

Introducing Students to Feedstock Recycling of End-of-Life Silicones via a Low-Temperature, Iron-Catalyzed Depolymerization Process

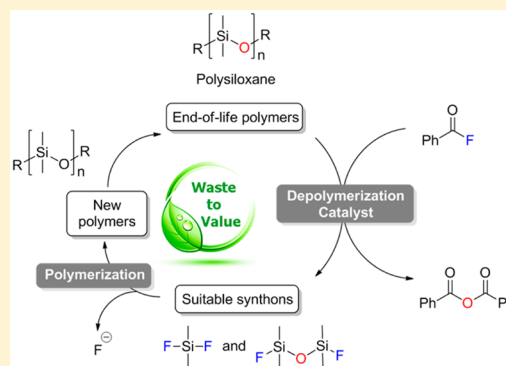
Peter Döhlert, Maik Weidauer, Raphael Peifer, Stephan Kohl, and Stephan Enthaler*

Technische Universität Berlin, Department of Chemistry, Cluster of Excellence "Unifying Concepts in Catalysis", Straße des 17. Juni 115/C2, D-10623 Berlin, Germany

S Supporting Information

ABSTRACT: The straightforward large-scale synthesis and the ability to adjust the properties of polymers make polymers very attractive materials. Polymers have been used in numerous applications and an increased demand is foreseeable. However, a serious issue is the accumulation of enormous amounts of end-of-life polymers, which are currently recycled by thermal degradation, undergo downcycling, or buried in landfills. In contrast, only a minor fraction of polymers is recycled by selective depolymerization processes to produce low molecular weight chemicals that can be polymerized to new polymers. Polysiloxanes (silicones) are widely used polymers, and recycling is challenging due to their intrinsic properties. A few high temperature or less environmentally friendly protocols have been reported for recycling silicones. To circumvent these problems, a low-temperature process was developed for the depolymerization of polysiloxanes using catalytic amounts of cheap, iron salts as a precatalyst and benzoyl fluoride as a depolymerization reagent. Low molecular weight products (difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane) are used for the synthesis of new polysiloxanes; hence, overall a recycling process is feasible. This inorganic chemistry experiment introduces second-year undergraduate students to the concept of feedstock recycling via depolymerization/polymerization processes and exemplifies modern advances in sustainable chemistry.

KEYWORDS: Second-Year Undergraduate, Inorganic Chemistry, Laboratory Instruction, Catalysis, Green Chemistry, Environmental Chemistry, Polymerization



BACKGROUND

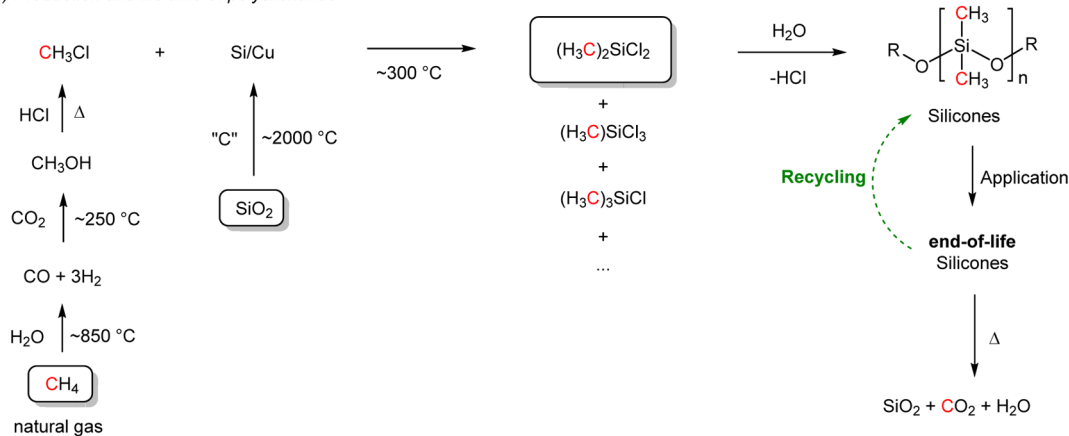
Every year, large amounts of end-of-life plastics are produced on a multiton scale by our consumer society.^{1–4} State-of-the-art waste management is composed of landfill storage, thermal recycling (decomposition for energy purposes), and downcycling to produce low-quality materials. In contrast, the selective degradation to valuable synthons (feedstock recycling) is only performed for a minor fraction of the waste.⁵ Noteworthy, low molecular weight chemicals can be applied as feedstock for new high-performance polymers, and therefore, a recycling of polymers is feasible. The development of efficient recycling technologies can be an opportunity to save steadily decreasing natural resources and to contribute to a greener society.⁵ The advantages of feedstock recycling are apparent; however, several issues hamper implementation, for example, high energy demand for depolymerizations, copolymers, and selectivity. The application of catalysis can be a useful tool to overcome these issues and to make the whole process more valuable.^{6,7} Widely used polymeric materials are polysiloxanes/silicones (e.g., silicone-oil, -rubber, -grease, -resin) with outstanding properties, for example, thermal stability, low chemical reactivity, low toxicity, stability to UV radiation, and electrical insulation. With these properties, a broad range of applications spanning from medicine, electronics, cookware,

