Short communication

Iron-catalyzed depolymerizations of end-of-life silicones with fatty alcohols

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Abstract

During the last decades, polymers became one of the major materials in our society and a future without polymers is hardly imaginable. However, as negative issue of this success enormous amount of end-of-life materials are accumulated, which are mainly treated by landfill storage, thermal recycling or down-cycling. On the other hand, feedstock recycling can be an interesting option to convert end-of-life polymers to high quality polymers, via depolymerization reactions to low-molecular weight building blocks and subsequent transformation via polymerization reactions. In this regard, we present herein the depolymerization of polysiloxanes (silicones) applying fatty alcohols as depolymerization reagents. In more detail, in the presence of catalytic amounts of simple iron salts, low-molecular weight products with the motif $R(OSiMe_2)_mOR$ (R = alkyl, m = 1–2) were attained. Remarkably, the reaction of $R(OSiMe_2)_mOR$ with water showed the formation of new cyclic siloxanes, which are useful starting materials for long-chain silicones, and the corresponding fatty alcohol as side product, which can be directly reused in subsequent depolymerization reactions. Importantly, a recycling of the silicones and a straightforward recycling of the depolymerization reagent are feasible.
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Keywords: Catalysis; Iron; Silicones; Depolymerization; Fatty alcohols; Polymerization; Recycling

1. Introduction

Widely-used polymers are polysiloxanes/silicones (e.g., silicone-oil, -rubber, -grease, -resin) and numerous applications spanning from medicine, electronics, cookware, coatings to construction industry have been accounted. After the silicones fulfilled their obligations, the end-of-life polysiloxanes are mainly treated by thermal decomposition. Importantly, at this point all parts in the polymer based on natural resources [e.g. $-CH_3$ in poly(dimethylsiloxane)s] are decomposed to carbon dioxide, which has a negative impact on the environment, and for new polysiloxanes, the decreasing natural resources will be consumed. An option to enhance the sustainability can be the depolymerization of end-of-life silicones to produce low-molecular chemicals, which can be polymerized to new high-quality materials in an associated process. Nonetheless, so far only a few number of high temperature (>200 °C) or less efficient methodologies have been presented [1–20]. Recently we reported on zinc- and iron-catalyzed depolymerization reactions of poly(dimethylsiloxane)s with different kinds of depolymerization reagents. For instance, depolymerization with acid fluorides as depolymerization reagents as low-molecular chemicals difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane, under non-inert and solvent-free conditions (<150 °C) were accessed, which can be easily polymerized to access new polysiloxanes (Fig. 1a) [21,22]. Similar reactivity at higher temperature (190 °C) was observed for more attractive acid chlorides as depolymerization reagents, which yields the industrially relevant Me_2SiCl_2. Noteworthy, acid fluorides/chlorides request for upstream chemistry to access these chemicals, which base primarily on decreasing

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a) Recycling of Poly(dimethylsiloxane)s
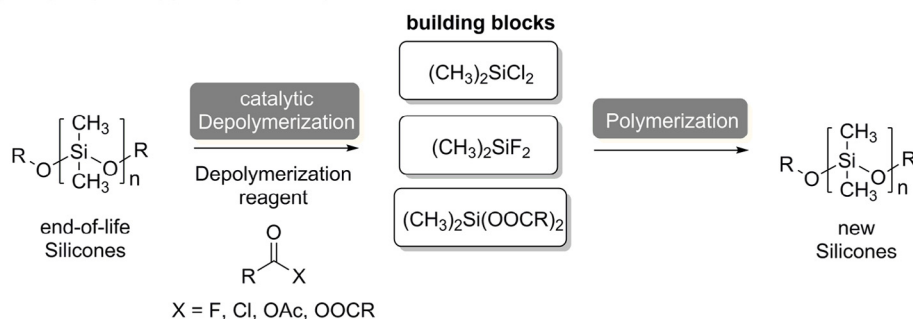
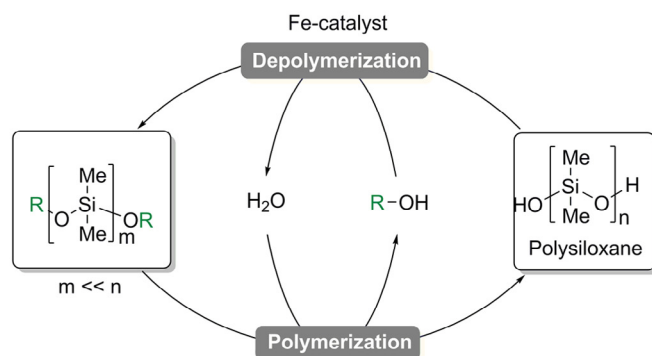b) Recycling of Poly(dimethylsiloxane)s based on fatty alcohols

