DOI: 10.1002/anie.201309299

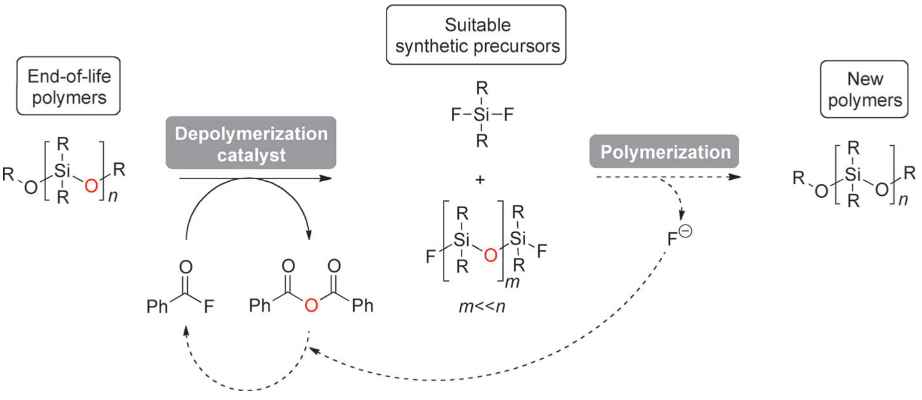
Zinc-Catalyzed Depolymerization of End-of-Life Polysiloxanes**

*Stephan Enthaler**

Abstract: *Polymers occupy an important role in our current society. Besides their great success, an issue is the accumulation of huge amounts of end-of-life polymers. Currently, the waste management is based primarily on landfills, thermal recycling, and downcycling. Notably, only a small portion of end-of-life materials is recycled by depolymerization, which refers to the creation of synthetic precursors that can be polymerized to new polymers to close the cycle. Widely used polymers in modern times are silicones (polysiloxanes), the intrinsic properties of which make their depolymerization demanding; only a few high-temperature or less environmentally friendly processes have been reported. In this regard, we have established an efficient low-temperature protocol for the depolymerization of silicones with benzoyl fluoride in the presence of cheap zinc salts as precatalysts to yield defined products. Notably, the products can be useful synthetic precursors for the preparation of new polymers, so that an overall recycling process is feasible.*

Polymers occupy an important and omnipresent role in our current society. Owing to the ready large-scale access and the straightforward adjustability of the properties of polymeric materials, countless applications have been developed in the past, and for the future, an increased demand is expected.[1–5] Besides the great success of polymers, one major issue is the accumulation of huge amounts of end-of-life polymeric materials on a multiton scale every year. At present, the waste-management system is based primarily on landfill storage, thermal recycling (thermal decomposition for energy purposes), and downcycling to produce low-quality materials.[6–9] Significantly, only a small portion of the end-of-life materials is recycled by depolymerization methodologies to create monomers or suitable synthetic precursors that can later be polymerized to high-quality materials to close the cycle. In this way, end-of-life polymers can be a potential feedstock for new polymers. As a consequence, the creation of efficient and resourceful recycling technologies is a challenging task for current society.[10] However, different issues hamper the scope of applications, for example, the high energy demand for depolymerization processes and the existence of mixed polymeric materials originating from different monomers. For the development of such recycling systems, the application of catalysis offers a possibility to perform depolymerization processes, especially for highly stable materials, in an efficient and sustainable manner, to reduce energy costs and to create overall economic advantages.[11]

Widely used polymeric materials in modern times are silicones (e.g., silicone oil, silicone rubber, silicone grease, silicone resin), which are accessible by the Müller–Rochow synthesis and subsequent hydrolysis.[12] After the silicones have fulfilled their purpose, one major option is their decomposition to produce, for example, silica. However, the synthesis of silicones requires a high energy input and consumes natural resources, especially in the case of the starting materials of the Müller–Rochow synthesis, e.g., chloromethane and silicon; hence low-temperature depolymerization processes can be a good low-energy alternative. Owing to the intrinsic properties of silicones, their depolymerization is challenging, and only a small number of high-temperature (>200 °C) or less environmentally friendly processes have been reported so far.[13,14] Recently, we demonstrated the application of catalysis in the depolymerization of end-of-life polyethers (e.g., poly(tetrahydrofuran), poly(ethylene oxide), poly(propylene oxide)) to produce suitable compounds as potential starting materials for polymerization chemistry. In the presence of catalytic amounts of



Scheme 1. Depolymerization approach for the conversion of polysiloxanes.

