JOURNAL OF Applied Polymer SCIENCE

Iron-Catalyzed Depolymerization of Polysiloxanes to Produce Dichlorodimethylsilane, Diacetoxydimethylsilane, or Dimethoxydimethylsilane

Stephan Enthaler
Department of Chemistry, Technische Universität Berlin, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 115/C2, D-10623, Berlin, Germany
Correspondence to: Stephan Enthaler (E-mail: stephan.enthaler@tu-berlin.de)

ABSTRACT: Polymers are one of the important pillars of our current society. Besides the great success a matter is the accumulation of huge amounts of end-of-life polymers. Current waste management bases primarily on landfills, thermal recycling, and down-cycling. Noteworthy, only a small part of the end-of-life materials is recycled by depolymerization, means low-molecular weight synthons are created, which can be polymerized to new polymers to close the cycle. Widely used polymers in modern life times are silicones (polysiloxanes). Based on the intrinsic properties the depolymerization is challenging and only a few high temperature or less environmental-friendly processes have been reported. In this regard, we have set up a capable low-temperature protocol for the depolymerization of silicones with acid chlorides, acetic acid, or methanol in the presence of cheap iron salts as precatalysts to yield dichlorodimethylsilane, diacetoxydimethylsilane, or dimethoxydimethylsilane as well-defined products. Notably, dichlorodimethylsilane, diacetoxydimethylsilane, and dimethoxydimethylsilane can be useful starting materials for synthesizing new polymers; overall a recycling is feasible. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41287.

KEYWORDS: catalysts; degradation; recycling

Received 9 April 2014; accepted 29 June 2014
DOI: 10.1002/app.41287

INTRODUCTION

The management of end-of-life plastics is one of the major issues for our current society, since every year multi million tons of waste are generated. Moreover, the primary origin is natural resources (e.g., crude oil and natural gas), which are steadily decreasing, hence for the future alternatives have to be considered. At present, for end-of-life plastics three major pathways have been established: (1) storage of the waste at landfills, (2) thermal recycling (thermal decomposition for energy purposes), and (3) down-cycling to produce low-quality materials. In contrast to that, the degradation of end-of-life plastics to monomers (feedstock recycling) is only carried out for a small portion of waste.[1–6] Importantly, the low-molecular weight degradation products represents a useful feedstock for new high-quality polymers and in consequence a recycling of the material is possible. Although the advantages of feedstock recycling are apparent several issues handicap the application, e.g., high energy demand for the degradation or co-polymers. A widely applied class of polymers are silicones (e.g., silicone oil, silicone rubber, silicone grease, and silicone resin), which are easily accessible by the Müller-Rochow synthesis and subsequent hydrolysis.[7,8] A high energy input and consumption of natural resources are required to produce the starting materials (e.g., chloromethane and silicium), while the treatment of the end-of-life silicones is mainly the thermal decomposition with an irretrievable loss of the integrated efforts. In this regard, low-temperature depolymerization methodologies can be an option to overcome these limitations, since a smaller amount of energy should be necessary to allow a recycling. Unfortunately, the intrinsic properties of silicones constrain the application of depolymerization processes, hence only a few high temperature (>200°C) or less environmental-friendly processes have been reported.[9–34] Recently, we studied the depolymerization of end-of-life polysiloxanes to produce suitable chemicals (e.g., Me_2SiF_2) as prospective starting materials for polymerization. Notably, zinc or iron catalysis was essential to realize low-temperature processes (130–150°C) under non-inert and solvent-free conditions.[35,36] In more detail, for cleaving silicon oxygen bonds in polysiloxanes the catalyst activates the Si–O bonds and allow the reaction with the depolymerization reagent benzoyl fluoride yielding Si–F bonds. By repeating this procedure the polymer is steadily degraded to low-molecular weight compounds, e.g., Me_2SiF_2. However, the application of acid chlorides as depolymerization reagents will be more useful,