Fig. 1. Recycling of poly(dimethylsiloxane)s.

fossil resources, hence increasing the cost and reducing the sustainability of such methods. In addition, during the polymerization process acids are formed as side product, which cannot be recycled easily to produce new acid chlorides for depolymerizations; hence a straightforward recycling of the depolymerization reagents is not feasible. To overcome these limitations, we recently investigated the application of fatty acid anhydride as depolymerization reagents resulting in the formation of low molecular products with the motif $RC(=O)(OSiMe_2)_mOC(=O)R$ (R = alkyl, m = 1–4), which easily react with water to obtain new silicones. Interestingly, as side product fatty acids are generated, which can be easily isolated and reconverted to the corresponding fatty acid anhydride to allow a recycling of the depolymerization reagents [23]. Importantly, the reformation of the fatty acid anhydride from the fatty acid requires high temperatures or additional reagents; hence the impact of the method is lowered with respect to environmental aspects. In this regard, the use of fatty alcohols can be a striking option to depolymerize silicones to generate products with the motif $R(OSiMe_2)_mOR$, which have been demonstrated to react easily with water to form new silicones. On the other hand, the fatty alcohol, due to the intrinsic properties, can be easily recovered and therefore reused in depolymerization reactions. In addition, the selection of the catalyst is crucial. In accordance to current process requirements, the use of cheap, abundant and low-toxic iron will be worthwhile [24]. Based on that, we report herein on the recycling of end-of-life poly(dimethylsiloxane)s via

straightforward iron-catalyzed depolymerization, applying fatty alcohols as depolymerization reagents and subsequent polymerization to new poly(dimethylsiloxane)s (Fig. 1b).

2. Experimental

2.1. General

Fatty alcohols, poly(dimethylsiloxane)s and iron salts were received from Sigma Aldrich, TCI and ABCR in their highest purity and were used without further purification steps. ^{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, 40–300 °C) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

2.2. General procedure for the depolymerization of poly(dimethylsiloxane)s

An open tube was charged with an appropriate amount of FeCl$_3$ (5.0 mol% with respect to the repeating unit, 0.34 mmol), the corresponding poly(dimethylsiloxane) (6.8 mmol with respect to the repeating unit) and 1-decanol (4 equiv. per repeating unit, 27.2 mmol). The reaction mixture was stirred at 200 °C for 24 hours. The mixture was cooled to room temperature and anisole (200 mg) was added as internal standard. An aliquot was dissolved in dichloromethane and subjected to

GC–MS analysis. The isolation (e.g., distillation, column chromatography) of the products **3**, **4**, **16a**, **16b** and **17a** was not possible due to instability and similarity. The accumulated sum of the peak areas of the products was referenced to the normalized peak area of the internal standard anisole to obtain the ratio between standard and products. Moreover, the ratio **3**:**4** (**16a**:**16b**) is based on the peak areas related to the peak area of the internal standard.

3: MS (ESI) m/z = 358 (100, M^+-CH_3). Retention time: 19.54 min.

4: MS (EI) m/z = 432 (71, M^+-CH_3), 151 (100). Retention time: 20.30 min.

15a: MS (EI) m/z = 414 (100, M^+-CH_3), 111 (12), 97 (23), 83 (23), 69 (23), 57 (23).

