

Recycling Concept for End-of-Life Silicones: Boron Trifluoride Diethyl Etherate as Depolymerization Reagent to Produce Difluorodimethylsilane as Useful Commodity

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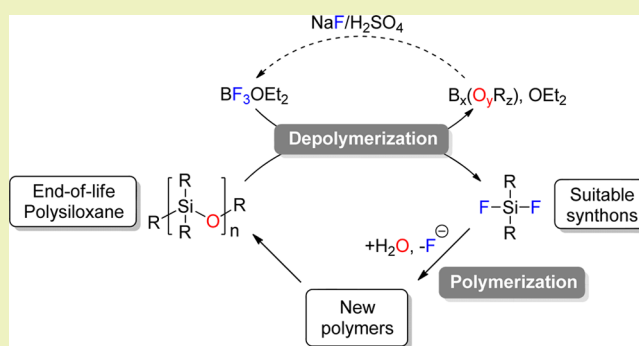
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S Supporting Information

ABSTRACT: The current waste management system is based primarily on landfills, thermal recycling and down-cycling. On the other hand, only a small portion of the end-of-life materials is recycled by depolymerization. In more detail, low-molecular weight commodities/monomers are produced by this process, which can be polymerized in a second step to produce new high quality polymers. Importantly, by applying these depolymerization/polymerization methodologies, contributions to more a sustainable, resource-conserving and environmental-benign society can be made. In this regard, we have set up a capable low-temperature (100 °C) protocol for the depolymerization of poly(dimethylsiloxane)s. In more detail, boron trifluoride diethyl etherate was applied as a depolymerization reagent in the conversion of numerous silicones to obtain difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane as well-defined products under solvent-free conditions in yields up to 85%. Moreover, it was demonstrated that difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane are useful starting materials for the synthesis of new silicones (polymerization). In consequence a recycling of silicones is feasible. The principle of operation of the recycling concept was demonstrated in the depolymerization/polymerization of 500 g of a polysiloxane.

KEYWORDS: Polysiloxanes, silicones, recycling, depolymerization, polymerization, boron trifluoride



INTRODUCTION

The state-of-the-art waste management system, for treatment of human-made end-of-life products, is mainly based on landfill storage, thermal recycling (decomposition for energy purposes), and down-cycling to produced low-quality materials.^{1–3} In contrast, the selective degradation/decomposition/depolymerization to obtain valuable building blocks is only carried out for a minor fraction of the waste.^{4–6} Noteworthy, the produced low-molecular weight chemicals can be used as feedstock for new polymers and therefore a recycling of polymers is feasible without lose of quality (feedstock/chemical recycling).

Moreover, the creation of capable recycling methodologies could be a chance to save steadily decreasing natural resources and contribute to a sustainable, resource-conserving and environmental-benign society.⁴ However, different issues hamper the successful implementation of feedstock recycling, e.g., 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). In the modern society, polysiloxanes/silicones are a widely applied class of polymers