---

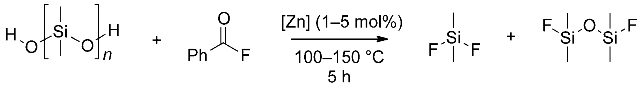
[*] Dr. S. Enthaler
Technische Universität Berlin, Department of Chemistry
Cluster of Excellence "Unifying Concepts in Catalysis"
Strasse des 17. Juni 115/C2, 10623 Berlin (Germany)
E-mail: stephan.enthaler@tu-berlin.de

[**] 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. Dr. R. Kretschmer (University of California San Diego) is thanked for supporting this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309299.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1: Zinc-catalyzed depolymerization of polysiloxane **1**.[a]



1, $M_n \approx 550$ g mol^{-1} **2** **3** **4**

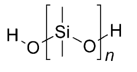
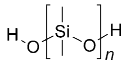
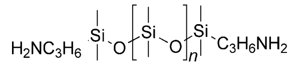
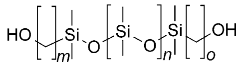
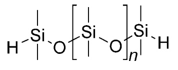
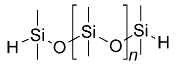
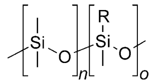
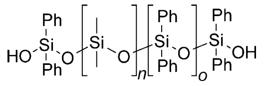
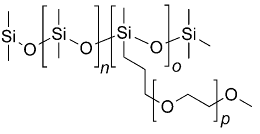
Entry	Precatalyst (mol %)	**2** [equiv]	*T* [°C]	Yield of **3** [%][b,c]	Yield of **4** [%][b,c]	Yield [%][d]
1	–	2	150	<1	<1	<1
2	$Zn(OTf)_2$ (5.0)	2	150	22	57	79
3	$ZnCl_2$ (5.0)	2	150	6	50	56
4	$Zn(OAc)_2$ (5.0)	2	150	46	9	55
5	$Zn(acac)_2$ (5.0)[e]	2	150	43	6	49
6	$Zn(OTf)_2$ (1.0)	2	150	6	1	7
7	$Zn(OTf)_2$ (5.0)	1	150	4	8	12
8	$Zn(OTf)_2$ (5.0)	3	150	78	21	99
9	$Zn(OTf)_2$ (5.0)	4	150	91	9	>99
10	$Zn(OTf)_2$ (5.0)	2	120	68	18	86
11	$Zn(OTf)_2$ (5.0)	2	100	24	1	25
12[f]	$Zn(OTf)_2$ (5.0)	2	150	70	8	78

[a] Reaction conditions: Zn salt (1.0–5.0 mol %, as based on the polymer subunit), polysiloxane **1** (1.0 g, $M_n \approx 550$ g mol^{-1}), **2** (1–4 equiv, as based on the polymer subunit), 5 h. [b] Yield of the product in an isolated mixture of **3** and **4**. [c] The yield was determined by ^{1}H NMR spectroscopy. [d] Combined yield of **3** and **4** as based on silicon. [e] $Zn(acac)_2$ was used as the hydrate. [f] Benzoyl chloride (2 equiv) was used instead of **2**, along with tetrabutylammonium fluoride hydrate (2 equiv).[21] acac = acetylacetonate, Tf = trifluoromethanesulfonyl.

simple zinc or iron salts, polyethers were readily converted with acid chlorides or anhydrides as depolymerization reagents into chloroesters under noninert and solvent-free conditions at low temperature (100–180 °C).[15] In this regard, we became interested in the transfer of this concept to the depolymerization of polysiloxanes (Scheme 1). In more detail, the Si—O bond could be activated by a suitable catalyst, whereupon a reaction with benzoyl fluoride should take place to cleave the Si—O and produce a Si—F bond. Through repetition of this process, the polymer would be steadily converted into low-molecular-weight compounds, such as R_2SiF_2 or $FR_2SiOSiR_2F$.[16] Interestingly, these compounds can be applied to produce new polymers, for example, through hydrolytic processes.[17] As side products, fluoride-containing compounds are formed, which can be potentially used for the regeneration of the depolymerization reagent.[18] We report herein our investigations on the zinc-catalyzed depolymerization of end-of-life polysiloxanes with benzoyl fluoride as the depolymerization reagent.

Initially, the depolymerization of polysiloxanes in the presence of different zinc salts was investigated (Table 1). For these reactions, a flask connected to a Vigreaux column and a distillation head was charged with the hydroxy-terminated poly(dimethylsiloxane) **1** ($M_n \approx 550$ g mol^{-1}), the corresponding zinc salt, and benzoyl fluoride (**2**) as the depolymerization reagent, and the mixture was stirred and heated to 150 °C (oil-bath temperature; internal temperature: ca. 115 °C). The generated low-boiling products were continuously distilled off and collected. After 5 h, the distillate was investigated by NMR spectroscopic techniques. In the case of $Zn(OTf)_2$ as the precatalyst, two products were observed: difluorodimethylsilane (**3**;[19] ^{1}H NMR: $\delta = 0.31$ ppm (t, $^3J_{H,F} = 6.24$ Hz);