15b: MS (EI) m/z = 488 (90, M^+-CH_3), 318 (40), 151 (100), 133 (13), 97 (12), 85 (21), 71 (41), 57 (81).

16a: MS (EI) m/z = 470 (100, M^+-CH_3), 111 (10), 97 (22), 83 (28), 77 (15), 69 (26), 57 (32).

3: ^1H NMR (200 MHz, C_6D_6) δ = 3.67 (t, 4H, J = 6.39 Hz, OCH_2), 1.50–1.60 (m, 4H, CH_2CH_3), 1.18–1.28 (m, 28H), 0.85 (t, 6H, J = 6.39 Hz, CH_2CH_3), 0.13 (s, 6H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δ = 62.3 (OCH_2), 32.8 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 14.0 (CH_3), −3.3 ($SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (40 MHz, C_6D_6) δ = −4.5 ppm.

2.3. Depolymerization of poly(dimethylsiloxane)s – recycling of the catalyst

An open tube was charged with Fe(II,III) oxide (5.0 mol% with respect to the repeating unit, 0.34 mmol), **1** (6.8 mmol with respect to the repeating unit) and 1-decanol (3 equiv. per repeating unit, 20.4 mmol). The reaction mixture was stirred at 200 °C for 24 hours. The mixture was cooled to room temperature and a magnet was placed outside of the pressure tube to fix the catalyst. The liquid compounds were collected by decantation and anisole (200 mg) was added as internal standard. An aliquot was dissolved in dichloromethane and subjected to GC–MS analysis. A new portion of **1** and **2** was added to the catalyst and the reaction was performed as described.

2.4. Procedure for the depolymerization of poly(dimethylsiloxane) 12 and subsequent polymerization

A flask was charged with $FeCl_3$ (5.0 mol% with respect to the repeating unit, 8 mmol), poly(dimethylsiloxane) **12** (160 mmol with respect to the repeating unit) and 1-decanol (4 equiv. per repeating unit, 640 mmol). The reaction mixture was stirred at 200 °C for 24 hours. The mixture was cooled to room temperature and a sample was taken for GC–MS analysis (**3**:**4** 56:44). Afterwards, water (100 mL) and HCl (37%, 1.0 mL) were added and the mixture was stirred for 12 h at ambient temperature. To the two phase system dichloromethane (50 mL) was added. The aqueous layer was extracted with dichloromethane (2 × 25 mL) and the combined organic layers were dried with Na_2SO_4. The dichloromethane was removed in vacuum. A GC–MS analysis revealed the presence of octamethylcyclotetrasiloxane **18** and 1-decanol **2**. The octamethylcyclotetrasiloxane **18** and 1-decanol **2** were separated by Kugelrohr distillation.

2.5. 1-Decanol 2

^1H NMR (200 MHz, $CDCl_3$) δ = 3.54 (t, 2H, J = 6.60 Hz), 2.45 (br, 1H), 1.42–1.53 (m, 2H), 1.20 (m, 14H), 0.78–0.84 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 62.8 (CH_2), 32.7 (CH_2), 32.2 (CH_2), 29.63 (CH_2), 29.57 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 25.8 (CH_2), 22.7 (CH_2), 14.0 (CH_3) ppm. MS (EI) m/z = 158 (1, M^+), 112 (14), 97 (26), 83 (50), 70 (81) 55 (100). The analytical data were compared with an authentic sample.

## 2.6. Octamethylcyclotetrasiloxane 18

^1H NMR (200 MHz, $CDCl_3$) δ = 0.04 (s) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 0.74 ppm. $^{29}Si\{^1H\}$ NMR (40 MHz, $CDCl_3$) δ = −21.2 ppm. MS (EI) m/z = 296 (1, M^+), 281 (100), 265 (11).