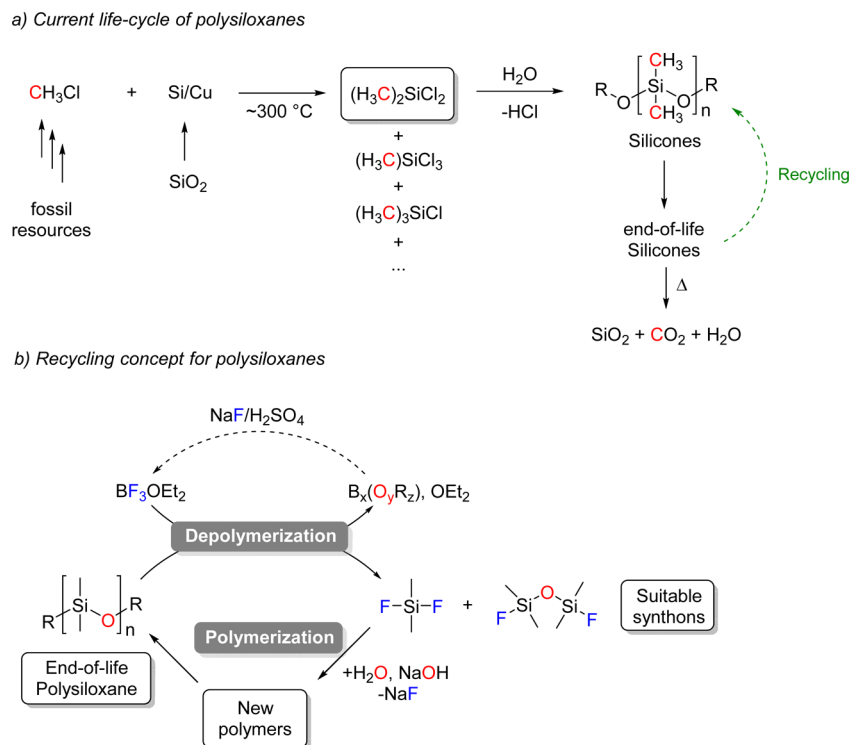
spanning from medicine, electronics, cookware, coatings to construction industry. Especially, the availability on a large-scale by Müller–Rochow synthesis, methyl chloride is reacted with silicon to access dichlorodimethylsilane as a major component, and subsequent hydrolysis makes polysiloxanes attractive materials.^{7–9} Importantly, additional steps and high energy input are required to produce the starting materials for Müller–Rochow synthesis, e.g., methyl chloride is accessible in a sequence from fossil resources, via synthesis gas and methanol.⁷ Moreover, a huge amount of energy is needed to produce silicon. Presently, one major treatment of end-of-life polysiloxanes is the thermal decomposition, after fulfilling their obligations. At this point, all integrated functions derived from fossil resources, e.g., $-\text{CH}_3$, are transformed to the polluting sink carbon dioxide and, for new silicones, fossil resources will be consumed. To overcome these matters, the depolymerization of silicones to low-molecular commodities can be a useful

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Scheme 1. Current Lifetime of Polysiloxanes and Recycling Concept for Polysiloxanes



alternative (vide supra).^{9–28} More recently, it was reported that in the presence of catalytic amounts of zinc or iron salts, the depolymerization of poly(dimethylsiloxane)s can be performed at low temperatures (<150 °C). In more detail, by applying benzoyl fluoride as a depolymerization reagent, difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane were obtained as valuable commodities, which were easily polymerized to produce new silicones, overall demonstrating a resource-conserving silicone recycling.^{29,30} Additionally, the expensive benzoyl fluoride can be substituted by in situ generation from cheaper benzoyl chloride or benzoic anhydride with potassium fluoride. Because only the fluorine will be part of the products (difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane), significant amounts of side products are formed; for instance, only 15% of benzoyl fluoride, 10% benzoyl chloride/KF and 7% benzoic anhydride/KF will be embedded in the product. Moreover, the presented depolymerization reagents are derived from fossil resources, hence decreasing the sustainability of the methods. In this regard, an interesting alternative can be the application of boron trifluoride diethyl etherate (BF_3OEt_2) (Scheme 1).^{10,31–36} On the one hand, BF_3OEt_2 can act as a Lewis acid in the activation of Si–O bonds in silicones and on the other hand as a “fossil-resources-independent” depolymerization reagent with high fluorine content 40% (BF_3OEt_2) or 84% (BF_3).³⁷ In addition, the cost with ~4 € per fluorine is low compared to the other systems, e.g., benzoyl fluoride (~482 €), benzoyl chloride/KF (~22 €), and benzoic anhydride/KF (~46 €).