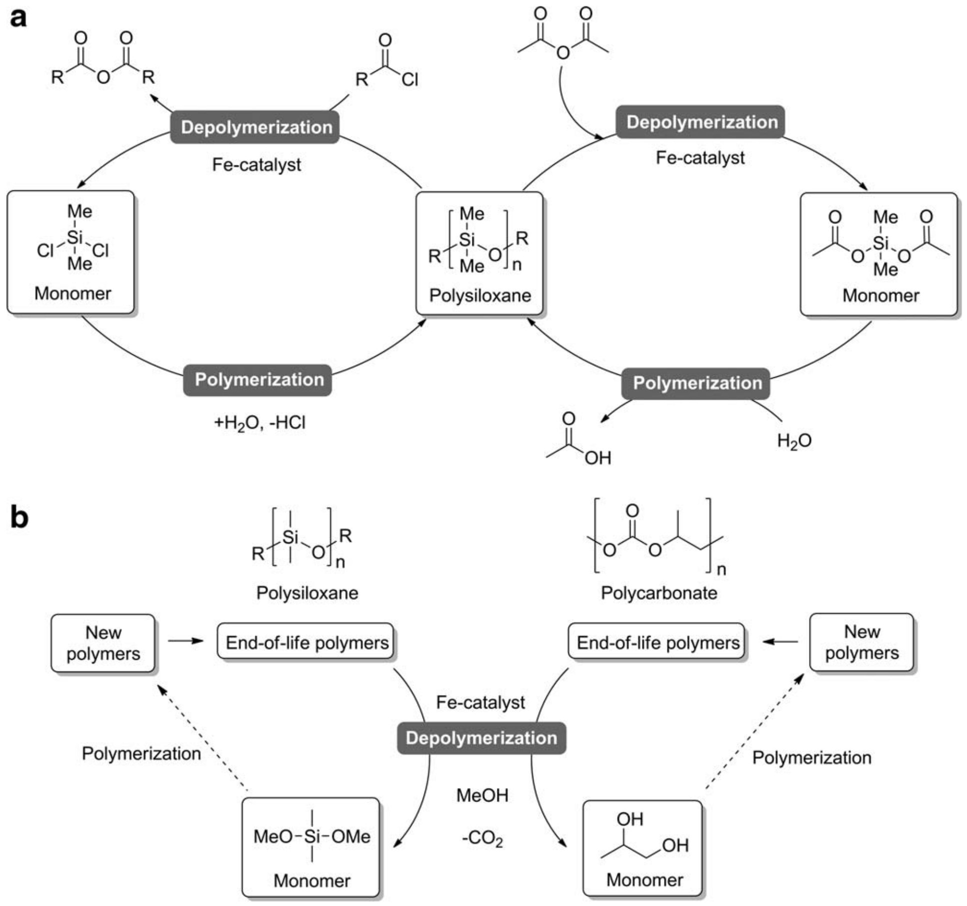


Figure 1. Depolymerization of polysiloxanes.

because the produced chemicals, e.g., Me_2SiCl_2, can be the feed for already established industrial polymerization technologies (*vide supra*) (Figure 1a).[29–34] Interestingly, in 1969 Borisov et al. reported on the iron catalyzed conversion of octamethylcyclotetrasiloxane to Me_2SiCl_2 and $Me_2ClSiOSiClMe_2$ applying acetyl chloride as reagent.[30] However, only low yields were observed (Me_2SiCl_2: 4%, $Me_2ClSiOSiClMe_2$: 12%). On the other hand, acid fluorides and acid chlorides as depolymerization reagents require upstream chemistry to access these compounds, hence increasing the cost of such depolymerization protocols.* An attractive alternative can be the application of acetic anhydride as depolymerization reagent (Figure 1a; 1 mol Ac_2O: ~ 3 €). In more detail, the reaction of a polysiloxane with acetic anhydride should provide diacetoxydimethylsilane as low-molecular weight product. Potentially, diacetoxydimethylsilane can be applied as starting material for new polysiloxanes producing as side product acetic acid, which can be converted to acetic anhydride, hence a recycling of the depolymerization reagent is feasible.[37] Initially, Borisov and coworkers described the application of acetic anhydride and catalytic amounts of iron(III) chloride for the conversion of octamethylcyclotetrasiloxane to obtain diacetoxydimethylsilane.[29–34] However, low yields of diacetoxydimethylsilane (<5%) were reported. A different approach for the depolymerization of polysiloxanes was reported by Okamato et al. and others.[38–41] In more detail, poly(dimethylsiloxanes) were reacted with dimethyl carbonate in the presence of strong acids or simple metal salts (e.g., KF, NaF) in methanol at 180°C to produce dimethoxydimethylsilane as product. However, the reaction required dimethyl carbonate as reagent, which has to be synthesized before; hence resources are consumed, additional costs are caused and overall the sustainability is reduced. Based on these initial achievements we wonder if it is possible to substitute the dimethyl carbonate by polycarbonates, such as poly(propylene carbonate). In general, a coupling of two different depolymerization processes can be envisaged, allowing the conversion of two end-of-life materials to useful starting materials for polymerization (Figure 1b). In more detail, a mixture of poly(dimethylsiloxane) and poly(propylene carbonate) will be reacted in the presence of a suitable catalyst in methanol to produce on the one hand dimethoxydimethylsilane, which can be applied as monomer for the synthesis of new polysiloxanes.[42,43] On the other hand, 1,3-propane diol is formed, which can be converted to propylene oxide a starting material for the ring-opening polymerization with carbon dioxide to yield new poly carbonates.[44–52]

Based on that initial works, we report herein on depolymerization of end-of-life polysiloxanes in the presence of

---

*see Ref. Y: 1 mol PhC(O)F: ~482 €; 1 mol PhC(O)Cl + 1 mol KF = ~22 €; 1 mol PhC(O)O(O)CPh + 1 mol KF = ~46 €. See Ref. Y: 1 mol PhC(O)Cl = ~10 €.

straightforward iron precatalysts applying acid chlorides, acetic anhydride, or methanol as depolymerization reagents (Figure 1).

EXPERIMENTAL

General: All chemicals were used as received without further manipulations. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker AFM 200 spectrometer (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{29}Si: 39.71 MHz) using the proton signals of the deuterated solvents as reference. GC-MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

General Procedure for the Depolymerization of Polysiloxanes with Acid Chlorides: A one-neck flask (10 mL) was charged with the corresponding polysiloxane (1.0 g), iron(III) fluoride (5.0 mol %, based on the polymer subunit), and benzoyl chloride (3 equiv. based on the polymer subunit) a Vigreux column and a distillation head were connected. The mixture was stirred and heated to 190°C (oil bath). The formed low-boiling compounds were continuously distilled off and collected. After the reaction was completed the yield was determined and the quality was analyzed by NMR. The yield was calculated by yield = [*n* (product)/*n* (polymer subunit)]*100%.

