5.0 mol%), **2** (7.2 mmol), 40–130 °C, 24 h. [b] Determined by GC methods using anisole as an internal standard. Products were compared with authentic samples. [c] 12 h.

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[a] *Dr. S. Enthaler, M. Weidauer*
Technische Universität Berlin
Department of Chemistry
Cluster of Excellence "Unifying Concepts in Catalysis"
Straße des 17. Juni 115, 10623 Berlin (Germany)
Fax: (+49) 30-31429732
E-mail: stephan.enthaler@tu-berlin.de

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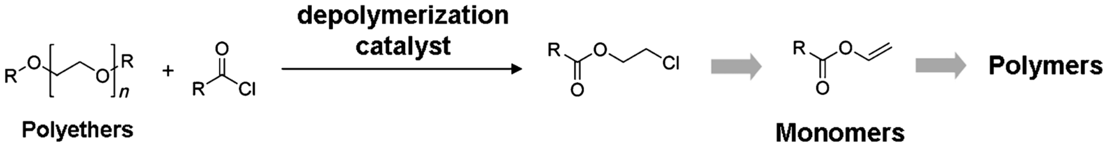
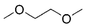
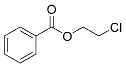
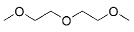
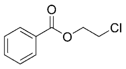
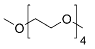
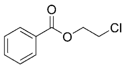
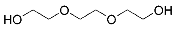
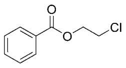
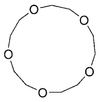
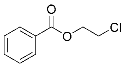
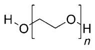
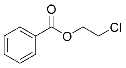
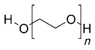
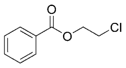
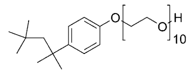
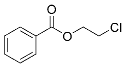
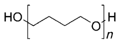
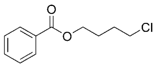
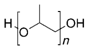
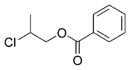
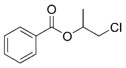
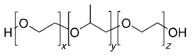
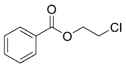
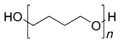
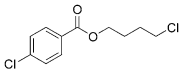
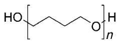
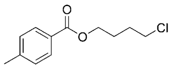
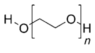
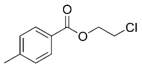
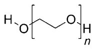
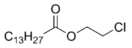


Figure 1. Depolymerization of polyethers in the presence of catalysts and acid chlorides and potential follow-up chemistry.

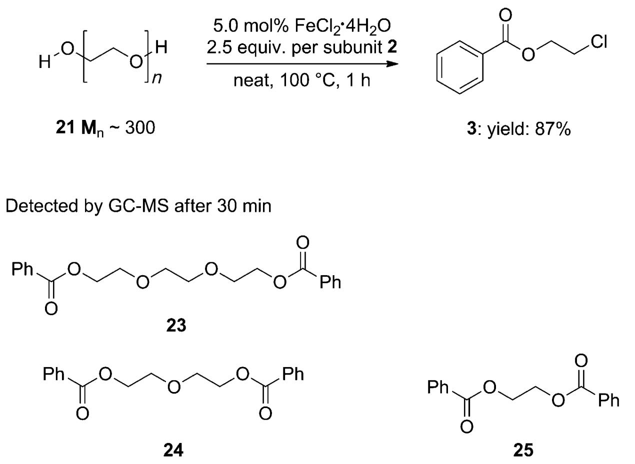
With the appropriate reaction conditions in hand (5.0 mol% $FeCl_2·4H_2O$, **2**, 100 °C, 24 h) we investigated the scope and limitation of the protocol in the depolymerization of diverse polyethers (Table 2). First, various molecularly defined ethers were fragmented by the depolymerization procedure (entries 1–5). Good results were achieved for ethers with methoxy or hydroxyl end-groups. Moreover, no significant difference in the yield of **3** was detected between cyclic and acyclic ethers (entries 3 and 5). After having demonstrated the potential of the iron catalyst in the depolymerization of well-defined ethers, we directed our attention to polymeric ethers (entries 6–15). Indeed, the system was capable to produce the corresponding chloroethers in yields of up to 95%. For polyethylene glycol with a number-average molecular weight of up to 1 000 000, the chloroester **3** was obtained in 89–95% yield (entries 6 and 7). A good performance was noticed for the depolymerization of polytetrahydrofuran, whereas for polypropylene oxide two different products in a ratio of ca. 1:1 were observed (entries 9 and 10). Additionally, the influence of the nucleophile was studied (entries 12–15). Notably, later on the nature of the alkyl or aryl function of the acid chloride can control the properties of the new polymer. Applying 4-chlorobenzoyl chloride as well as 4-methylbenzoyl chloride resulted in similar yields as for unmodified benzoyl chloride. Moreover, myristic acid chloride was applied as nucleophile, which is easily obtained from renewable resources, to depolymerize polyethylene glycol (entry 15).