3. Results and discussion

Initially the depolymerization of poly(dimethylsiloxane) hydroxy terminated **1** (M_n ~550 g/mol) with 1-decanol **2** was studied in the presence of catalytic amounts of iron salts in an open flask (Table 1, entries 1–12). Noteworthy, in the absence of any iron source low product formation was observed (Table 1, entry 1). In contrast, the addition of 5.0 mol% iron(II) or iron(III) salts based on the polymer subunit revealed the degradation of the polymer chain and the compounds **3** and **4** were detected containing the $RO(SiMe_2)_mOR$ motif with m = 1 (**3**), and m = 2 (**4**) and R = decyl. Importantly, in contrast to earlier works, no additional reagent is necessary to remove the produced water, while in this approach the water is released to the atmosphere. Furthermore, it is noteworthy that the reaction is performed under solvent-free and protection gas free conditions. In more detail, no significant difference was observed in case of FeF_2 and FeF_3 with **3** as the major product (Table 1, entries 2–3). In contrast, for iron chlorides a better reactivity was found for the water-free metal precursors (Table 1, entries 4–6). In case of iron salts with acetyl acetonate ligands, a better performance was observed for the Fe(III) salt (Table 1, entries 7–8). Moreover, iron oxides were applied as precatalysts exhibiting lower yields, but in case of Fe(II,III) oxide a simple recycling by magnetic separation of the catalyst was feasible and the residue showed still catalytic activity after run 3 (Table 1, entries 11–14). Noteworthy, for numerous iron salts as side product didecyl ether was observed, this can be formed by the reaction of two molecules 1-decanol and elimination of water. In addition, the amount of depolymerization reagent was varied. In increasing the amount to 4 equivalents, an increased yield was monitored, while a decrease to 1–2 equivalents showed no product formation (Table 1, entries 15–18). Finally, the influence of the reaction temperature was investigated, demonstrating best performance at 200 °C (Table 1, entries 19–21). After investigation of the reaction conditions of the iron-catalyzed depolymerization of silicones, we directed our attention to study the scope and limitations of the methodology (Table 2).

Table 1
Iron-catalyzed depolymerization of polysiloxane **1**.
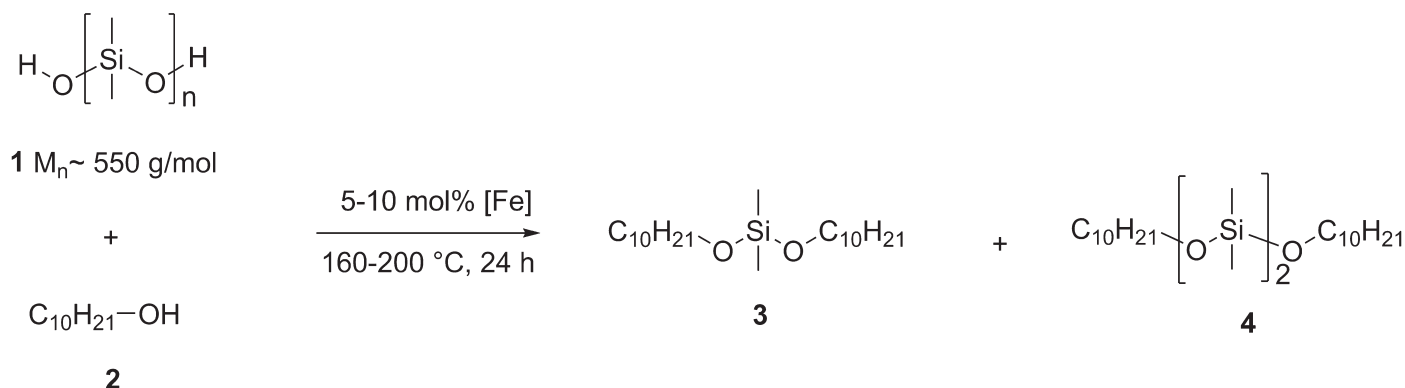
Entry[a]	Iron source [mol%]	**2** [equiv.]	T [°C]	t [h]	Ratio[b] standard: products	Ratio **3**:**4**[c]
1	-	3	200	24	1:3	72:27
2	FeF$_2$ (5)	3	200	24	1:13	65:35
3	FeF$_3$ (5)	3	200	24	1:10	64:36
4	FeCl$_2$ (5)	3	200	24	1:17	52:48
5	FeCl$_2$ 4H$_2$O (5)	3	200	24	1:10	56:44
6	FeCl$_3$ (5)	3	200	24	1:18	62:38
7[d]	Fe(acac)$_2$ (5)	3	200	24	1:11	73:27
8[d]	Fe(acac)$_3$ (5)	3	200	24	1:27	59:41
9	Fe(OAc)$_2$ (5)	3	200	24	1:17	68:32
10	Fe(OTf)$_2$ (5)	3	200	24	1:20	72:28
11	Fe(III)oxide (5)	3	200	24	1:7	66:33
12	Fe(II,III)oxide (5) [1. Run]	3	200	24	1:7	76:24
13	Fe(II,III)oxide (5) [2. Run]	3	200	24	1:8	66:34
14	Fe(II,III)oxide (5) [3. Run]	3	200	24	1:12	68:31
15	FeF$_3$ (5)	4	200	24	1:15	68:32
16	FeCl$_3$ (5)	4	200	24	1:50	63:37
17	FeCl$_3$ (5)	2	200	24	<1	<1
18	FeCl$_3$ (5)	1	200	24	<1	<1
19	FeCl$_3$ (5)	3	180	24	1:10	49:51
20	FeCl$_3$ (5)	3	160	24	1:5	53:47
21	FeCl$_3$ (5)	3	140	24	<1	<1