Dichlorodimethylsilane 3:[53–55] ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 0.78$ (d, $^{2}J_{Si,H} = 7.60$ Hz) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25°C) $\delta = 6.7$ (d, $^{1}J_{Si,C} = 68.29$ Hz) ppm. ^{29}Si{^{1}H} NMR (40 MHz, $CDCl_3$, 25°C) $\delta = 32.2$ ppm.

General Procedure for the Depolymerization of Polysiloxanes with Acetic Anhydride: An Ace pressure tube (volume ~15 mL) was charged with the corresponding polysiloxane (1.0 g), iron(III) chloride (7.5 mol %, based on the polymer subunit) and acetic anhydride (3 equiv. based on the polymer subunit). The mixture was stirred and heated to 160°C (oil bath). After 16 hr the mixture was cooled to room temperature and anisole (100 µL, internal standard) was added. An aliquot was dissolved in CH_2Cl_2 and the yield was determined by GC MS. The yield was calculated by yield = [*n* (product)/*n* (polymer subunit)]*100%.

Diacetoxydimethylsilane 24:[56,57] ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 2.07$ (m, 6H), 0.47 (m, 6H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25°C) $\delta = 170.8$, 22.5, -1.5 ppm. ^{29}Si{^{1}H} NMR (40 MHz, $CDCl_3$, 25°C) $\delta = 5.1$ ppm. MS (ESI) m/z = 176 (M^{+}, 1), 161 (11), 119 (100), 77 (70).

Polymerization of 24: A flask (50 mL) equipped with a condenser was charged with diacetoxydimethylsilane (11.4 mmol) and water (25 mL). The mixture was refluxed for 1 hr and afterward cooled to room temperature. The aqueous solution was extracted with diethylether (3x 20 mL) and the organic layer was dried over Na_2SO_4. After filtration the solvent was removed to obtain colorless oil. The overall yield was calculated by yield = [n (polymer subunit)/n (**24**)]*100%.

Octamethylcyclotetrasiloxane 25:[58,59] yield: 55%. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 0.04$ (m, 24H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25°C) $\delta = 0.6$ ppm. ^{29}Si{^{1}H} NMR (40 MHz, $CDCl_3$, 25°C) $\delta = -19.1$ ppm. MS (ESI) m/z = 296 (M^{+}, <1), 281 (100), 265 (10).

General Procedure for the Depolymerization of Polysiloxanes with Methanol: An autoclave with a Teflon-inlet (25 mL) was charged with the polysiloxane **1** (1.0 g), iron(III) fluoride (7.5 mol %, based on the polymer subunit), poly(propylene carbonate) **26** (3 equiv. based on the polymer subunit of **1**, $M_n \sim$ 50,000 g/mol) and methanol (2.0 mL). The autoclave was sealed and placed in a preheated oven (180°C). After 24 hr the autoclave was cooled to room temperature and anisole (0.1 mL) was added as internal standard. A sample diluted with dichloromethane and was analyzed by GC-MS. The yield was calculated by yield = [*n* (product)/*n* (polymer subunit)]*100%.

Dimethoxydimethylsilane 27:[†] ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 3.41$ (s, OCH_3, 6H) 0.03 (s, CH_3, 6H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25°C) $\delta = 49.9$, -4.3 ppm. ^{29}Si{^{1}H} NMR (40 MHz, $CDCl_3$, 25°C) $\delta = -0.2$ ppm. MS (ESI) m/z = 120 (M^{+}, <1), 105 (100), 75 (64), 59 (27).

Polymerization of 27: A flask (50 mL) equipped with a condenser was charged with dimethoxydimethylsilane (11.4 mmol) and water (25 mL). The mixture was refluxed for 1 hr and afterward cooled to room temperature. The aqueous solution was extracted with diethylether (3x 20 mL) and the organic layer was dried over Na_2SO_4. After filtration the solvent was removed. **30**: yield: 71%. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): $\delta = 0.01$–0.15 (m) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25°C) $\delta = 0.2$–1.2 (m) ppm. ^{29}Si{^{1}H} NMR (40 MHz, $CDCl_3$, 25°C) $\delta = -8.2$, -19.0 ppm. The overall yield was calculated by yield = [*n* (polymer subunit)/ *n* (**27**)]*100%.

RESULTS AND DISCUSSION

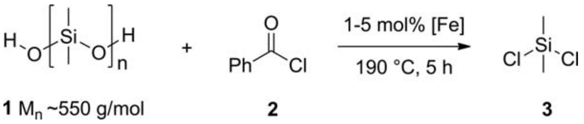
In our initial study on the depolymerization of poly(dimethylsiloxane) hydroxy terminated **1** ($M_n \sim$ 550 g/mol) with benzoyl fluoride as depolymerization reagent we have shown that under optimized reaction conditions (5.0 mol % $FeCl_3$, 130°C) the conversion of **1** with benzoyl chloride was not successful (Table I, entry 2). Hence the reaction temperature was stepwise increased to 190°C.[‡] Interestingly, at 190°C the polysiloxane **1** was selectively converted to dichlorodimethylsilane **3** in 32% yield (Table I, entries 3–5). Noteworthy, in the absence of $FeCl_3$ no product formation was observed. Next the catalytic abilities of various iron salts were investigated (Table I, entries 5–12). For all salts moderate yields of **3** (24–49%) were obtained, while in tendency a higher activity for iron(III) salts is observed. In contrast, with iron(III) fluoride a good yield of 60% were realized after 5 hr at 190°C (Table I, entry 6). Increasing the catalyst loading to 7.5 mol % the yield was significantly increased to 86%, while decreasing the catalyst loading reduced the amount of product (Table I, entries 13 and 15). On the other hand, elongation of the reaction time to 10 hr resulted in a comparable yield of 62% as found after 5 hr (Table I, entry 14). Moreover, the influence of the depolymerization reagent benzoyl chloride was studied. Decreasing and increasing the amount of

---

[†] Compared with an authentic sample.