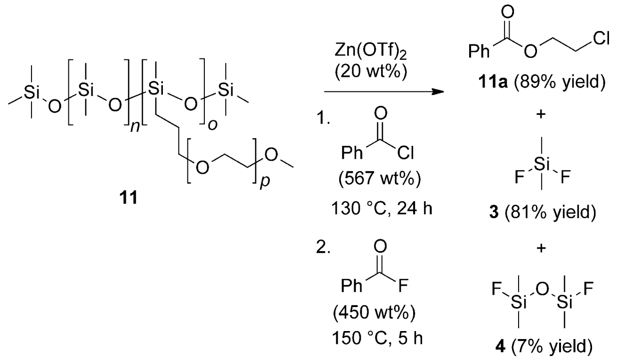
Table 2: Scope and limitations of the zinc-catalyzed depolymerization of polysiloxanes.[a]

Entry	Substrate	Yield [%][b,c]	Yield [%][d]
1	 **1** ($M_n \approx 550$ g mol^{-1})	78 (**3**) 21 (**4**)	99
2	 **5** ($M_n \approx 110.000$ g mol^{-1})	57 (**3**) 17 (**4**)	74
3	 **6** ($M_n \approx 2.500$ g mol^{-1})	82 (**3**) 14 (**4**)	96
4	 **7** ($M_n \approx 5.600$ g mol^{-1})	54 (**3**) 41 (**4**)	95
5	 **8** ($M_n \approx 580$ g mol^{-1})	5 (**3**) 2 (**4**)	7
6[e]	 **8** ($M_n \approx 580$ g mol^{-1})	65 (**3**) 17 (**4**)	82
7[f]	 **9** R = C_{16}–C_{18}	1 (**3**) 4 (**4**)	5
8[f,g]	 **10**	47 (**3**) 2 (**4**) 93 (**10a**)[h]	54
9[f,i]	 **11**	<1 (**3**) 91 (**4**)	91
10	silicone oil M100 (**12**)	55 (**3**) 23 (**4**)	78
11	silicone oil (viscosity 30 000 cSt), **13**	64 (**3**) 18 (**4**)	82
12[j]	silicone baking cups, **14**	524 mg (**3**) 126 mg (**4**)	650 mg

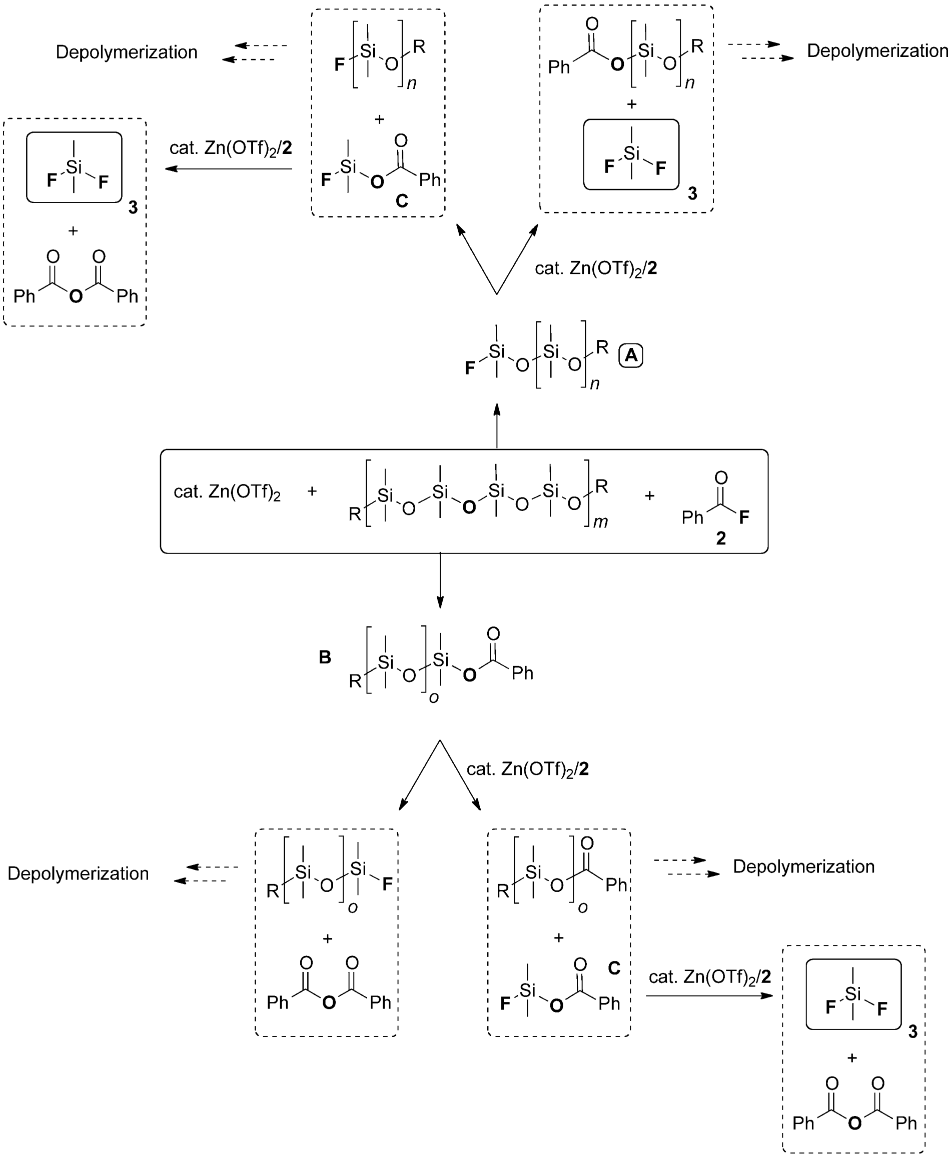
[a] Reaction conditions: $Zn(OTf)_2$ (5.0 mol %, as based on the polymer subunit), polysiloxane (1.0 g), **2** (3 equiv, as based on the polymer subunit), 150 °C, 5 h.[b] Yield of the product in an isolated mixture of **3** and **4**. [c] The yield was determined by ^{1}H NMR spectroscopy. [d] Combined yield of **3** and **4** as based on silicon. [e] Acetophenone (20 wt %) was added. [f] $Zn(OTf)_2$ (20 wt %), **2** (450 wt %). [g] The starting polymer contained dimethylsiloxane and diphenylsiloxane in a 95:5 molar ratio. [h] Product **10a** is Ph_2SiF_2. [i] The starting polymer contained approximately 20 wt % $[(CH_3)_2SiO]_n$. [j] The reaction was carried out with 1 g of the silicone (Xenos Home Collection).