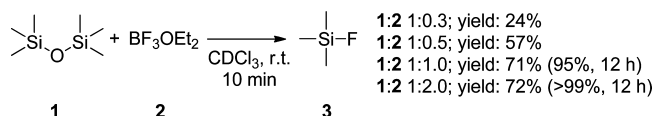
A boron containing side product $\text{B}_x(\text{O}_y\text{R}_z)$ is formed, which can be easily reconverted to BF_3 by $\text{NaF}/\text{H}_2\text{SO}_4$.³⁸ Based on that, the boron of the depolymerization reagent can be recycled, hence increasing the sustainability of the methodology. On the other hand, the desired products difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane are

produced, which can be polymerized with water and, for example, sodium hydroxide, to obtain new high-quality silicones (Scheme 1b). On the basis of this concept, we present herein an improved depolymerization of end-of-life polysiloxanes with boron trifluoride diethyl etherate.

RESULTS AND DISCUSSION

Depolymerization of the Model Compound Hexamethyldisiloxane. Initially, as the model reaction for the depolymerization of silicones, the conversion of hexamethyldisiloxane (**1**) was studied (Scheme 2). In more detail, to a

Scheme 2. Reaction of Hexamethyldisiloxane (**1**) with Boron Trifluoride Diethyl Etherate (**2**)



solution of hexamethyldisiloxane (**1**) in chloroform- d_1 was added boron trifluoride diethyl etherate (**2**) in various ratios at room temperature. After addition, the mixtures were analyzed by different NMR techniques. For instance, the reaction of hexamethyldisiloxane (**1**) with boron trifluoride diethyl etherate in a ratio of 1:1 showed the formation of a new signal in the ^1H NMR. Along to the singlet for hexamethyldisiloxane (**1**) with a chemical shift of 0.05 ppm, a doublet was observed at $\delta = 0.19$ ppm and a coupling constant of $^3J_{\text{H-F}} = 7.42$ Hz, which can be assigned to fluorotrimethylsilane (**3**). A ratio of 0.41:1 (hexamethyldisiloxane (**1**):fluorotrimethylsilane (**3**)) was monitored, which corresponds to a yield of 71% of **3**. Moreover, the characteristic signals for diethyl ether were observed at $\delta = 1.28$ ppm (6H, t, $J = 7.07$ Hz) and $\delta = 3.80$ ppm (4H, q, $J = 7.07$ Hz), but no distinction was possible

Table 1. Depolymerization of Polysiloxane (4) with Boron Trifluoride Diethyl Etherate: Optimization of Reaction Conditions

$$\text{H-O-Si(CH}_3\text{)}_2\text{-O}_n\text{-Si(CH}_3\text{)}_2\text{-H} + \text{BF}_3\text{OEt}_2 \xrightarrow[15-60 \text{ min}]{40-100 \text{ }^\circ\text{C}}$$

$$\text{F-Si(CH}_3\text{)}_2\text{-F} + \text{F-Si(CH}_3\text{)}_2\text{-O-Si(CH}_3\text{)}_2\text{-F} + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$$

4 $M_n \sim 550$ g/mol **2** **5** **6**

Entry ^a	2 [equiv.]	T [°C]	t [min]	Yield 5 [%] ^b	Yield 6 [%] ^b
1	1.0	100	60	85	2
2	0.75	100	60	80	6
3	0.66	100	60	64	13
4	0.5	100	60	28	8
5	0.33	100	60	21	10
6	2.0	100	60	66	20
7	1.0	80	60	61	8
8	1.0	60	60	37	5
9	1.0	40	60	<1	<1
10	1.0	100	30	71	4
11	1.0	100	15	59	11



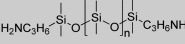
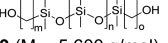



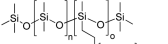
^aReaction conditions: Polysiloxane (4) (1.0 g, $M_n \sim 550$ g/mol), BF_3OEt_2 (2) (0.33–2.0 equiv based on the polymer subunit), 15–60 min, 40–100 °C. ^bIsolated yield. Determined by ¹H NMR.