[‡] The maximum temperature was set to 190°C, because of the boiling point of benzoyl chloride at 197°C.

Table I. Iron-Catalyzed Depolymerization of Polysiloxane 1



Entry[a]	Iron source (mol %)	**2** (equiv.)	*T* (°C)	Yield (%)[b]
1	–	3	190	<1
2	$FeCl_3$ (5)	3	130	<1
3	$FeCl_3$ (5)	3	150	<1
4	$FeCl_3$ (5)	3	170	6
5	$FeCl_3$ (5)	3	190	32
6	FeF_3 (5)	3	190	60
7	$FeCl_2$ $4H_2O$ (5)	3	190	24
8	Fe(acac)$_2$ (5)	3	190	34
9	Fe(acac)$_3$ (5)	3	190	49
10	Fe(OAc)$_2$ (5)	3	190	25
11	Fe(II)oxide (5)	3	190	46
12	Fe(II,III)oxide (5)	3	190	39
13	FeF_3 (1)	3	190	50
14[c]	FeF_3 (5)	3	190	62
15[d]	FeF_3 (7.5)	3	190	86
16	FeF_3 (5)	2	190	23
17	FeF_3 (5)	4	190	48

[a] Reaction conditions: iron-salt (1.0–5.0 mol % based on the polymer subunit), polysiloxane **1** (1.0 g, $M_n \sim 550$ g/mol), benzoyl chloride **2** (2–4 equiv. based on the polymer subunit), 5 hr, 130–190°C.

[b] Isolated yield. Determined by ^1H NMR.

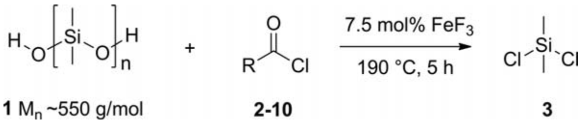
[c] 10 hr.

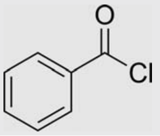
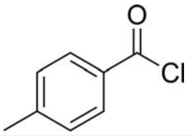
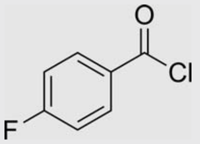
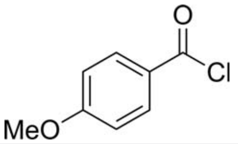
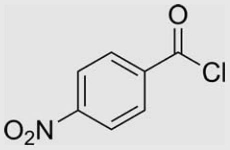
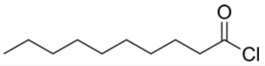
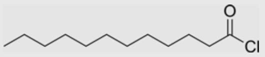
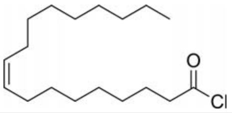
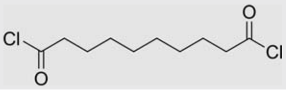
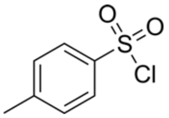
[d] Me_2SiF_2 was observed in traces.

2 showed no positive effect on the reaction outcome, while 3.0 equiv. were still the best amount (Table I, entries 16–17).

In addition the influence of the acid chloride was investigated (Table II). First the influence of substitution on the phenyl ring of benzoyl chloride was studied (Table II, entries 1–5). However, for electron-donating as well as electron-withdrawing groups in *para*-position no positive effect on the reaction outcome was observed, since in all cases yields in the range of 20–59% were achieved. Moreover, acid chlorides derived from renewable resources were applied as depolymerization reagent (Table II, entries 6–9). Here yields in the range of 23–39% were monitored. Based on that results for further studies benzoyl chloride **2** was utilized.

Table II. Iron-Catalyzed Depolymerization—Influence of the Acid Chloride



Entry[a]	Acid chloride	Yield (%)[b]
1	 **2**	86
2	 **4**	35
3	 **5**	20
4	 **6**	59
5	 **7**	40
6	 **8**	38
7	 **9**	23
8	 **10**	23
9[c]	 **11**	39
10	 **12**	15

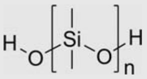
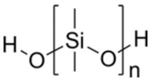
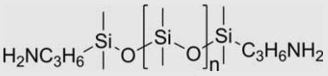
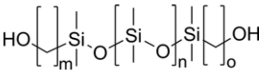
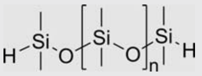
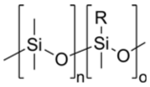
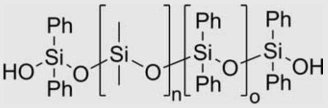
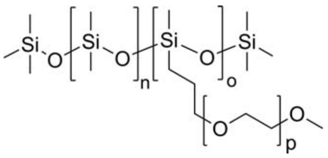
[a] Reaction conditions: FeF_3 (7.5 mol % based on the polymer subunit), polysiloxane **1** (1.0 g), acid chloride (3.0 equiv. based on the polymer subunit), 190°C, 5 hr.

[b] Isolated yield. Determined by ^1H NMR. Me_2SiF_2 was observed in traces.

[c] 1.5 equiv. of the acid chloride.