$^{13}C\{^1H\}$ NMR: $\delta = -3.45$ ppm (t, $^2J_{C,F} = 16.67$ Hz); ^{19}F NMR: $\delta = -131.4$ ppm (sept, $^3J_{H,F} = 6.18$ Hz, $^1J_{Si,F} = 289.9$ Hz); $^{29}Si\{^1H\}$ NMR: $\delta = -2.4$ ppm) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**4**;[20] ^1H NMR: $\delta = 0.21$ ppm (d, $J = 6.20$ Hz); $^{13}C\{^1H\}$ NMR: $\delta = -1.69$ ppm (d, $^2J_{C,F} = 18.81$ Hz); ^{19}F NMR: $\delta = -131.1$ ppm (sept, $^3J_{H,F} = 6.01$ Hz, $^1J_{Si,F} = 278.1$ Hz); $^{29}Si\{^1H\}$ NMR: $\delta = -9.3$ ppm). Interestingly, both obtained products are potential starting materials for polymerization reactions to produce new silicones.[17] Moreover, from the reaction residue, benzoic anhydride was isolated. In contrast, in the absence of a zinc salt, no product formation was observed (Table 1, entry 1). To further verify the influence of the zinc precatalyst, $ZnCl_2$, $Zn(OAc)_2$, and $Zn(acac)_2 \cdot x\,H_2O$ were tested under the same conditions (Table 1, entries 3–5). To some extent, lower yields were observed. With $Zn(OAc)_2$ and $Zn(acac)_2 \cdot x\,H_2O$, difluorodimethylsilane (**3**) was observed as the major compound. A reduction in the catalyst loading to 1.0 mol% resulted in a diminished yield (Table 1, entry 6). The influence of different amounts of the depolymerization reagent **2** was also investigated (Table 1, entries 7–9). When the amount of **2** was increased to 3 or 4 equivalents with respect to the polymer subunit, excellent yields (up to > 99%) were observed, whereas a 1:1 ratio of **2** to the polymer subunit led to low yields of the products. Moreover, a study of the reaction outcome at different temperatures revealed an increased yield when the reaction was carried out at 120°C rather than 150°C. Interestingly, under these conditions, compound **3** was observed as the major product, whereas at 150°C, compound **4** was dominant. This difference is probably caused by the longer retention time of **4** in the reaction mixture at lower temperature; as a consequence, more time is available for the transformation into **3**.

The scope and limitations of the method were studied under the established conditions (Table 1, entry 8) with $Zn(OTf)_2$ (5.0 mol%) and the depolymerization reagent **2** (3.0 equiv) at 150°C (Table 2). Thus, a hydroxy-terminated poly(dimethylsiloxane) with a higher molecular weight was successfully converted into compounds **3** and **4** in a combined yield of 74% (Table 2, entry 2). Poly(dimethylsiloxane)s with different terminating groups were also depolymerized to **3** and **4** in good to excellent yields (Table 2, entries 3–6). Notably, in the case of hydrosilanes as the terminating groups, the addition of



Scheme 2. Depolymerization approach for the conversion of polysiloxane polyether copolymers.