[a] Reaction conditions: iron source (5–10 mol% based on the polymer subunit), polysiloxane **1** (6.8 mmol), 1-decanol **2** (1-4 equiv. based on the polymer subunit), 140–200 °C, 24 h.
[b] Ratio determined by GC–MS using anisole (200 mg) as internal standard. Products = **3** + **4**.
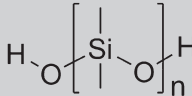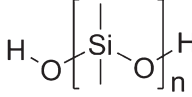[c] Determined by GC–MS.
[d] acac = acetylacetonate.

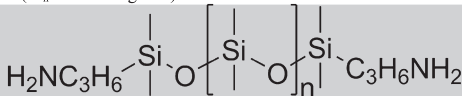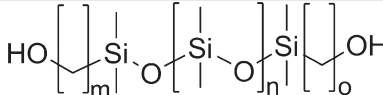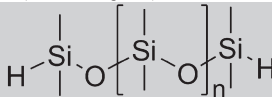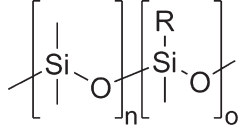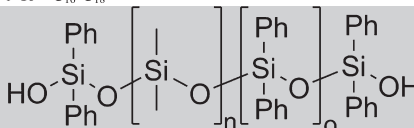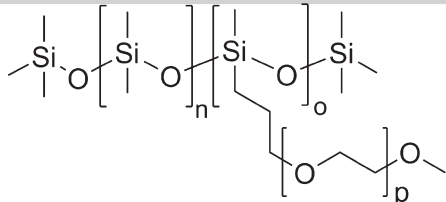For instance, increasing the length of the polymer chain (M_n ~110.000 g/mol) resulted in lower yields of **3** and **4** (Table 2, entry 2). In contrast to that, a significant influence of the end group was observed (Table 2, entries 3–5). For instance with hydrides as end function, an excellent performance was observed (Table 2, entry 5). Moreover, two different silicone oils and a silicone baking cup were converted in good yields to the desired products (Table 2, entries 9–11).