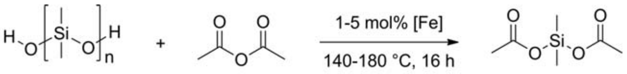
After setting up a suitable system (7.5 mol % FeF_3, 3.0 equiv. **2**, 190°C, 5 hr) the scope and limitations were tested for various polysiloxanes (Table III). For instance increasing the length of the polymer chain ($M_n \sim$ 100.000 g/mol) the catalyst was capable to produce **3** in 82% yield (Table III, entry 2). In contrast to that, a significant influence of the kind of the end group was observed (Table III, entries 3–5). Interestingly, in case of the polymer **19** with two different co-polymers, e.g., a polysiloxane (~20 wt %) and a poly(ethylene glycol) residue (~80 wt %), both co-polymers can be depolymerized by our protocol (Table III, entry 8). On the one hand, the poly(ethylene glycol) residue is converted to 2-chloroethyl benzoate in 91% yield with benzoyl chloride in the presence of the iron catalyst. Interestingly,

Table III. Scope and Limitations of the Iron-Catalyzed Depolymerization

Entry[a]	Substrate	**3** Yield (%)[b]
1	 **1** ($M_n \sim 550$ g/mol)	86
2	 **13** ($M_n \sim 110.000$ g/mol)	82
3	 **14** ($M_n \sim 2.500$ g/mol)	27
4	 **15** ($M_n \sim 5.600$ g/mol)	49
5	 **16** ($M_n \sim 580$ g/mol)	54
6[c]	 **17** R = C_{16}–C_{18}	71 mg
7[d]	 **18**	45
8[e]	 **19**	44[f]
9	Silicone oil M100 **20**	39
10	Silicone oil (viscosity 30.000 cSt) **21**	51
11[c,g]	Silicone baking cup **22**	502 mg

[a] Reaction conditions: FeF_3 (7.5 mol % based on the polymer subunit), polysiloxane (1.0 g), benzoyl chloride **2** (3.0 equiv. based on the polymer subunit), 190°C, 5 hr.
[b] Isolated yield of **3**. Determined by ^1H NMR. Me_2SiF_2 was observed in traces.
[c] 11 wt % FeF_3, 567 wt % **2**.
[d] 95:5 mole ratio of dimethylsiloxane:diphenylsiloxane.
[e] ~20 wt % $[(CH_3)_2SiO]_n$.
[f] 2-Chloroethyl benzoate: 91%.
[g] 1 g silicone (Xenos Home Collection).

Table IV. Iron-Catalyzed Depolymerization of Polysiloxane 1



1 $M_n \sim 550$ g/mol **23** **24**

Entry[a]	Iron source (mol %)	**23** (equiv.)	*T* (°C)	Yield **24** (%)[b]
1	-	2	160	<1
2	$FeCl_3$ (5)	2	160	22
3	$FeCl_3$ (5)	2	180	4
4	$FeCl_3$ (5)	2	140	<1
5	FeF_3 (5)	2	160	<1
6	$FeCl_2 \bullet 4H_2O$ (5)	2	160	36
7	$Fe(acac)_2$ (5)	2	160	<1
8	$Fe(acac)_3$ (5)	2	160	<1
9	$Fe(OAc)_2$ (5)	2	160	<1
10	Fe(II)oxide (5)	2	160	<1
11	Fe(II,III)oxide (5)	2	160	<1
12	$FeCl_3$ (5)	3	160	9
13	$FeCl_3$ (2.5)	2	160	51
14	$FeCl_3$ (1.0)	2	160	9

[a] Reaction conditions: iron-salt (1.0–5.0 mol % based on the polymer subunit), polysiloxane **1** (1.0 g, $M_n \sim 550$ g/mol), **23** (2–3 equiv. based on the polymer subunit), 16 hr, 140–180°C.
[b] Determined by GC-MS with anisole as internal standard.

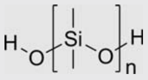
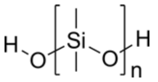
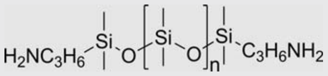
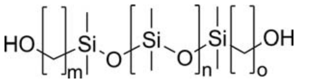
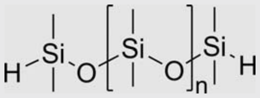
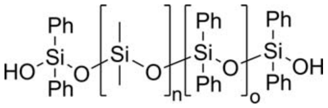
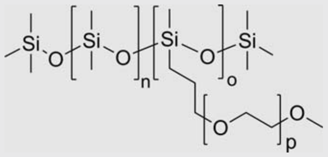
2-chloroethyl benzoate can be a suitable precursor for polymerization chemistry.[60–65] On the other hand, the polysiloxane residue is depolymerized to **3** with benzoyl chloride in the presence of the iron catalyst. In addition, poly(dimethylsiloxane) with different silicon based copolymers was tested (Table III, entries 6 and 7).[§] However, lower yields of **3** were observed. Moreover, silicon oils and a silicon baking cup were converted in good yields to the desired compound **3** (Table III, entries 9–11). With respect to the reaction mechanism we assume a similar process as described for the production of Me_2SiF_2 as described in earlier works.[35,36]