Scheme 3. Proposed depolymerization process for the conversion of polysiloxanes.

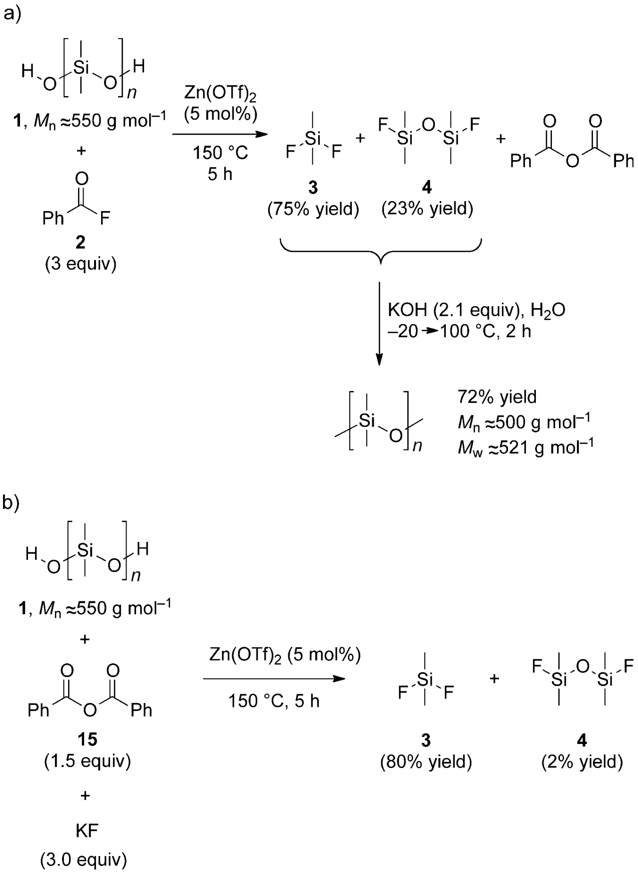
© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

acetophenone was necessary for the reaction to proceed in good yield, probably for deactivation of the Si–H functionality (Table 2, entries 5 and 6). Furthermore, the substitution pattern of the polymer subunit was examined (Table 2, entries 7–9). A good yield was observed for the reaction of poly(dimethylsiloxane-*co*-diphenylsiloxane) (**10**), and along with compounds **3** and **4**, diphenyldifluorosilane (**10a**) was isolated. Compounds **3** and **4** were also isolated from the depolymerization of the copolymerized material **11** containing siloxane units (ca. 20 wt %). Moreover, the protocol was applied to the depolymerization of goods of daily use, such as silicone oils and silicone baking cups. In the case of silicon oils based on poly(dimethylsiloxane), a good performance of the zinc catalyst was observed (Table 2, entries 10 and 11). Interestingly, from 1 g of a silicone baking cup **14**, 0.65 g of a mixture of **3** and **4** was obtained, thus demonstrating the usefulness und applicability of the depolymerization method.

Attempts were made at a step-by-step depolymerization of the copolymer material **11** (Table 2, entry 9) containing a polysiloxane (ca. 20 wt %) and a poly(ethylene glycol) residue (ca. 80 wt %; Scheme 2). First, the poly(ethylene glycol) residue was depolymerized by applying our recently established protocol.[15a] The polymer was treated with a catalytic amount of Zn(OTf)$_2$ (20 wt %) and benzoyl chloride at 130 °C for 24 h. Subsequently, benzoyl fluoride was added, and heating (150 °C) was continued for 5 h. From the reaction mixture, compounds **3** and **4** were distilled off in 88 % combined yield. The chloroester **11a**, a suitable precursor for polymerization reactions,[15] was also isolated in 89 % yield.

With respect to the reaction mechanism, we propose the activation of a Si–O bond of the polysiloxane by Lewis acidic Zn(OTf)$_2$ to enable the reaction with benzoyl fluoride (Scheme 3).[14,15,22] Indeed, initial calculations have shown that the bond-dissociation energy of the Si–O bond is significantly decreased by coordination of the oxygen atom to a zinc atom.[23] The Si–O bond is cleaved and forms on the one hand a [Si–F] unit **A** and on the other hand a [SiOC(O)Ph] unit **B** with lower molecular weights.[24] Subsequently, the [Si–F] unit **A** can react with benzoyl fluoride in the presence of the catalyst to cleave the Si–O bond adjacent to the fluorine atom and form difluorodimethylsilane (**3**), which is removed by distillation from the reaction mixture, and a [SiOC(O)Ph] unit. On the other hand, the Si–O bond adjacent to the fluorine atom can be cleaved to form a [F–SiOC(O)Ph] unit **C**, which can be attacked by **2** to form **3** and benzoic anhydride. Overall, by repetition of the reaction sequences, a depolymerization process is feasible with **3** as the product. ^{19}F NMR spectroscopic investigations at different reaction times revealed the formation of various fluorine-containing intermediates, which were converted over time into the desired compounds **3** and **4**.[25]

