

Depolymerization protocol for linear, branched, and crosslinked end-of-life silicones with boron trifluoride diethyl etherate as the depolymerization reagent

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ABSTRACT: An important issue for current society is the accumulation of large amounts of end-of-life polymers, which are mainly deposited in landfills, converted by thermal recycling or down cycling to low-quality materials. In contrast to that, the feedstock recycling of end-of-life polymers to produce new high-quality polymers is only applied to a small portion of waste. In more detail, low-molecular weight chemicals are generated by this methodology; they can be polymerized in a second step to produce new high-quality polymers. Notably, with these depolymerization-polymerization processes, contributions to a more sustainable, resource-conserving, and environmentally benign society can be made. In this regard, we have set up a capable protocol for the depolymerization of polysiloxanes, which are applied extensively in numerous technological applications. Boron trifluoride diethyl etherate was used as a depolymerization reagent to transform Si—O bonds in linear, branched, and crosslinked silicones to Si—F bonds. As depolymerization products, difluorodimethyl silane for linear polysiloxanes and methyl trifluorosilane for branched polysiloxanes were obtained; these were suitable synthons for new polymers and will allow an overall recycling of polysiloxanes. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42814.

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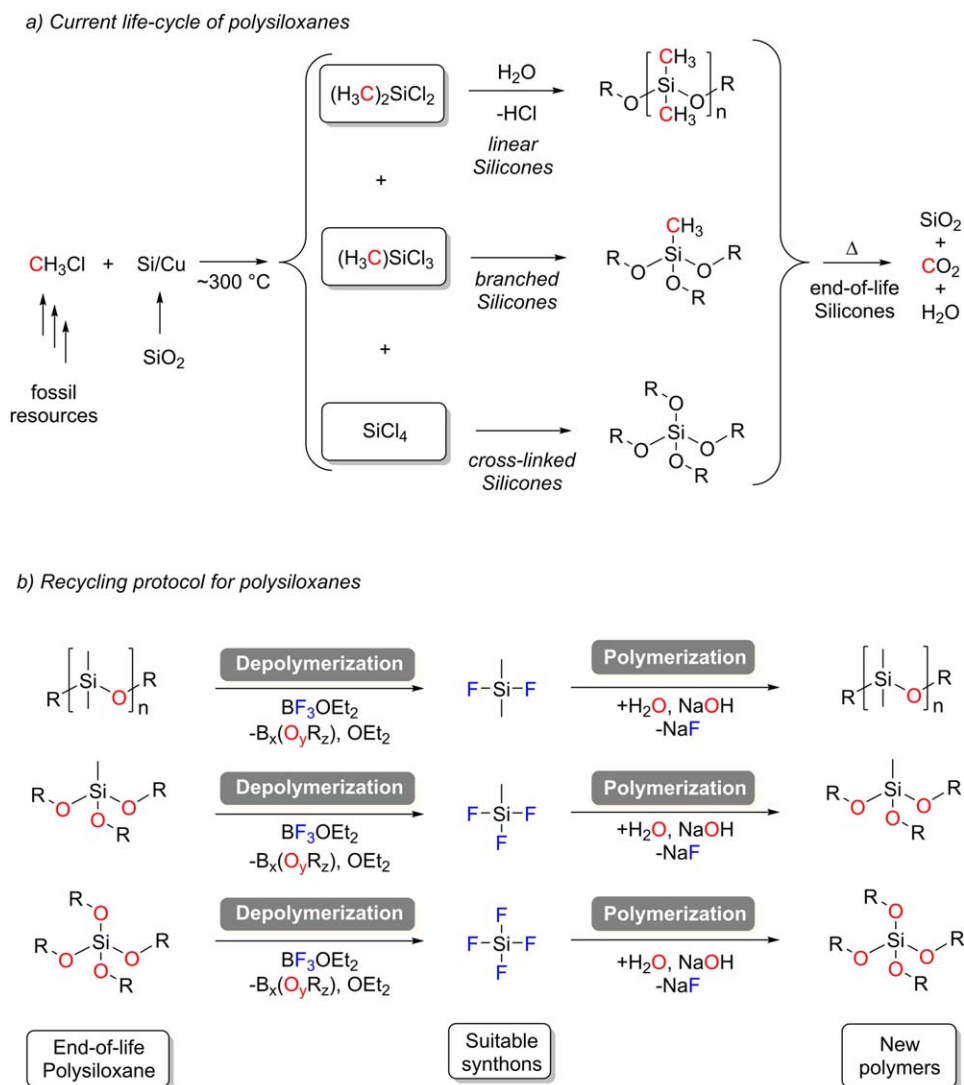
INTRODUCTION