Initially the depolymerization of poly(dimethylsiloxane) hydroxy terminated **1** ($M_n \sim 550$ g/mol) with acetic anhydride was studied in the presence of catalytic amounts of iron(III) chloride at different reaction temperatures (Table IV, entries 1–4). Noteworthy, in the absence of $FeCl_3$ no product formation was observed, while significant amounts of the polysiloxane are converted to cyclic siloxanes, e.g., $[Me_2SiO]_4$, $[Me_2SiO]_6$ (Table IV, entry 1). In contrast, addition of 5.0 mol % $FeCl_3$ based on the polymer subunit revealed the formation of diacetoxydimethylsilane (**24**) in 22% yield at 160°C (Table IV, entry 2). Along with **24** cyclic siloxanes were observed by GC-MS, e.g., $[Me_2SiO]_4$, $[Me_2SiO]_6$. Noteworthy, the starting polymer **1** was completely converted. Moreover, increasing or decreasing the reaction temperature to 180°C or 140°C, respectively, showed no improvement of the yield of compound **24** (Table IV, entries 3 and 4). In contrast to the acid chloride approach (Table III) a different set-up, means a pressure tube, was applied, because of the lower boiling point of acetic anhydride (~140°C) in comparison to diacetoxydimethylsilane (163°C) and the high reaction temperature (160°C); hence with the acid chloride approach acetic anhydride will be distilled-off. In addition, different iron sources were tested (Table IV, entries 5–11). However, only in case of $FeCl_3$ and

---

[§] The amount of $[Me_2SiO]_n$ units in the polymer is unknown.

Table V. Scope and Limitations of the Iron-Catalyzed Depolymerization

Entry[a]	Substrate	Yield **24** (%)[b] ($FeCl_3$)	Yield **24** (%)[b] ($FeCl_2•4H_2O$)
1	 **1** ($M_n \sim$ 550 g/mol)	51	36
2	 **13** ($M_n \sim$ 110.000 g/mol)	14	29
3	 **14** ($M_n \sim$ 2.500 g/mol)	21	17
4	 **15** ($M_n \sim$ 5.600 g/mol)	37	15
5	 **16** ($M_n \sim$ 580 g/mol)	35	13
6[c]	 **17**	16	<1
7[d]	 **19**	<1	<1
8	Silicone oil M100 **20**	<1	21
9	Silicone oil (viscosity 30.000 cSt) **21**	<1	19
10[e]	Silicone baking cups **22**	<1	<1

[a] Reaction conditions: $FeCl_3$ or $FeCl_2•4H_2O$ (5.0 mol % based on the polymer subunit), polysiloxane (1.0 g), acetic anhydride **23** (2.0 equiv. based on the polymer subunit), 180°C, 24 hr.

[b] Determined by GC-MS with anisole as internal standard.

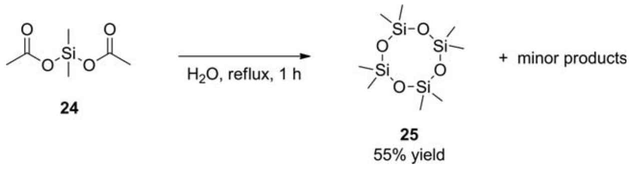
[c] 95:5 mole ratio of dimethylsiloxane:diphenylsiloxane.

[d] ~20 wt % $[(CH_3)_2SiO]_n$.

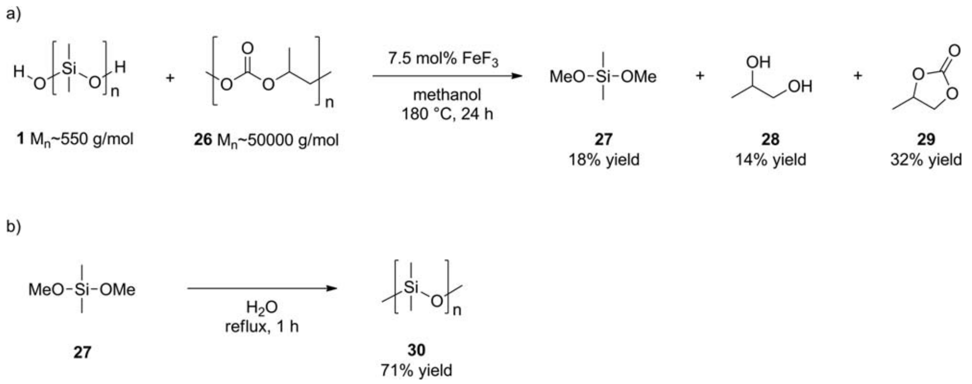
[e] 1 g silicone (Xenos Home Collection).

$FeCl_2•4H_2O$ product **24** is formed in up to 36% yield (Table IV, entries 2 and 6). Interestingly, by decreasing the catalyst loading to 2.5 mol % $FeCl_3$ the yield was increased to 51% (Table IV, entry 13).

In order to demonstrate the scope and limitations of the depolymerization system different polysiloxanes were reacted with catalytic amounts of $FeCl_3$ (5.0 mol %) or $FeCl_2•4H_2O$ (5.0 mol %) and acetic anhydride (Table V). In contrast to the acid chloride approach lower yields of the depolymerization products were realized. For instance the long chain polymer **13** was converted with $FeCl_2•4H_2O$ in 29% yield to **24** (Table V, entry 2). On the other hand, for the polymers with different end functionalities **24** was obtained in up to 37% yield (Table V, entries 3–5). Noteworthy, for this depolymerization a better performance was observed for $FeCl_3$. In case of silicon oils only $FeCl_2•4H_2O$ was capable to allow product formation (Table V,



Scheme 1. Oligomerization of diacetoxydimethylsilane.