between BF_3 coordinated and uncoordinated diethyl ether. In addition, ¹⁹F NMR proves the formation of fluorotrimethylsilane (3) by a complex signal at -157.8 Hz. The decet showed a fluorine hydrogen coupling of $^3J_{\text{F-H}} = 7.40$ Hz and a doublet of decet results from a fluorine silicon coupling of $^1J_{\text{F-Si}} = 274.60$ Hz. In addition, a signal was dedicated to BF_3OEt_2 $\delta = -153.0$ ppm (BF_3OEt_2 in CDCl_3 $\delta = -152.7$ ppm) with a ratio of 1:1.03 (boron trifluoride diethyl etherate 2:fluorotrimethylsilane (3)) and an unknown signal at -146.9 ppm with a ratio of 0.32:1 (unknown compound:fluorotrimethylsilane (3)). On the other hand, with ¹¹B NMR, two different signals were observed with a chemical shift of 0.23 ppm and -0.91 ppm. The ¹³C{¹H} NMR revealed a doublet at -0.01 ppm with a coupling constant of $J = 15.22$ Hz and, in the ²⁹Si{¹H} NMR, a signal with a chemical shift of 36.7 ppm was observed, which can be assigned to compound 3. Interestingly, the yield of 71% of fluorotrimethylsilane (3) indicates the conversion of both silicon functions of hexamethyldisiloxane (1) and the transfer of more than one fluorine atom from boron trifluoride diethyl etherate (2). This fact was also underlined by a 95% yield of 3 after a reaction time of 12 h. Moreover, a decrease in the amount of boron trifluoride diethyl etherate (2) to 0.5 equiv or 0.3 equiv, respectively, decreased the yield of fluorotrimethylsilane (3) to 57% or 24%, respectively, after 10 min. In the case of the 0.3 equiv boron trifluoride diethyl etherate (2), it was completely consumed, because only 3 was observed by ¹⁹F NMR and, with ¹¹B NMR, no signal was detected. In contrast, increasing the amount of boron trifluoride diethyl etherate (2) with respect to compound 1 revealed an improved yield. In more detail, with a ratio of 1:2 (hexamethyldisiloxane (1):boron trifluoride diethyl etherate (2)), a yield of 72% for fluorotrimethylsilane (3) after 10 min at room temperature was achieved, whereas after 12 h, complete conversion of hexamethyldisiloxane (1) was achieved. In addition, by ¹¹B NMR and ¹⁹F NMR, BF_3OEt_2 was detectable, for instance, in the ¹⁹F NMR in a 0.48:1 (boron trifluoride

diethyl etherate (2):fluorotrimethylsilane (3)) ratio. Note-worthy, a minor signal ($\delta = -152.92$ ppm) was found close to BF_3OEt_2 ($\delta = -152.98$ ppm). At this point, the fate of the boron and the oxygen atom of compound hexamethyldisiloxane (1) were unclear. Hence the reaction was performed on a larger scale. A flask was charged with hexamethyldisiloxane (1) (1 equiv), boron trifluoride diethyl etherate (2) (2 equiv), and 1,2-dichloroethane as the solvent and a Vigreux column and a distillation head were connected and the mixture was heated to 80 °C. The collecting flask was cooled to -78 °C, and after 2 h, fluorotrimethylsilane (3) was isolated in 88% yield. The temperature was increased to 120 and 140 °C to isolate the solvent 1,2-dichloroethane and BF_3OEt_2 .