The state-of-the-art waste management system for end-of-life polymers is mainly based on landfill storage, thermal recycling, and down cycling to generate low-quality materials. In contrast, methodologies for the selective degradation–decomposition–depolymerization to produce valuable chemicals are only carried out for a minor fraction of the waste. Importantly, the generated low-molecular-weight products can be applied as starting materials for new polymers without a loss of quality (feedstock/chemical recycling).^{1–5} Moreover, the design of efficient recycling processes could be a possibility for saving our steadily decreasing natural resources and could contribute to a more sustainable and environmentally benign society. Nevertheless, different matters hamper the implementation of feedstock recycling, for example, high energy demand for the degradation processes, copolymers, additives, selectivity, and the current low price for fossil resources for the production of new polymers (e.g., crude oil, natural gas, coal).⁶ Polysiloxanes (silicones) are attractive materials and are, therefore, used extensively in

numerous technological applications.⁷ In particular, the easy availability on a large-scale by Müller–Rochow synthesis and subsequent hydrolysis are factors of success [Scheme 1(a)]. In more detail, methyl chloride is reacted with silicon to access, for example, dichlorodimethyl silane, methyl trichlorosilane, tetrachlorosilane, or chlorotrimethyl silane. For instance, the polymerization of dichlorodimethyl silane affords linear polysiloxanes, whereas that with methyl trichlorosilane branched polysiloxanes and with tetrachlorosilane, crosslinked polysiloxanes are available.⁷ Moreover, chlorotrimethyl silane can be used as an end cap. On the basis of this range of chlorosilanes, a wide variety of products with tailor-made abilities are feasible. Notably, additional synthetic steps and high energy input are required to produce the starting materials for Müller–Rochow synthesis; for example, methyl chloride is accessible in a sequence from fossil resources, and a huge amount of energy is needed to produce silicon. Currently, one major treatment of end-of-life polysiloxanes is thermal decomposition, which destroys all functions derived from fossil resources, for example, —CH₃, and generates the pollution sink, carbon dioxide.⁸

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Scheme 1. Current lifetimes and recycling protocols of the polysiloxanes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Moreover, for new silicones, fossil resources will be consumed. To overcome these issues, the depolymerization of silicones can be an interesting option (see previous).^{9–11} In this regard, we recently established a feedstock recycling concept for linear poly(dimethyl siloxane)s (**4s**) with the aid of zinc or iron catalysis.^{12–15} In more detail, the depolymerization of **4s** can be realized in the presence of depolymerization reagents, for example, benzoyl fluoride, benzoyl chloride/potassium fluoride, benzoic anhydride/potassium fluoride, or boron trifluoride dietherate, to obtain difluorodimethyl silane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyl disiloxane (**6**) as products. Interestingly, **5** and **6** are useful starting materials for new silicones.¹⁶ Moreover, an interesting depolymerization reagent is boron trifluoride diethyl etherate (BF_3OEt_2 ; **2**) for the formation of monomers **5** and **6** as products. On the one hand, **2** can operate as a Lewis acid in the activation of Si—O bonds in silicones and, on the other hand, as a fossil-resource-independent reagent with high fluorine contents of 40% (**2**) or 84% [boron trifluor-

ide (BF_3)]. Diethyl ether could be easily reused for the synthesis of new **2**.¹⁷ As a side product, a $\text{B}_x(\text{O}_y\text{R}_z)$ compound is formed and could easily be reconverted to BF_3 by $\text{NaF}/\text{H}_2\text{SO}_4$.¹⁸ On this basis, the boron of the depolymerization reagent could be reused and, hence, increase the sustainability of the methodology. However, the presented protocols are limited to linear **4s**. On this basis, we wondered whether this method could be transferred to polymers containing branched or crosslinked units to create suitable synthons, which could be used as a starting chemicals for new polymers [Scheme 1(b)].

EXPERIMENTAL

General

All chemicals were used as received without further manipulation. $^1\text{H-NMR}$, $^{19}\text{F-NMR}$, $^{13}\text{C-NMR}$ and $^{29}\text{Si-NMR}$ spectra were recorded on a Bruker Avance 200-MHz instrument ($^1\text{H-NMR}$: 200.13 MHz, $^{13}\text{C-NMR}$: 50.32 MHz, $^{19}\text{F-NMR}$: 188.31 MHz, and $^{29}\text{Si-NMR}$: 39.71 MHz) with the proton signals of the deuterated

solvents as reference or external standards and on a Bruker Avance 400-MHz solid-state instrument (^1H -SSNMR: 399.86 MHz, ^{13}C -SSNMR: 100.54 MHz, and ^{29}Si -SSNMR: 79.44 MHz, SSNMR = Solid State NMR). For the NMR spectra of the compounds, see the Supporting Information.