Scheme 2. Depolymerization of polysiloxane **1** and polycarbonate **26** and polymerization of **27**.

entries 8 and 9). With respect to the reaction mechanism we assume a similar process as described for the production of Me_2SiF_2 as described in earlier works.[35,36]

After studying the depolymerization of polysiloxanes with iron salts and acetic anhydride to form diacetoxydimethylsilane **24** as product, the application of **24** as starting material for new polymers was examined to close the cycle as depicted in Figure 1. In more detail, **24** was reacted with water at refluxing conditions for 1 hr (Scheme 1). Afterward the cyclic oligomer **25** was isolated in 55% yield along with some minor oligosiloxanes/polysiloxanes, demonstrating the applicability of **24** for polymerization chemistry.

Initially the depolymerization of poly(dimethylsiloxane) hydroxy terminated **1** ($M_n \sim 550$ g/mol) with methanol (excess) and poly(propylene carbonate) **26** (3.0 equiv. based on the polymeric unit of polymer **1**) was studied in the presence of catalytic amounts of different iron salts at 180°C for 24 hr (Table IV, entries 1–4). Due to the high reaction temperature and the low boiling point of methanol, the reaction was performed in an autoclave. However, only a moderate yield of 18% of the desired dimethoxydimethylsilane **27** were observed in the presence of iron(III) fluoride (Scheme 2). Aside **27** 1,2-propanediol **28** and propylene carbonate **29** were observed as depolymerization products of polymer **26**. Unfortunately, an optimization study leads not to a significant improvement of the product yield. Moreover, the potential of dimethoxydimethylsilane as precursor for new polysiloxanes was investigated (Scheme 2b).

CONCLUSIONS

In summary, we demonstrated the usefulness of iron salts in the depolymerization of polysiloxanes to produce useful low-molecular weight silicone commodities, which can be easily applied as feed in polymerization reactions to obtain new silicones. Based on that, an overall recycling of silicones is feasible. Three different approaches have been established. On the one hand, acid chlorides have been applied as depolymerization reagents to obtain dichlorodimethylsilane as major chemical, which is the starting material for current silicone production. The second approach bases on the application of acetic anhydride as depolymerization reagent, which results in the formation of diacetoxydimethylsilane as product. Interestingly, this approach avoids any formation of halide by-products during polymerization process and the side product acetic acid can be reconverted to acetic anhydride. On the other hand, dimethoxydimethylsilane can be accessed as depolymerization product from the reaction of polysiloxanes with polycarbonates in methanol. Comparing the three approaches the acid chloride system was superior with respect to the yield of the product and the easy collection of the product.

ACKNOWLEDGMENTS

Financial support from the Cluster of Excellence “Unifying Concepts in Catalysis” (funded by the Deutsche Forschungsgemeinschaft and administered by the Technische Universität Berlin) is gratefully acknowledged.

REFERENCES

1. Barnes, D. K. A.; Galgani, F.; Thompson, R. C.; Barlaz, M. *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 1985.
2. Newborough, M.; Highgate, D.; Vaughan, P. *Appl. Therm. Eng.* **2002**, *22*, 1875.
3. Kaminsky, W.; Hartmann, F. *Angew. Chem.* **2000**, *112*, 339.
4. Kaminsky, W.; Hartmann, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 331.
5. Brandrup, J., Ed. Recycling and Recovery of Plastics, Hanser/Gardner, München, **1996**.
6. Hopewell, J.; Dvorak, R.; Kosior, E. *Philos. Trans. R. Soc. London Ser B* **2009**, *364*, 2115.
7. Moretto, H.-H.; Schulze, M.; Wagner, G. “Silicones” Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2005**.
8. Kalchauer, W.; Pachaly, B. Handbook of Heterogeneous Catalysis, 2nd ed.; Ertl G., Knözinger, H., Schüth, F., Weitkamp, J., Eds.; 2008, 2635, Wiley VCH, Weinheim.
9. Farooq, O. *J. Organomet. Chem.* **2000**, *613*, 239.
10. Sommer, L. H.; Ansul, G. R. *J. Am. Chem. Soc.* **1955**, *77*, 2482.
11. Alexander, M. R.; Mair, F. S.; Pritchard, R. G.; Warren J. E., *Appl. Organomet. Chem.* **2003**, *17*, 730.
12. Jenkner, H. Z. *Naturforsch.* **1959**, *146*, 133.