Depolymerization of Silicones. After we demonstrated the potential of boron trifluoride diethyl etherate in the cleavage of Si–O bonds and transformation to Si–F bonds in the model reaction, the concept was transferred to polysiloxanes. Initially, the depolymerization of polysiloxane (4) in the presence of boron trifluoride diethyl etherate (2) was investigated (Table 1). In more detail, a flask was charged with poly(dimethylsiloxane) hydroxy terminated 4 ($M_n \sim 550$ g/mol) connected with a Vigreux column and a distillation head and depolymerization reagent boron trifluoride diethyl etherate (2) was added. The mixture was stirred and heated to 100 °C (oil bath temperature) and the generated low-boiling products were continuously distilled off and collected at low temperature (-40 °C). After 60 min, the distillate was investigated by NMR techniques. Three products were observed, on the one hand difluorodimethylsilane (5)²⁹ (¹H NMR $\delta = 0.31$ (t, $^3J_{\text{HF}} = 6.24$ Hz) ppm, ¹³C{¹H} $\delta = -3.45$ (t, $^2J_{\text{CF}} = 16.67$ Hz) ppm, ¹⁹F NMR $\delta = -131.4$ (sept, $^3J_{\text{HF}} = 6.18$ Hz, $^1J_{\text{SiF}} = 289.9$ Hz) ppm, ²⁹Si{¹H} NMR $\delta = -2.4$ ppm) and traces of 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (6)³⁰ (¹H NMR $\delta = 0.21$ (d, $J = 6.20$ Hz) ppm, ¹³C{¹H} $\delta = -1.69$ (d, $^2J_{\text{CF}} = 18.81$ Hz) ppm, ¹⁹F NMR $\delta = -131.1$ (sept, $^3J_{\text{HF}} = 6.01$ Hz, $^1J_{\text{SiF}} = 278.1$ Hz) ppm, ²⁹Si{¹H} NMR $\delta = -9.3$ ppm). On

Table 2. Depolymerization of Polysiloxanes with Boron Trifluoride Diethyl Etherate: Scope and Limitations

entry ^a	substrate	Yield 5 [%] ^b
1	 4 ($M_n \sim 550$ g/mol)	71 (4)
2	 7 ($M_n \sim 110,000$ g/mol)	50 (13)
3	 8 ($M_n \sim 2,500$ g/mol)	34 (7)
4	 9 ($M_n \sim 5,600$ g/mol)	39 (6)
5	 10 ($M_n \sim 580$ g/mol)	53 (24)
6	 11 R = C ₁₆ -C ₁₈	32 mg (5), 50 mg (6)
7 ^c	 12	38 (25)
8 ^d	 13	<1 (93)
9	Silicone oil M100 14	68 (26)
10	Silicone oil (250 °C, Baysilon) 15	62 (10)
11 ^e	Silicone oil (250 °C, Baysilon) 15	75 (6)
12 ^f	Silicone baking cup 16	0.54 g (5), 0.11 g (6)

^aReaction conditions: Polysiloxane (1.0 g), BF₃OEt₂ (**2**) (1.0 equiv based on the polymer subunit), 30 min, 100 °C. ^bIsolated yield. Determined by ¹H NMR. In brackets the yield of **6** is given. ^c95:5 mol ratio of dimethylsiloxane:diphenylsiloxane. ^d~20 wt % [(CH₃)₂SiO]_n. ^e10 g, 2 h. ^f1 g of silicone (Xenos Home Collection).