To demonstrate the possibility of a recycling process as depicted in Scheme 1, the polysiloxane **1** was depolymerized with benzoyl fluoride **2** and a catalytic amount of Zn(OTf)$_2$ as described in Table 1, entry 8. Subsequently, the products **3** and **4** were subjected to polymerization to form new polysiloxanes (Scheme 4 a). After polymerization, cyclic polysiloxanes were obtained with a number-average molecular weight of approximately 500 g mol^{-1} and a weight-average molecular weight of approximately 521 g mol^{-1}.[12a]



Scheme 4. Recycling of polysiloxane by depolymerization and polymerization.

Moreover, the side products of the depolymerization reaction (benzoic anhydride) and of the polymerization process (potassium fluoride) can be applied for the depolymerization of polysiloxanes (Scheme 4 b). Thus, **1** was depolymerized with a mixture of benzoic anhydride (1.5 equiv) and potassium fluoride (3.0 equiv) at 150 °C within 5 h to provide **3** and **4** in a total yield of 82 %. Importantly, this result demonstrates the possibility of recycling the fluorine component, as depicted in Scheme 1.

In summary, we have established an effective protocol for the depolymerization of polysiloxanes with benzoyl fluoride as the depolymerization reagent in the presence of catalytic amounts of abundant and cheap zinc salts to yield defined products. Notably, the obtained products can be useful synthetic precursors for polymerization reactions to prepare new polymers; overall, the recycling of polymers is feasible. Future investigations will focus on the search for suitable depolymerization reagents for large-scale applications and the establishment of milder reaction conditions.

Experimental Section

General procedure: A polysiloxane (1.0 g), benzoyl fluoride (3 equiv, as based on the polymer subunit), and zinc(II) triflate (5.0 mol %, as based on the polymer subunit) were placed in a flask, and a Vigreaux column (4 cm) and a distillation head were connected. The mixture was stirred and heated to 150 °C (oil bath). The generated low-boiling compounds were continuously distilled off and collected. The yield and quality of the products were determined by NMR spectroscopy.

Received: October 24, 2013
Revised: December 18, 2013
Published online: February 5, 2014

Keywords: depolymerization · recycling · silicones · sustainable chemistry · zinc catalysis

---

[1] M. Delferro, T. J. Marks, *Chem. Rev.* **2011**, *111*, 2450 – 2485.

[2] J.-i. Kadokawa, *Chem. Rev.* **2011**, *111*, 4308 – 4345.

[3] B. Carsten, F. He, H. Jung Son, T. Xu, L. Yu, *Chem. Rev.* **2011**, *111*, 1493 – 1528.

[4] N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270 – 2299.

[5] M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963 – 5050.

[6] D. K. A. Barnes, F. Galgani, R. C. Thompson, M. Barlaz, *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 1985 – 1998.

[7] M. Newborough, D. Highgate, P. Vaughan, *Appl. Therm. Eng.* **2002**, *22*, 1875 – 1883.

[8] W. Kaminsky, F. Hartmann, *Angew. Chem.* **2000**, *112*, 339 – 341; *Angew. Chem. Int. Ed.* **2000**, *39*, 331 – 333.

[9] *Recycling and Recovery of Plastics* (Ed.: J. Brandrup), Hanser/Gardner, München, **1996**.

[10] J. Hopewell, R. Dvorak, E. Kosior, *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 2115 – 2126.

[11] a) *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**; b) *Multiphase Homogeneous Catalysis* (Eds.: B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt), Wiley-VCH, Weinheim, **2005**.

[12] a) "Silicones": H.-H. Moretto, M. Schulze, G. Wagner in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2005**; b) W. Kalchauer, B. Pachaly, *Handbook of Heterogeneous Catalysis*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 2635 – 2647.