and coatings to the construction industry has been established. Moreover, the straightforward availability of polysiloxanes on a large scale by the Müller–Rochow Process and subsequent hydrolysis makes them attractive materials (Scheme 1a).^{8–10} In more detail, methyl chloride is reacted with silicon at elevated temperature to produce a mixture of silanes (Me_2SiCl_2 , MeSiCl_3 , SiCl_4 , Me_4Si) with dichlorodimethylsilane as the major component. Additional synthetic steps and high energy input are required to access the starting materials; for example, methyl chloride is formed in a sequence from natural resources via synthesis gas and methanol.⁸ In addition, a very large amount of energy is required to convert SiO_2 to silicon. After the synthesis of Me_2SiCl_2 , the addition of water produces the desired polysiloxanes, with hydrogen chloride as byproduct. After polysiloxanes have fulfilled their uses, the notation changes to end-of-life polysiloxanes. Currently, one major treatment for end-of-life polysiloxanes is thermal decomposition. At this stage, all integrated functions derived from natural resources (e.g., $-\text{CH}_3$) are converted to carbon dioxide, which has a negative impact on the environment, and for new polysiloxanes, natural resources will be consumed. To overcome these issues, depolymerization to low molecular weight

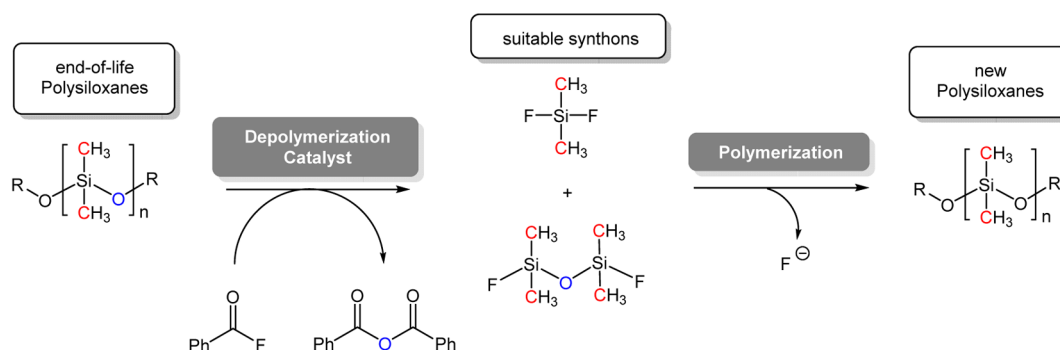
Published: March 6, 2015

Scheme 1. Lifetime of Polysiloxanes and Recycling Concept

a) Production and life time of polysiloxanes



b) Recycling approach for polysiloxanes



synthons can be an interesting option (Scheme 1b). However, only a few high temperature (>200 °C) or less environmentally friendly protocols have been established so far.^{10–29} Recently, it was reported that zinc- and iron-catalyzed low-temperature (<150 °C) depolymerizations of polysiloxanes yield useful monomers, for example, difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane, which were easily polymerized to access new polysiloxanes, and overall a recycling process was demonstrated (Scheme 1b).^{30,31}

■ AIMS OF THE EXPERIMENTS

A few recycling experiments for students have been established, primarily based on the depolymerization of poly(ethylene terephthalate) to produce low molecular weight chemicals.^{32–35}