In addition, the influence of the fatty alcohol component was studied (Fig. 2). In more detail, the chain length of the fatty alcohol was increased towards C12 (lauryl alcohol **16**) and C14 (myristyl alcohol **17**). In comparison to 1-decanol, lower yields were observed for the corresponding depolymerization products, but in a similar ratio of **16a**:**16b**. In order to demonstrate the possibility of subsequent polymerization process after the depolymerization process, the experiment presented in Table 2

entry 9 was performed on a larger scale and coupled with a polymerization process to produce new silicones (Fig. 3). In more detail, iron(III) chloride, silicone **14** and 1-decanol were heated for 24 hours at 200 °C. Analysis of the reaction mixture by GC–MS revealed the formation of the depolymerization products **3**:**4** in a ratio of 56:44 after 24 hours. Subsequently, the polymerization was performed by addition of water, HCl and stirring for 12 hours at ambient temperature [25]. A GC–MS analysis revealed the formation of the cyclic oligosiloxane **18**. Afterwards, the fatty alcohol layer was easily separated from the aqueous layer and the oligosiloxane was removed by distillation and isolated in 69% yield. Interestingly, the cyclic oligosiloxane **18** presents a useful precursor for polysiloxanes [26,27]. Moreover, the fatty alcohol was isolated in 81% and can be directly applied for a new batch of iron-catalyzed depolymerizations.

Table 2
Iron-catalyzed depolymerization – scope and limitations.

Polysiloxane

2 (4 equiv.)
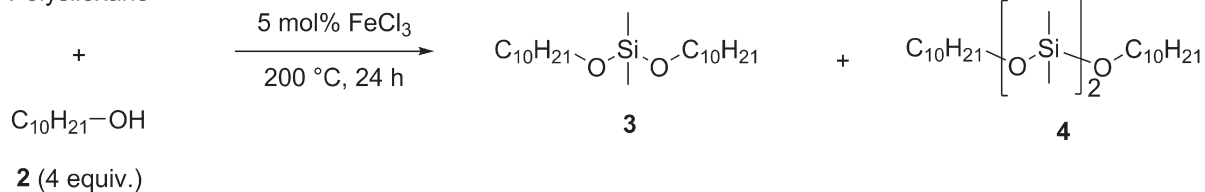
Entry[a]	Substrate	Ratio[b] standard: products	Ratio[c] **3**:**4**
1	**1** (M_n ~550 g/mol)	1:50	63:37
2	**5** (M_n ~110.000 g/mol)	1:32	61:39
3	**6** (M_n ~2.500 g/mol)	1:12	55:45
4	**7** (M_n ~5.600 g/mol)	1:13	57:43
5	**8** (M_n ~580 g/mol)	1:99	57:43
6	**9** R = C_{16}-C_{18}	<1	<1
7[d]	**10**	1:12	62:38
8[e]	**11**	<1	<1
9	Silicone oil M100 **12**	1:19	61:39
10	Silicone oil (Baysilon) **13**	1:32	63:37
11[f]	Silicone baking cup **14**	1:16	63:37
12[g]	Rainbow Loom® **15**	1:32	71:29

[a] Reaction conditions: FeCl₃ (5 mol% based on the polymer subunit), polysiloxane (6.8 mmol), 1-decanol **2** (4 equiv. based on the polymer subunit), 200 °C, 24 h.