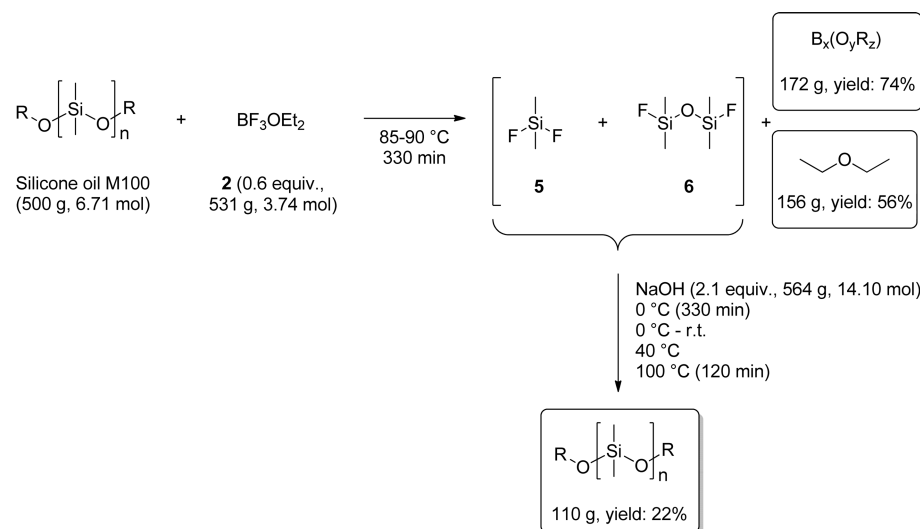
the other hand, diethyl ether was detected (¹H NMR $\delta = 1.16$ (6H, t, $J = 7.01$ Hz), 3.44 (4H, q, $J = 7.01$ Hz) ppm). Noteworthy, both obtained products (difluorodimethylsilane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**)) can be applied as starting materials for polymerization chemistry to produce new silicones.²⁹ Importantly, the reaction proceeds under solvent-free and protection-gas-free conditions, which increases the impact on sustainability. Applying 1 equiv of boron trifluoride diethyl etherate (**2**), with respect to the polymer subunit, a yield of 85% of difluorodimethylsilane (**5**) was realized (Table 1, entry 1). Interestingly, based on this result, more than one fluorine of the BF₃ can be transferred to the silicon (silicon:fluorine 1:3), hence decreasing the amount of boron trifluoride diethyl etherate (**2**) to 0.66 equiv (silicon:fluorine 1:2) revealed a similar yield (Table 1, entry 2). A further decrease to 0.33 equiv of boron trifluoride diethyl etherate (**2**) resulted in low yields of difluorodimethylsilane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**) (Table 1, entries 4 and 5). Moreover, the influence of the reaction temperature was studied (Table 1, entries 7–9). In the cases of 60 and 80 °C, lower yields were observed, whereas at 40 °C, no product formation was monitored. Importantly, at the end of the reaction, an off-white precipitate was observed. Powder X-ray diffraction (PXRD) analysis of the white precipitate revealed a crystalline product. The precipitate crystallized in a

triclinic cell and reflexes were found to match references for B(OH)₃ (Sassolite) from the ICDD database (International Centre for Diffraction Data, pdf 30-199) as well as reflexes from an authentic commercially available B(OH)₃ sample.

After optimization of the reaction conditions (1.0 equiv boron trifluoride diethyl etherate (**2**), 100 °C, 30 min), the scope and limitations were tested for various polysiloxanes (Table 2). For instance, increasing the length of the polymer chain ($M_n \sim 110,000$ g/mol) resulted in a similar yield of difluorodimethylsilane (**5**) (Table 2, entry 2). In contrast to that, a significant influence of the kind of the end group was observed (Table 2, entries 3–5). Interestingly, in the case of the polymer **13** with two different copolymers, e.g., a polysiloxane (~20 wt %) and a poly(ethylene glycol) residue (~80 wt %), the polysiloxane part was converted selectively to 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**) (Table 2, entry 8). Moreover, silicone oils and a silicone baking cup were converted in good yields to the desired compound difluorodimethylsilane (**5**) (Table 2, entries 9–12).