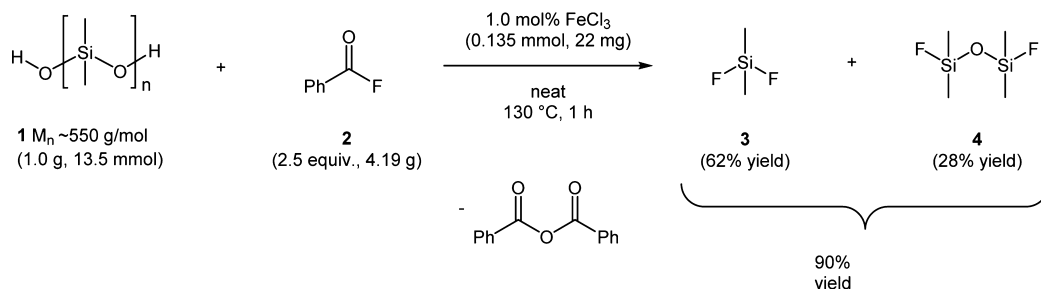
The central aim of the experiment described herein is to introduce an additional class of polymer and to demonstrate an entire recycling process, including depolymerization and polymerization. This laboratory experiment is based on the recently reported recycling concept for polysiloxanes depicted in Scheme 1b.^{30,31} The main pedagogic aim is to introduce a recycling strategy of polymer waste to students based on two coupled processes, on the one hand the depolymerization of polysiloxanes and on the other hand the polymerization of the depolymerization products. In this regard, students can discuss the advantages/disadvantages of established waste management systems and design potential options for the future. As a consequence, fundamental social issues can be underlined.³⁶ The terms “green chemistry, sustainability, environmentally friendly, and environmentally benign chemistry” can be valuable to highlight the challenges for current and future

academic, as well as industrial, chemistry.³⁷ One subaim is to acquaint students with the concept of metal-catalyzed depolymerizations to produce practical monomers, which is underrepresented in introductory-level chemistry textbooks. At this stage, a discussion on the advantageous application of catalysis can be helpful.³⁸ The current trend in catalysis to substitute expensive, rare, and toxic metals with cheap, abundant, and low-toxicity metals can add new aspects for understanding of catalyst selection (see, for instance: metal costs (e.g., Fe 0.005 €/mol, Rh 2484 €/mol, Ru 150 €/mol, Ir 2052 €/mol),³⁹ metal availability (e.g., Fe 4.7%, Rh 0.001 ppm, Ru 0.02 ppm, Ir 0.001 ppm),⁴⁰ and toxicity (e.g., permitted daily oral exposure: Rh, Ru, Ir 10 ppm, Fe 1300 ppm)⁴¹). On the other hand, the monomers obtained can be applied in a polymerization reaction to produce new polysiloxanes. In this regard, students gain experience in polymer chemistry. For both experiments (depolymerization and polymerization), different analytical techniques for characterization, for example, NMR spectroscopy or mass spectrometry, are utilized. Students can (im)prove their skills in interpretation of ¹H NMR and ¹³C{¹H} NMR spectra and practical knowledge can be obtained with ¹⁹F NMR and ²⁹Si{¹H} NMR techniques.

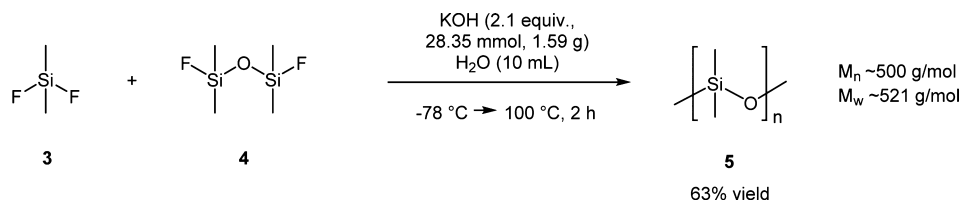
■ EXPERIMENTAL OVERVIEW

Second-year students performed the depolymerization of polysiloxanes and the polymerization reactions with standard lab glassware during one 8 h laboratory session in line with an advanced inorganic practical course. Detailed experimental procedures are given in the Supporting Information.

Scheme 2. Iron-Catalyzed Depolymerization of Polysiloxane 1



Scheme 3. Polymerization of 3 and 4



Depolymerization

A typical depolymerization reaction (Scheme 2) is performed by students working individually. A round-bottom flask connected with a Vigreux column and a distillation head is charged with poly(dimethylsiloxane) hydroxy-terminated **1** (M_n ~550 g/mol, 13.5 mmol based on the polymer subunit, 1.0 g) and iron(III) chloride (1 mol %, 0.135 mmol, 22 mg with respect to the polymer subunit). Benzoyl fluoride (2.5 equiv based on the polymer subunit) is added via the distillation head and the mixture is stirred and heated to 130 °C in a preheated oil bath. The low-boiling compounds formed, difluorodimethylsilane (**3**) and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane (**4**), are continuously distilled off and collected in a cooled flask (-78 °C). After 1 h, the products are characterized by ¹H, ¹³C{¹H}, ¹⁹F, and ²⁹Si{¹H} NMR spectroscopy by dissolving an aliquot in CDCl₃.