13. Aishima, I.; Sakurai, H.; Takashi, Y.; Monita, H.; Hirotsu, Y.; Hamada, T. 1972 US Pat. 3661878.
14. Apblett, A. W.; Barron, A. R.; *Organometallics* **1990**, *9*, 2137.
15. Mulhaupt, R.; Calabrese, J.; Ittel, S. D. *Organometallics* **1991**, *10*, 3403.
16. McMahon, C. N.; Bott, S. G.; Alemany, L. B.; Roesky, H. W.; Barron, A. R. *Organometallics* **1999**, *18*, 5395.
17. Brook, M. A.; Zhao, S.; Liu, L.; Chen, Y. *Can. J. Chem.* **2012**, *90*, 153.
18. Okamoto, M.; Suzuki, S.; Suzuki, E.; *Appl. Catal. A* **2004**, *261*, 239.
19. Pappas, P. S.; Just, R. L. *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 527.
20. Chang, C.-L.; Lee, H. S.-J.; Chen, C.-K. *J. Polym. Res.* **2005**, *12*, 433.
21. Chang, C. L.; Lin, Y. K. *Polym. Degrad. Stab.* **2005**, *87*, 207.
22. Okamoto, M.; Miyazaki, K.; Kado, A.; Suzuki, S.; Suzuki, E. *Catal. Lett.* **2003**, *88*, 115.
23. Okamoto, M.; Miyazaki, K.; Kado, A.; Suzuki, E. *Chem. Commun.* **2001**, 1838.
24. Schimmel, K. H. *Acta Polym.* **1987**, *38*, 495.
25. Fouquet, T.; Bour, J.; Toniazzo, V.; Ruch, D.; Charles, L. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 2057.
26. Chang, C. L.; Lee, H. S.; Chen, C. K. *Polym. Degrad. Stab.* **1999**, *65*, 1.
27. Schimmel, K. H.; Schulz, J. *Acta Polym.* **1987**, *38*, 536.
28. Schimmel, K. H.; Schroeder, E.; Schulz, J.; Souvimonh, T. *Acta Polym.* **1988**, *39*, 310.
29. Ashby, B. A. GB 990657, **1965**.
30. Borisov, S. N.; Voronkov, M. G.; Sviridova, N. G. *Zh. Obshch. Khim.* **1969**, *39*, 559.
31. Voronkov, M. G.; Trukhina, A. A.; Belousova, L. I.; Kuznetsova, G. A.; Vlasova, N. N. *Russ. J. Org. Chem.* **2007**, *43*, 501.
32. Voronkov, M. G.; Dubinskaya, E. I.; Chuikova, N. A. *Zh. Obshch. Khim.* **1977**, *47*, 2335.
33. Borisov, S. N.; Sviridova, N. G.; Voronkov, M. G. *Zh. Obshch. Khim.* **1968**, *38*, 2794.
34. Voronkov, M. G.; Sviridova, N. G.;Yuzhelevskii, Y. A.; Borisov, S. N. *Zh. Obshch. Khim.* **1969**, *39*, 564.
35. Enthaler, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 2716.
36. Enthaler, S.; Kretschmer, R. **2014**, *7*, 2030.
37. Oishi, K.; Yamazaki, T. Jpn. Kokai Tokkyo Koho, 2011213701, **2011**.
38. Okamoto, M.; Suzuki, S.; Suzuki, E. *Appl. Catal. A* **2004**, *261*, 239.
39. Okamoto, M.; Miyazaki, K.; Kado, A.; Suzuki, S.; Suzuki, E. *Catal. Lett.* **2003**, *88*, 115.
40. Tsuji, Y. Jpn. Pat. 1997, **1997**.
41. Kawamoto, T. Jpn. Pat. 2000, **2000**.
42. Chen, X.; Zhou, S.; You, B.; Wu, L. *Prog. Org. Coat.* **2012**, *74*, 540.
43. Zhang, Y.; Yang, X.; Zhao, X.; Huang, W. *Polym. Int.* **2012**, *61*, 294.
44. Robinson, P. L.; Kelly, J. W.; Evans Jr., S. A. *Phosphorus Sulfur Silicon Related Elements* **1986**, *26*, 15.
45. Lee, S. H.; Cyriac, A.; Jeon, J. Y.; Lee, B. Y. *Polym. Chem.* **2012**, *3*, 1215.
46. Cotterill, A. S.; Gill, M.; Milanovic, N. M. *J. Chem. Soc. Perkin Trans. 1* **1995**, 1215.
47. Simon, E. S.; Whitesides, G. M.; Cameron, D. C.; Weitz, D. J.; Cooney, C. L. *J. Org. Chem.* **1987**, *52*, 4042.
48. Kelly, J. W.; Robinson, P. L.; Evans Jr., S. A. *J. Org. Chem.* **1986**, *51*, 4473.
49. Lee, L. G.; Whitesides, G. M. *J. Org. Chem.* **1986**, *51*, 25.
50. Kelly, J. W.; Robinson, P. L.; Evans Jr., S. A. *J. Org. Chem.* **1985**, *50*, 5007.
51. Robinson, P. L.; Barry, C. N.; Kelly, J. W.; Evans Jr., S. A. *J. Am. Chem. Soc.* **1985**, *107*, 5210.
52. Voss, G.; Gerlach, H. *Helv. Chim. Acta* **1983**, *66*, 2294.
53. Fortier, S.; Zhang, Y.; Sharma, H. K.; Pannell, K. H. *Organometallics*, **2010**, *29*, 1041.
54. Rakita, P. E.; Worsham, L. S. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 547.
55. Xing, W. Y.; Song, L.; Hu, Y.; Zhou, S.; Wu, K.; Chen, L. *Polym. Degrad. Stab.* **2009**, *94*, 1503.
56. Goldman, D.; Dawson, K.; Nirula, A. WO2013/119677 A1, **2013**.
57. Scheim, U.; Grosse-Ruyken, H.; Ruehlmann, K.; Porzel, A. *J. Organomet. Chem.* **1985**, *293*, 29.
58. Fattakhova, D. S.; Jouikov, V. V.; Voronkov, M. G. *J. Organomet. Chem.* **2000**, *613*, 170.
59. Bassindale, A. R.;Pannell, K. H. *J. Chem. Soc. Perkin Trans.* **1990**, *2*, 1801.
60. Enthaler, S.; Weidauer, M. *Chem. Eur. J.* **2012**, *18*, 1910.
61. Enthaler, S.; Weidauer, M. *ChemSusChem* **2012**, *5*, 1195.
62. Enthaler, S. *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 239.
63. Enthaler, S.; Trautner, A. *ChemSusChem* **2013**, *6*, 1334.
64. Enthaler, S. *J. Appl. Polym. Sci.* **2014**, 131, doi: 10.1002/app.39791.
65. Enthaler, S. *Catal. Lett.* **2014**, *144*, 850.