Synthesis of Polysiloxanes: Procedure for the Synthesis of Trimethyl Silyl Terminated Poly(dimethyl siloxane) (7), Poly(dimethyl siloxane-co-methyl siloxane) (10), and Poly(dimethyl siloxane-co-siloxane) (13)

A flask was charged with hydroxyl-terminated **4** (3.0 g or 50.0 mmol for **7** and 10.0 g or 167.0 mmol on the basis of the polymer subunit for **10** and **13**) and a stirring bar. To the starting material, the corresponding silyl chloride (2.1 mL or 16.4 mmol of trimethyl silyl chloride for **7**, 1.4 mL, 12.1 mmol of methyl trichlorosilane for **10**, and 1.0 mL or 9.1 mmol of tetrachlorosilane for **13**) was added dropwise. The reaction mixture was stirred at room temperature (r.t.) for 3 days; this was followed by heating at 50°C for 1 day. After the solutions were cooled to r.t., volatile compounds were removed by reduced pressure.

7. Yield = 2.8 g (93 wt %) of a colorless oil. ^1H -NMR [200 MHz, chloroform- d_1 (CDCl_3), 25°C, δ , ppm]: 0.07 (s, br, br, = broad), 0.06 (s, br), 0.03 (s, br). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50 MHz, CDCl_3 , 25°C, δ , ppm): 1.88 (s), 1.74 (s), 1.09 (s), 1.01 (s), 0.90 (s), 0.81 (s), 0.70 (s). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (40 MHz, CDCl_3 , 25°C, δ , ppm): 7.2, -19.1, -21.5, -21.6, -22.1, -22.2.

10. Yield = 8.6 g (86 wt %) of a colorless solid. ^1H -NMR (400 MHz SSNMR, 25°C, δ , ppm): -0.29 (s, br), -0.32 (s, br), -0.33 (s, br), -0.40 (s, br), -0.42 (s, br). $^{13}\text{C}\{^1\text{H}\}$ -NMR (^1H -NMR; 100 MHz SSNMR, 25°C, δ , ppm): -1.43 (s), -5.37 (s, br). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (^1H -NMR; 80 MHz SSNMR, 25°C, δ , ppm): -24.8, -68.6, -69.9.

13. Yield = 7.9 g (79 wt %) of a colorless gel. ^1H -NMR (400 MHz SSNMR, 25°C, δ , ppm): -0.41 (s, br), -0.47 (s, br), -0.49 (s, br). $^{13}\text{C}\{^1\text{H}\}$ -NMR (^1H -NMR, 100 MHz SSNMR, 25°C, δ , ppm): -1.53 (s). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (80 MHz SSNMR, 25°C, δ , ppm): -17.4, -100.6.

Depolymerization of Polysiloxane Model Compounds

NMR Scale: Procedure for the Conversion of Methyl tris(trimethyl siloxy)silane (8) or tetrakis(trimethyl siloxy)silane (11). An NMR tube was charged with CDCl_3 (0.5 mL), **8** or **11** (0.19 mmol), and **2** (1.3–4.6 equiv., 0.25–0.87 mmol). After 10 min at r.t., the samples were investigated by NMR methods. The yields and ratio were determined by integrals of the proton signals of the methyl groups of the starting material and products.

Fluorotrimethyl silane (3). ^1H -NMR (200 MHz, CDCl_3 , 25°C, δ , ppm): 0.20 (d, $^3J_{\text{HF}} = 7.4$ Hz, $J_{\text{HF}} =$ coupling constant for the coupling between H and F). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50 MHz, CDCl_3 , 25°C, δ , ppm): -0.01 (d, $^2J_{\text{CF}} = 15.2$ Hz). ^{19}F -NMR (188 MHz, CDCl_3 , 25°C, δ , ppm): -157.8 (dec, $^3J_{\text{HF}} = 7.4$ Hz, ddec, $^1J_{\text{SiF}} = 274.6$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (40 MHz, CDCl_3 , 25°C, δ , ppm): 36.7.