[13] See, for example: a) O. Farooq, *J. Organomet. Chem.* **2000**, *613*, 239 – 243; b) L. H. Sommer, G. R. Ansul, *J. Am. Chem. Soc.* **1955**, *77*, 2482 – 2485; c) M. R. Alexander, F. S. Mair, R. G. Pritchard, J. E. Warren, *Appl. Organomet. Chem.* **2003**, *17*, 730 – 734; d) H. Jenkner, *Z. Naturforsch.* **1959**, *14*, 133; e) I. Aishima, H. Sakurai, Y. Takashi, H. Monita, Y. Hirotsu, T. Hamada, US Patent 3661878, **1972**; f) A. W. Apblett, A. R. Barron, *Organometallics* **1990**, *9*, 2137 – 2141; g) R. Mulhaupt, J. Calabrese, S. D. Ittel, *Organometallics* **1991**, *10*, 3403 – 3406; h) C. N. McMahon, S. G. Bott, L. B. Alemany, H. W. Roesky, A. R. Barron, *Organometallics* **1999**, *18*, 5395 – 5408; i) M. A. Brook, S. Zhao, L. Liu, Y. Chen, *Can. J. Chem.* **2012**, *90*, 153 – 160; j) M. Okamoto, S. Suzuki, E. Suzuki, *Appl. Catal. A* **2004**, *261*, 239 – 245; k) P. S. Pappas, R. L. Just, *J. Poly. Sci. Polym. Chem. Ed.* **1980**, *18*, 527 – 531; l) C.-L. Chang, H. S.-J. Lee, C.-K. Chen, *J. Polym. Res.* **2005**, *12*, 433 – 438; m) C. L. Chang, Y. K. Lin, *Polym. Degrad. Stab.* **2004**, *87*, 207 – 211; n) M. Okamoto, K. Miyazaki, A. Kado, S. Suzuki, E. Suzuki, *Catal. Lett.* **2003**, *88*, 115 – 118; o) M. Okamoto, K. Miyazaki, A. Kado, E. Suzuki, *Chem. Commun.* **2001**, 1838 – 1839; p) K. H. Schimmel, *Acta Polym.* **1987**, *38*, 495 – 498; q) T. Fouquet, J. Bour, V. Toniazzo, D. Ruch, L. Charles, *Rapid Commun. Mass Spectrom.* **2012**, *26*, 2057 – 2067; r) C. L. Chang, H. S. Lee, C. K. Chen, *Polym. Degrad. Stab.* **1999**, *65*, 1 – 4; s) K. H. Schimmel, J. Schulz, *Acta Polym.* **1987**, *38*, 536 – 538; t) K. H. Schimmel, E. Schroeder, J. Schulz, T. Souvimonh, *Acta Polym.* **1988**, *39*, 310 – 314.

[14] a) B. A. Ashby, GB 990657, **1965**; b) S. N. Borisov, M. G. Voronkov, N. G. Sviridova, *Zh. Obshch. Khim.* **1969**, *39*, 559 – 564; c) M. G. Voronkov, A. A. Trukhina, L. I. Belousova, G. A. Kuznetsova, N. N. Vlasova, *Russ. J. Org. Chem.* **2007**, *43*, 501 – 506; d) M. G. Voronkov, E. I. Dubinskaya, N. A. Chuikova, *Zh. Obshch. Khim.* **1977**, *47*, 2335; e) S. N. Borisov, N. G. Sviridova, M. G. Voronkov, *Zh. Obshch. Khim.* **1968**, *38*, 2794 – 2800; f) M. G. Voronkov, N. G. Sviridova, Y. A. Yuzhelevskii, S. N. Borisov, *Zh. Obshch. Khim.* **1969**, *39*, 564 – 571.

[15] a) S. Enthaler, M. Weidauer, *Chem. Eur. J.* **2012**, *18*, 1910 – 1913; b) S. Enthaler, M. Weidauer, *ChemSusChem* **2012**, *5*, 1195 – 1198; c) S. Enthaler, *Eur. J. Lipid Sci. Technol.* **2013**, *115*, 239 – 245; d) S. Enthaler, A. Trautner, *ChemSusChem* **2013**, *6*, 1334 – 1336; e) S. Enthaler, *J. Appl. Polym. Sci.* **2014**, DOI: 10.1002/app.39791; f) S. Enthaler, *ACS Catal.* **2013**, *3*, 150 – 158.

[16] a) K. Dippel, O. Graalmann, U. Klingebiel, *Z. Anorg. Allg. Chem.* **1987**, *552*, 195 – 200; b) R. J. P. Corriu, A. Kpoton, M. Poirier, G. Royo, A. de Saxcé, J. C. Young, *J. Organomet. Chem.* **1990**, *395*, 1 – 26.

[17] a) R. Pietschnig, F. Belaj, J. J. Tirrée, *Organometallics* **2004**, *23*, 4897 – 4901; b) R. Pietschnig, K. Merz, *Organometallics* **2004**, *23*, 1373 – 1377; c) H. Kunowski, DE1019652, **1957**; d) H. Kunowski, DE1063600, **1959**; e) O. Graalmann, U. Klingebiel, W. Clegg, M. Haase, G. M. Sheldrick, *Chem. Ber.* **1984**, *117*, 2988 – 2997; f) O. Graalmann, U. Klingebiel, M. Meyer, *Chem. Ber.* **1986**, *119*, 872 – 877; g) D. Schmidt-Baese, U. Klingebiel, *Chem. Ber.* **1989**, *122*, 815 – 821; h) U. Klingebiel, *Chem. Ber.* **1981**, *114*, 3366 – 3371; i) M. Cypryk, *J. Phys. Chem. A* **2005**, *109*, 12020 – 12026.