The usefulness of the protocol was demonstrated in a scale-up experiment (45.0 mmol). Polyethylene glycol (**21**) was reacted with benzoyl chloride (**2**) in the presence of catalytic amounts of

Table 2. Iron-catalyzed depolymerization of polyethers—scope and limitations.

Entry[a]	Substrate		Product		Yield [%][b]
1		**5**		**3**	79[c]
2		**6**		**3**	81[c]
3		**1**		**3**	78[c]
4		**7**		**3**	73
5		**8**		**3**	82
6		**9** ($M_n \approx 100000$)		**3**	89
7		**10** ($M_n \approx 1000000$)		**3**	95
8		**11** (TRITON X-100)		**3**	91
9		**12** ($M_n \approx 1000$)		**13**	83
10[d]		**14** ($M_n \approx 2500$)	 	**15** **16**	68 68
11		**17** ($M_n \approx 2500$)		**3**	92
12[e]		**12** ($M_n \approx 1000$)		**18**	92
13[f]		**12** ($M_n \approx 1000$)		**19**	89
14[f]		**9** ($M_n \approx 100000$)		**20**	91
15[g]		**21** ($M_n \approx 300$)		**22**	78

[a] Reaction conditions: substrate (0.72 mmol, based on the subunits), $FeCl_2·4H_2O$ (5.0 mol% per subunit), **2** (1.5 equiv per subunit), 100 °C, 24 h. [b] Isolated product yield. [c] As side product **4** was detected. [d] A mixture of two isomers in a ratio of ca. 1:1 was observed. [e] 4-Chlorobenzoyl chloride was used as nucleophile. [f] 4-Methylbenzoyl chloride was used as nucleophile. [g] Myristic acid chloride was used as nucleophile.



Scheme 1. Depolymerization of polyethylene glycol **21**.

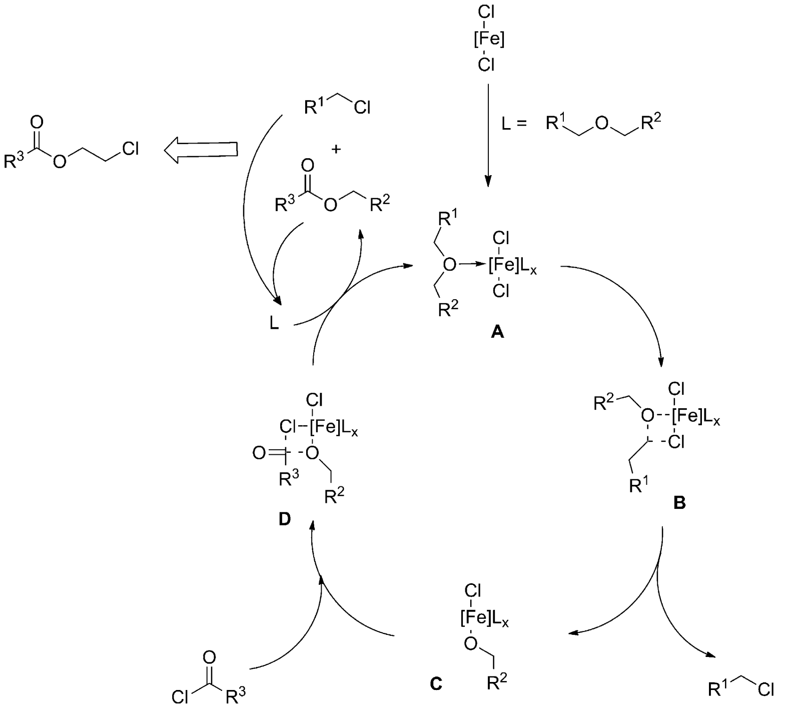
$FeCl_2$·4 H_2O at 100 °C (Scheme 1). After 1 h full conversion was reached, accompanied by 87% isolated yield. A sample taken after 30 min and analyzed by GC–MS showed the presence of intermediates **23**, **24**, and **25** with decreased chain length compared to the starting material.