Diethyl ether ^1H -NMR (200 MHz, CDCl_3 , 25°C, δ , ppm): 3.69 (q, $^3J_{\text{HH}} = 7.0$ Hz, CH_2), 1.26 (t, $^3J_{\text{HH}} = 7.0$ Hz, CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (50 MHz, CDCl_3 , 25°C, δ , ppm): 67.0 (CH_2), 14.7 (CH_3).

Flask Scale: Procedure for the Conversion of 8 and 11. A flask was charged with the corresponding silane (**8**: 1.0 g or 3.2 mmol; **11**: 0.65 g or 1.7 mmol) and a stirring bar, and a Vigreux column and a distillation head were connected. The flask was heated to 100°C (the oil-bath temperature), and **2** (for **8**, 3.0 equiv or 9.6 mmol; for **11**, 4.0 equiv or 6.76 mmol) was added. The mixture was stirred and heated for 60 min. The formed low-boiling compounds were continuously distilled off and collected. After 1 h, we measured the overall yield by weighing the collecting flask. The quality and the ratio (integrals of the proton signals of the methyl groups) were determined by NMR.

For 8. 3 (see previous), methyl trifluorosilane (**9**)¹⁹, diethyl ether (see previous).

^1H -NMR (200 MHz, CDCl_3 , 25°C, δ , ppm): 0.50 (q, $^3J_{\text{HF}} = 4.0$ Hz). ^{19}F -NMR (188 MHz, CDCl_3 , 25°C, δ , ppm): -133.5 (q, $^3J_{\text{HF}} = 4.0$ Hz, dq, $^1J_{\text{SiF}} = 272.0$ Hz).

For 11. 3 (see previous) and diethyl ether (see previous).

Depolymerization of Polysiloxanes: Procedure for the Depolymerization of Hydroxyl-Terminated 4, 7, 10, and 13

The experiments were carried out in accordance with the section on Flask Scale: Procedure for the Conversion of **8** and **11**. We used polysiloxane (for **4**, 1.0 g; for **7**, 1.0 g; for **10**, 1.0 g; for **13**, 1.0 g) the reaction temperature was 100 or 120°C (the oil-bath temperature), and 300 wt % of **2**.

For 4. 5: ^1H -NMR (200 MHz, CDCl_3 , 25°C, δ , ppm): 0.31 (t, $^3J_{\text{HF}} = 6.2$ Hz). ^{19}F -NMR (188 MHz, CDCl_3 , 25°C, δ , ppm): -131.4 (sept, $^3J_{\text{HF}} = 6.2$ Hz, ddec, $^1J_{\text{SiF}} = 289.9$ Hz).

6: ^1H -NMR (200 MHz, CDCl_3 , 25°C, δ , ppm): 0.20 (d, $^3J_{\text{HF}} = 6.2$ Hz, overlapped by **3**). ^{19}F -NMR (188 MHz, CDCl_3 , 25°C, δ , ppm): -131.1 (sept, $^3J_{\text{HF}} = 6.2$ Hz). Diethyl ether (see previous).

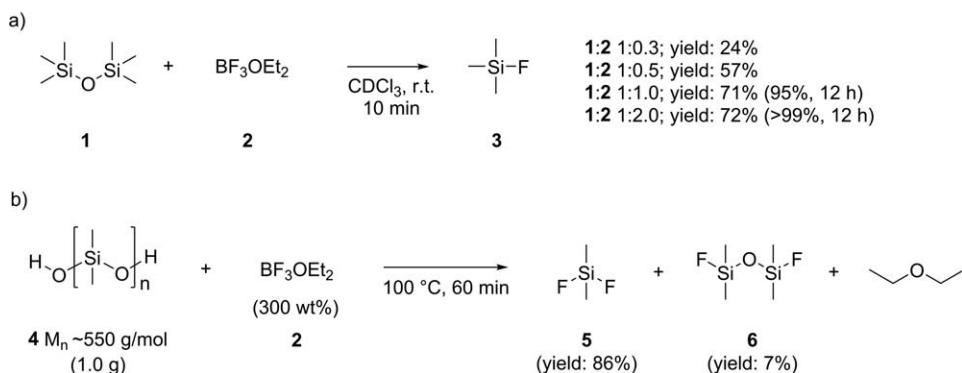
For 7. 3 (see previous), **5** (see previous), **6** (see previous), and diethyl ether (see previous).

For 10. 9 (see previous), **5** (see previous), **6** (see previous), and diethyl ether (see previous).

For 13. 5 (see previous) and diethyl ether (see previous).