[18] See, for example: a) G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes, J. A. Olah, *J. Org. Chem.* **1979**, *44*, 3872 – 3881; b) C. Chen, C.-T. Chien, C.-H. Su, *J. Fluorine Chem.* **2002**, *115*, 75 – 77; c) T. Hidaka, N. Fushimi, T. Yoshimura, T. Kawai, JP 2003064034, **2003**.

[19] a) E. N. Suslova, A. I. Albanov, B. A. Shainyan, *J. Organomet. Chem.* **2009**, *694*, 420 – 426; b) B. A. Suvorov, *Russ. J. Gen. Chem.* **2006**, *76*, 1401 – 1406; c) E. N. Suslova, A. I. Albanov, B. A. Shainyan, *Russ. J. Gen. Chem.* **2008**, *78*, 1675 – 1681; d) I. A. Kudasheva, R. S. Musavirov, E. P. Nedogrei, R. T. Akhmatdinov, E. A. Kantor, D. L. Rakhmankulov, *Zh. Obshch. Khim.* **1986**, *56*, 617 – 621; e) E. L. Myers, C. P. Butts, V. K. Aggarwal, *Chem. Commun.* **2006**, *42*, 4434 – 4436; f) N. C. Craig, O. P. Abiog, B. Hu, S. C. Stone, W. J. Lafferty, L.-H. Xu, *J. Phys. Chem.* **1996**, *100*, 5310 – 5317; g) A. A. Krolevets, V. N. Chmykhov, E. N. Glotov, A. F. Gontar, B. I. Martynov, *Russ. J. Gen. Chem.* **1993**, *63*, 597 – 599; h) K. R. Muddukrishna, D. K. Padma, *J. Fluorine Chem.* **1992**, *56*, 51 – 54; i) N. Wang, J. R. Hwu, E. H. White, *J. Org. Chem.* **1991**, *56*, 471 – 475; j) J. A. Soderquist, E. I. Miranda, *Tetrahedron Lett.* **1986**, *27*, 6305 – 6306.

[20] a) A. M. Filippov, V. N. Bochkarev, *Zh. Obshch. Khim.* **1990**, *60*, 865 – 867; b) A. M. Filippov, V. N. Bochkarev, *Zh. Obshch. Khim.* **1990**, *60*, 861 – 865; c) K. Tamao, M. Kumada, T. Takahashi, *J. Organomet. Chem.* **1975**, *94*, 367 – 376; d) P. A. McCusker, T. Ostdick, *J. Am. Chem. Soc.* **1959**, *81*, 5550 – 5553; e) R. Müller, C. Dathe, *Z. Anorg. Allg. Chem.* **1964**, *330*, 195 – 209; f) J. E. Bulkowski, R. Stacy, C. H. Van Dyke, *J. Organomet. Chem.* **1975**, *87*, 137 – 143.

[21] H. Sun, S. G. DiMagno, *J. Am. Chem. Soc.* **2005**, *127*, 2050 – 2051.

[22] After the reaction, $Zn(OTf)_2$ was detected by ^{19}F NMR spectroscopy ([D_8]THF; $\delta = -81.1$ ppm) in the reaction mixture, thus indicating potential Lewis acid catalysis: a) S. Enthaler, *Catal. Sci. Technol.* **2011**, *1*, 104 – 110; b) S. Enthaler, M. Weidauer, *Catal. Lett.* **2012**, *142*, 168 – 175; c) S. Enthaler, S. Inoue, *Chem. Asian J.* **2012**, *7*, 169 – 175.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[23] $Me_3SiOSi(Me_2)\mathbf{OSi}(Me_2)OSi(Me_2)OSiMe_3$ was chosen as a model, and the bond-dissociation energy (BDE) of the silicon–oxygen bond was calculated (B3LYP/TZVP level of theory). Unmodified compound: BDE = 505.8 kJ mol^{-1}; $ZnCl_2$ complex: BDE: 471.9 kJ mol^{-1}.

[24] As a model for the [SiO(O)CPh] unit **B**, $PhCOOSiMe_3$ (H. H. Anderson, *J. Am. Chem. Soc.* **1952**, *74*, 2371 – 2372) was synthesized and treated with **2** in the presence of $Zn(OTf)_2$ under the optimized conditions. The cleavage of the O–Si bond resulted in the formation of $Me_3Si{-}F$, which was detected by ^{19}F NMR spectroscopy ($\delta = -157.0 - -157.3$ ppm (m); see Ref. [18b]).

[25] ^{1}H NMR: $\delta = 0.13$–0.35 ppm (m); ^{19}F NMR: $\delta = -132.0$–-130.3 ppm (m).