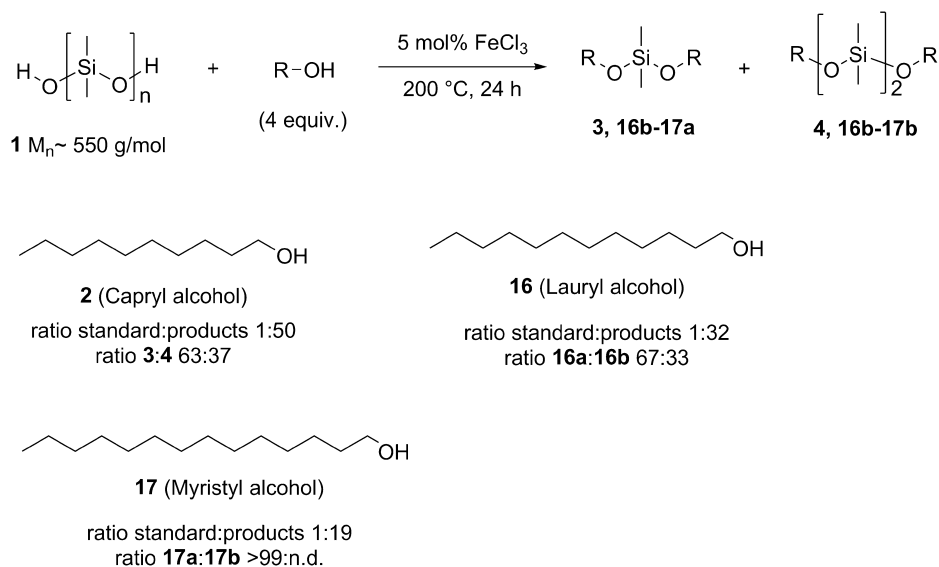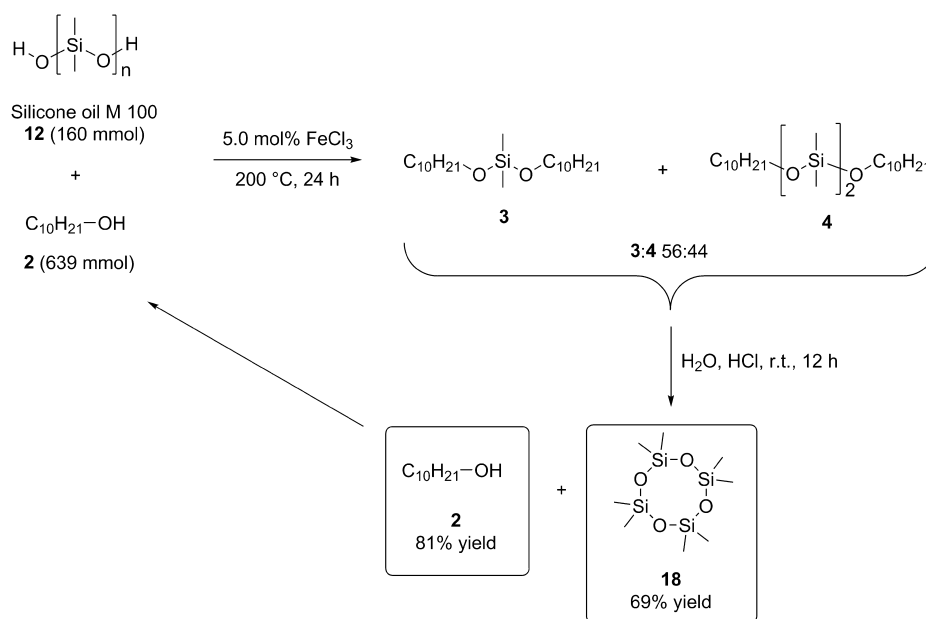[b] Ratio determined by GC–MS using anisole (200 mg) as internal standard. Products = **3** + **4**.

[c] Determined by GC–MS.

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

[e] ~ 20 wt% [(CH₃)₂SiO]ₙ.

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

[g] 1 g silicone (Rainbow Loom).

Fig. 2. Depolymerization of poly(dimethylsiloxane) **1** – fatty alcohol variation.

Fig. 3. Recycling of poly(dimethylsiloxane) **12**.

4. Conclusions

In summary, we installed a concept for the recycling of end-of-life polysiloxanes via a coupling of depolymerization and polymerization processes. In more detail, iron catalysis was established as valuable for the depolymerization process using fatty alcohols, based on renewable resources, as depolymerization reagent. Especially the application of iron(II,III) oxide is promising in terms of recyclability and operability. Interestingly, the attained low-molecular weight chemicals were successfully polymerized to an oligosiloxane, which is a suitable building block for long-chain silicones. In addition, as side product the corresponding fatty alcohol is formed; this can be applied for new depolymerization processes. Overall, recycling of silicones and recycling of the depolymerization reagents are feasible.

Appendix: Supplementary materials

Supplementary data to this article can be found online at doi:10.1016/j.reffit.2015.09.002.

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