RESULTS AND DISCUSSION

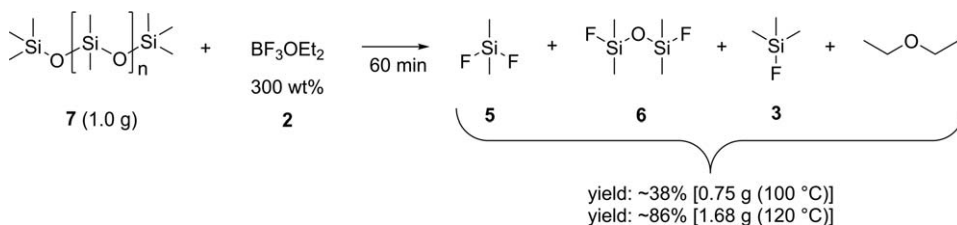
Recently, we studied the conversion of hexamethyl disiloxane (**1**) with **2** as a model for the depolymerization of dimethyl siloxane units in linear silicones (Scheme 2).¹⁵ We have found that with 2 equiv of **2**, the Si—O bonds were cleaved and transformed to Si—F bonds in excellent yields (**3**: >99%); this demonstrated the potential for depolymerization reactions. A transfer of this model approach to linear **4** was carried out on an NMR scale. In more detail, silicone **4** was reacted with **2** at r.t. in CDCl_3 as the solvent (see Supporting Information). ^1H -NMR and ^{19}F -NMR measurements at different reaction times (0, 10, and 60 min and 18 h) revealed the successive conversion of the silicone, as observed by the appearance of new signals for the protons of the methyl functionalities and the disappearance of the Si—OH function in ^1H -NMR. In addition, a precipitate was formed during the proceeding reaction. After 18 h, the characteristic signal for the depolymerization product **5** was observed. However, no full conversion

Scheme 2. Reaction of 1 and 4 with 2.¹⁵

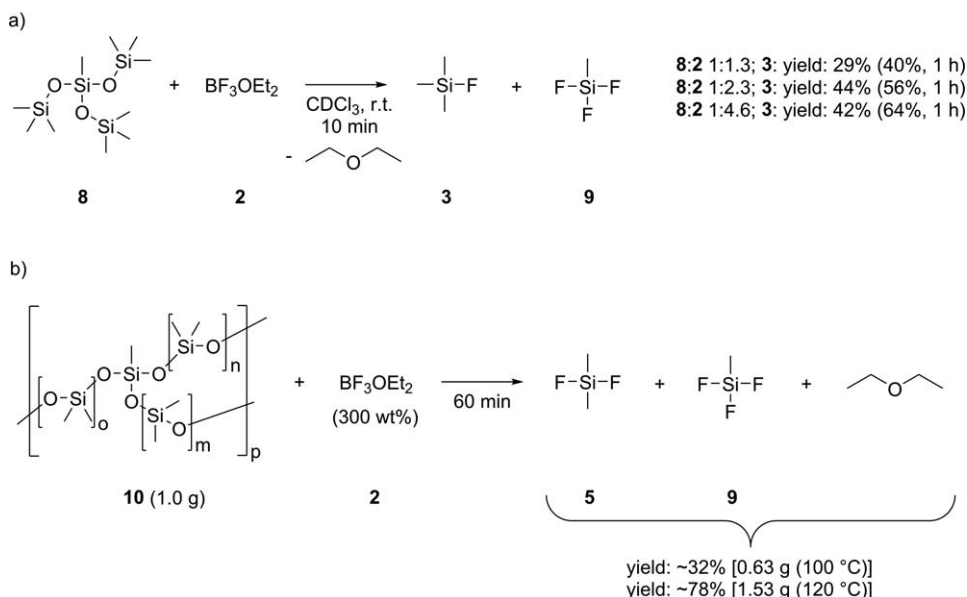
of the silicone to 5 was achieved. On this basis, the reaction temperature was increased to accelerate the reaction. In more detail, a flask was charged with hydroxyl-terminated 4 (1.0 g) connected with a Vigreux column, and a distillation head and the depolymerization reagent 2 (300 wt %) was added (Scheme 1b). The mixture was stirred and heated to 100°C (the oil-bath temperature) under solvent-free and noninert conditions. By this approach, the generated low-boiling products 5 and 6 were continuously distilled off and collected at low temperature (−196°C) in 86% yield (5) and 7% yield (6) along with diethyl ether. Interestingly, the depolymerization products 5 and 6 are interesting building blocks for new silicones.¹⁵ In the reaction flask, an off-white solid $[B_x(O_yR_z)]$ was formed; it could be reconverted to BF_3 by NaF/H_2SO_4 . Stimulated by these results, we became interested in the transfer of the method toward branched and cross-linked silicones. As presented in Scheme 2a, 1 can be seen on the one hand as a model for the linear Si—O—Si polymer unit and, on the other hand, as a trimethyl silyl end cap, which can modify the properties of the silicones.²⁰ On this basis, hydroxyl-terminated 4 (number-average molecular weight $\approx 550 \text{ g/mol}$) was reacted with methyl trichlorosilane to introduce trimethyl silyl end caps. The successful protection of the hydroxyl groups was proven by $^1\text{H-NMR}$, $^{13}\text{C}\{^1\text{H}\}$ -NMR, and $^{29}\text{Si}\{^1\text{H}\}$ -NMR (see Supporting Information). Afterward, polymer 7 was subjected to depolymerization in accordance with the reaction presented for silicone 4 (Scheme 3). In more detail, silicone 7 was reacted with 2 at r.t. in CDCl_3 (Supporting Information). $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ measurements at different reaction times (0, 10, and 60 min and 18 h) revealed, as expected, the successively depolymerization of 7, and after 18 h, traces of 5 were detected, but no full conversion was detected. Moreover, with $^{19}\text{F-NMR}$, it was shown that the trimethyl silyl end cap was converted to Me_3SiF ; this demonstrated the possibility of fully converting the silicone. On this basis, the reaction temperature was increased, and a flask