To investigate the effect of the counterion of the iron on the reaction outcome, substoichiometric amounts of $FeBr_3$ (0.5 equiv) were added to a mixture of **1** and **2** (see conditions Table 1, entry 3). After performing the reaction for 24 h the reaction mixture was analyzed by GC–MS, revealing the formation of chloroester **2** and to some extent (5%) the corresponding bromoester. Based on that result an abstraction of the chloride from the acid chloride by the metal can be assumed.[16] With regard to the underlying processes in Scheme 2 a reaction mechanism is proposed. First, the oxygen functionality of the ether is coordinated to the metal center (**A**), effecting an activation of the oxygen and the adjacent carbon.[17] In the next step a chloride is transferred from the metal center (**B**) to the activated carbon under cleavage of the C–O ether bond, to produce an alkyl chloride fragment and an iron alkoxide (**C**). Afterwards the iron alkoxide (**C**) reacts with the acid chloride via intermediate **D**. Consequently, a new C–O bond is formed to obtain an ester fragment. The chloride of the acid chloride is abstracted by the iron, which allows regeneration of **A**. Overall, the former ether is cleaved, creating two fragments that will feed again into the catalytic cycle, finally resulting in the formation of monomeric chloroesters.

In summary, we report an efficient methodology for the depolymerization of artificial polyethers using acid chlorides as nucleophiles in the presence of catalytic amounts of abundant and cheap iron salts under mild reaction conditions. Noteworthy, well-defined chloroesters are obtained as major product, which are valuable building blocks in polymerization chemistry for the synthesis of new polymers. Future investigations will focus on further evaluation of the reaction mechanism and the application of the protocol to the conversion of polyethers originated from biomass (e.g., lignin).

Experimental Section

General procedure for the depolymerization of tetraethylene glycol dimethyl ether (1): A pressure tube was charged with an appropriate amount of iron precursor (0.036 mmol, 5.0 mol%), tetraethylene glycol dimethyl ether (0.72 mmol), and benzoyl chloride (5.0 equiv, 3.6 mmol). The reaction mixture was stirred in a preheated oil bath at 130 °C for 24 h. The mixture was cooled on an ice bath and anisol (internal standard) was added. The solution was diluted with dichloromethane and an aliquot was taken for GC analysis (30 m Rxi-5 ms column, 40–300 °C).



Scheme 2. Mechanistic proposal for the iron-catalyzed depolymerization of polyethers.

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Keywords: depolymerization · homogeneous catalysis · iron · polyethers · polymers

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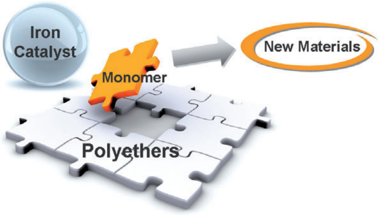
Iron will: The iron-catalyzed depolymerization of a range of polyethers is studied. The products of the depolymerization reactions are chloroesters, which can be used as starting materials for new polymers. In the presence of simple iron salts extraordinary catalyst activities and selectivities are feasible at low temperature.



S. Enthaler, M. Weidauer*

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Low-Temperature Iron-Catalyzed Depolymerization of Polyethers