Recycling of Silicones: Depolymerization-Polymerization. After the usefulness of boron trifluoride diethyl etherate in the depolymerization of poly(dimethylsiloxane)s was demonstrated, the reaction for the conversion of silicone oil M100 (**14**) was scaled-up (Scheme 2). In more detail, 500 g of the silicone oil M100 was placed in a flask and boron

Scheme 3. Coupling of the Depolymerization and Polymerization



trifluoride diethyl etherate (1.0 equiv based on the polymer subunit) was added carefully via a dropping funnel at room temperature. Afterward, the mixture was stirred and heated to 90 °C (oil bath temperature) and the generated low-boiling products (diethyl ether, difluorodimethylsilane (**5**), 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**)) were continuously distilled-off. In contrast to the isolation-approach presented in Table 2, entry 9, the products difluorodimethylsilane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**) were directly subjected to polymerization, meaning the distilled-off compounds were dropped into an ice-cooled sodium hydroxide solution (2.1 equiv based on the polymer subunit). After 330 min, the reaction mixture was cooled to room temperature and the excess of boron trifluoride diethyl etherate was removed from the off-white precipitate, which was purified by washing and dried in vacuum to obtain $\text{B}_x(\text{O}_y\text{R}_z)$ (172 g, yield: 74%), which can potentially be reconverted to BF_3 with in situ generated HF from, e.g., $\text{NaF}/\text{H}_2\text{SO}_4$.³⁸ Based on that protocol, the required amount of BF_3 for the depolymerization process can be synthesized just in time and in close proximity to the place of demand (“production on demand”), hence minimizing the contact with the environment. On the other hand, the polymerization flask was slowly warmed to room temperature and the diethyl ether was distilled-off and collected (156 g, yield: 56%), which can be reused for the formation of BF_3OEt_2 . In addition, the temperature of the polymerization flask was increased to 100 °C and the mixture was stirred for 2 h. Afterward, the suspension was filtered and the solid residue was washed with dichloromethane. Interestingly, the residue (NaF) can potentially be applied in the formation of new BF_3 (vide supra).³⁸ After extraction of the aqueous solution with dichloromethane, the solvent of combined organic layers were removed in vacuum to obtain a colorless liquid (110 g, yield: 22%). The light viscous liquid was investigated by different NMR techniques and gas chromatography–mass spectrometry (GC–MS). In the ^1H NMR, brought singlets were detected near to 0.0 ppm (−0.002, +0.026, +0.051, +0.065 ppm), which can be assigned to $[(\text{CH}_3)_2\text{SiO}]$ units. Moreover, in the $^{13}\text{C}\{^1\text{H}\}$ NMR, multiple signals with chemical shifts of 1.96, 1.32, 1.23, 1.04, 0.92, and 0.49 ppm and in the $^{29}\text{Si}\{^1\text{H}\}$ NMR with chemical shifts at −22.0 and −22.1 ppm were monitored, while as expected, no signal was detected with the

^{19}F NMR.³⁹ In addition, with GC–MS analysis, various chemicals were detected containing the $[(\text{CH}_3)_2\text{SiO}]$ units including, for instance, cyclic oligosiloxanes $[\text{Me}_2\text{SiO}]_4$ to $[\text{Me}_2\text{SiO}]_7$.⁴⁰

CONCLUSION

In summary, we have set up a straightforward method based on depolymerization and polymerization for the recycling of end-of-life polysiloxanes. On the one hand, depolymerization was carried out with boron trifluoride diethyl etherate as a depolymerization reagent to obtain well-defined products, e.g., difluorodimethylsilane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**). Moreover, $\text{B}_x(\text{O}_y\text{R}_z)$ is formed as a side product, which can be potentially recycled by reformation to BF_3 , which is in contrast to earlier investigations. Advantageously, the process is performed under solvent-free conditions, at low temperature (100 °C), with “fossil-resources-free” reagents and potential recycling of the depolymerization reagent is feasible, which can add value to sustainable aspects. On the other hand, difluorodimethylsilane (**5**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**6**) can be applied as starting materials for polymerization chemistry to produce new polysiloxanes. The principle of operation of the recycling concept was demonstrated in the depolymerization/polymerization of 500 g of a polysiloxane. Future studies will focus on the improvement of the coupling of the depolymerization and polymerization process and the establishment of a continuous method of operation. Moreover, a life cycle assessment will be carried out to evaluate the potential for industrial applications.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

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Notes

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