with a Vigreux column and a distillation head was charged with polymer 7, and the depolymerization reagent 2 (300 wt %) was added. The mixture was stirred and heated to 100°C (the oil-bath temperature), and the generated low-boiling products were continuously distilled off and collected at low temperature (−196°C). After 60 min, the colorless distillate was investigated by NMR techniques, and four products were assigned: 5, traces of 6 and 3, and diethyl ether. This observation revealed, on the one hand, the depolymerization of 4 and, on the other hand, the transformation of the OSiMe₃ end cap and the scope of the depolymerization protocol. The products 3, 5, and 6 were formed in a yield of about 38% (an estimation of the product ratio was not feasible because of the overlapping shifts in $^1\text{H-NMR}$ of 3 and 6). In comparison to silicone 4, a reduced yield was observed; this was probably caused by the TMS (trimethylsilyl) end caps. Interestingly, increasing the reaction temperature to 120°C revealed an increase in the yield to about 86%. It was noteworthy that all of the obtained products (5, 6, 9, and 3) could be applied as starting materials for polymerization chemistry to produce new silicones.⁷

Next, we focused on the depolymerization of branched silicones. As model for the depolymerization of branched silicones, the conversion of 8, because of the mimicry of the MeSiO_3 unit, was examined [Scheme 4(a)]. A solution of 8 in CDCl_3 was added to 2 in various ratios at r.t. After this addition, the mixtures were analyzed by NMR techniques. For instance, the reaction of 8 with 2 in a ratio of 1 : 1.3 showed the formation of a new signal in the $^1\text{H-NMR}$ spectrum. Interestingly, the signals for 8 [$\delta = 0.08$ (OCH₃), −0.02 (SiCH₃) ppm] disappeared, and new signals arose in the range of δ of 0.04–0.09 ppm. Along with these signals, a doublet was observed at a δ of 0.18 ppm, and a coupling constant of $^3J_{\text{HF}} = 7.44 \text{ Hz}$, which could be assigned to 3, was also clarified by $^{19}\text{F-NMR}$ by a complex signal at −157.8 ppm. Interestingly, increasing the reaction time or



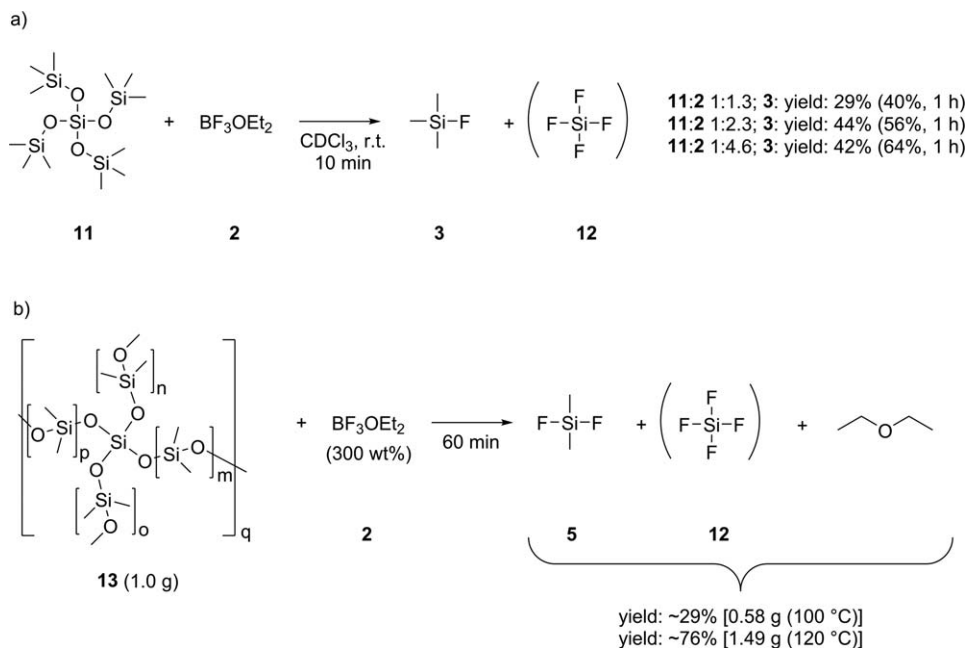
Scheme 3. Reaction of 7 with 2.



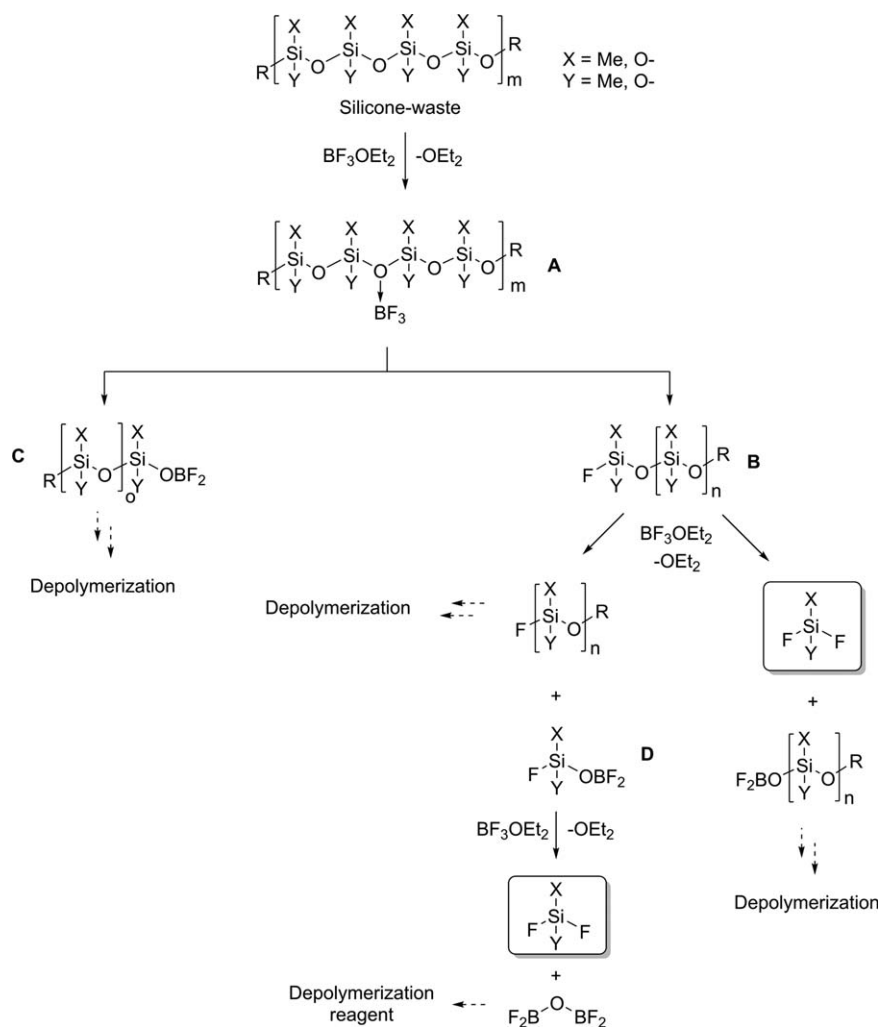
Scheme 4. Reaction of 8 and branched polymer 10 with 2.

the amount of 2 revealed an increase in the formation of 3. Unfortunately, at this point, the formation of 9 was not detected; this was probably due to the low concentration and low solubility at r.t. in CDCl₃ (the amount of 9 was not determined by NMR methods because of the low boiling point of -30°C).²¹ On this basis, the reaction was scaled up. A flask with a Vigreux column and a distillation head was charged with 8, and the depolymerization reagent 2 (3 equiv) was added. The mixture was stirred and heated to 100°C (the oil-bath temperature), and the generated low-boiling products were continuously distilled off and collected at low temperature (-196°C). After 60 min, the distillate was investigated by NMR techniques, and along with 3, compound 9 was observed. It was noteworthy that this result shows the transformation of the Si—O bonds of

the MeSiO₃ units to MeSiF₃. Afterward, the model was transferred to the branched silicone 10, which was synthesized by the reaction of hydroxyl-terminated 4 (number-average molecular weight ≈ 550 g/mol) with methyl trichlorosilane [Scheme 4(b), see Supporting Information]. First, silicone 10 was reacted with 2 at r.t. in CDCl₃, and the depolymerization was followed by ¹H-NMR and ¹⁹F-NMR spectroscopy (see Supporting Information), which showed the conversion of the silicone 10. After 18 h, small amounts of 5 were detected. On the basis of the low yield of the depolymerization product 5, the reaction temperature was increased to 100 or 120°C, respectively (see flask approach for polymers 4 and 7). After 60 min at 100°C, 5, 9, and diethyl ether were detected by NMR methods (see previous) and obtained in a yield of about 32%, whereas at 120°C, the



Scheme 5. Reaction of 11 with 2.



Scheme 6. Proposed mechanism for the depolymerization process.

yield was improved to about 78%. In contrast to silicones **4** and **7**, lower yields were observed. This was probably due to the lower solubility of **10** in **2** and the accessibility of the Si—O bonds. Initially, as a model for the depolymerization of crosslinked silicones, the conversion of **11**, as the SiO₄ mimic, was examined (Scheme 5). In accordance with the models **1** and **8**, **2** was added in different amounts at r.t. to a solution of **11** in CDCl₃. By different NMR techniques, the conversion of the Si—O bonds to Si—F bonds was noticed, and as a major compound, **3** was detected. In contrast, tetrafluorosilane was not detected by the NMR methods; this was probably because of the low boiling point (−86°C).²² Also, in the flask scale, tetrafluorosilane was not detectable. Afterward, the hydroxyl-terminated **4** (number-average molecular weight ≈ 550 g/mol) was reacted with tetrachlorosilane to access a crosslinked silicone **13** [Scheme 5(b), see Supporting Information].²³ The depolymerization of **13** was carried out in accordance with polymers **4**, **7**, and **10**. After 60 min at 100°C, **5** and diethyl ether were detected by the NMR methods (see previous) and obtained in a yield of about 29%. The yield was improved to about 76% when the reaction temperature was increased to 120°C. However, in contrast to silicones **4**, **7**, and **10**, lower

yields were observed; this was probably due to the lower solubility in **2** and the lower accessibility of the Si—O bonds in the polymer. With respect to the reaction mechanism, we propose the activation of an Si—O bond of the polysiloxane by Lewis acidic BF₃ via the coordination of BF₃ to oxygen (Scheme 6).²⁴ The Si—O bond was cleaved and formed, on the one hand, an Si—F unit **B** and, on the other hand, an SiOBF₂ unit **C** with lower molecular weights. Subsequently, the Si—F unit **A** could react with BF₃ to cleave the Si—O bond adjacent to the fluorine atom and form **5** (for branched and crosslinked units, additional steps were required to form MeSiF₃ or SiF₄), which was removed by distillation from the reaction mixture, and an SiOBF₂ unit. On the other hand, the Si—O bond adjacent to the fluorine atom was cleaved to form an FSiOBF₂ unit **D**, which could be attacked by BF₃ to form **5** (for branched and crosslinked units, additional steps were required to form MeSiF₃ or SiF₄). Overall, by repetition of the reaction sequences, a depolymerization process was feasible with **5** (**9**, **12**) as a product.

CONCLUSIONS

In summary, we set up a capable protocol for the depolymerization of polysiloxanes, which are extensively applied in numerous

technological applications. **2** was used as the depolymerization reagent to transform Si—O bonds in linear, branched, and crosslinked silicones to Si—F bonds. As depolymerization products, **5** for linear polysiloxanes and **9** for branched polysiloxanes were obtained; these are suitable synthons for new polymers and will allow an overall recycling of polysiloxanes.

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