Polymerization

A typical polymerization reaction (Scheme 3) is performed by students working individually. To the cooled flask (-78 °C) from the depolymerization reaction (vide supra) containing the mixture of **3** and **4** is added an aqueous solution of potassium hydroxide (2.1 equiv in 10 mL water). The mixture is slowly warmed to room temperature and subsequently heated to 100 °C for 2 h. After extraction with dichloromethane, cyclic poly(dimethylsiloxane)s (**5**) are characterized by GC-MS to obtain a number-average molecular weight (M_n) and a weight-average molecular weight (M_w), and further characterized by ¹H and ¹³C{¹H} NMR spectroscopy by dissolving an aliquot in CDCl₃.

HAZARDS

Due to the corrosive and toxic nature of the chemicals used in this experiment, safety goggles and gloves should be worn at all times. The reactions should be performed in a well-ventilated fume hood to prevent inhalation and skin contact with all materials or irritant solvents. Iron(III) chloride causes skin corrosion and is harmful if swallowed. Benzoyl fluoride is flammable and caustic. Potassium hydroxide represents a strong base; prevent contact with skin because of its caustic effect. The safety data for **3** and **4** are unknown, but it will be advised to

work in a well-ventilated hood. Benzoic anhydride may be harmful if swallowed and causes skin irritation and serious eye damage. Dichloromethane and chloroform-d₁ are potential carcinogens and irritants to eyes, skin, and respiratory tract. Chemicals should be disposed of in designated waste containers. The final product mixture **5** does not include any fluorine-containing compounds **3** or **4** (see ¹⁹F NMR in the Supporting Information). The similarity of **5** to the low toxicity of the starting material **1** supposes a low toxicity for **5**.

DISCUSSION

The recycling concept for polysiloxanes via depolymerization and polymerization reactions has been completed five times by a total of five students working individually within a typical 8 h laboratory session. The depolymerization process of polysiloxanes was studied in the presence of catalytic amounts of iron(III) chloride and poly(dimethylsiloxane) hydroxy-terminated (**1**) as a typical polysiloxane representative (Scheme 2). Importantly, in addition to **1**, the depolymerization method can be used for the conversion of various polysiloxanes, including goods from daily life, such as silicone baking cups, which demonstrates the usefulness of the methodology.³¹ Benzoyl fluoride (**2**) was added and the mixture was heated to start the reaction. Alternatively, because benzoyl fluoride is expensive (~482 €/mol), it can be generated in situ by the reaction of benzoyl chloride that is cheaper and potassium fluoride (~22 €/mol); following this procedure, benzoyl chloride (3.0 equiv with respect to the polymer subunit) can be added to a mixture of **1** and potassium fluoride (3.0 equiv with respect to the polymer subunit).³¹ Moreover, the solvent-free and protection-gas-free reaction conditions provide several benefits in terms of "green chemistry". As the reaction proceeds, students noticed that the volume in the reaction flask decreased and, at the end of the depolymerization, a red-brown solid remained, composed of the catalyst and benzoic anhydride, which can be isolated and investigated by ¹H NMR and ¹³C{¹H} NMR spectroscopy, with a characteristic chemical shift for the C=O function at 162.3 ppm. Importantly, students realized that the bridging oxygen atom in benzoic anhydride is originally from the silicon-oxygen bond in the polysiloxane and one of the driving forces of the reaction is the formation of strong Si-F

Table 1. NMR Shifts and Coupling Constants of Compounds 3, 4, and 5^a

NMR method	3		4		5	
	δ [ppm] ^b	J [Hz]	δ [ppm] ^b	J [Hz]	δ [ppm] ^b	J [Hz]
¹ H	0.32 (t)	6.3 (³ J _{HF})	0.21 (d)	6.2 (³ J _{HF})	0.111 (s), 0.068 (s), 0.063 (s), 0.060 (s), 0.052 (s), 0.046 (s)	
¹³ C{ ¹ H}	−3.1 (t)	16.7 (² J _{CF})	−1.3 (d)	18.6 (² J _{CF})	1.04 (s), 0.99 (s), 0.74 (s), 0.31 (s)	
¹⁹ F	−131.4 (sept)	5.8 (³ J _{HF}) (¹ J _{SiF}) 289.6	−131.1 (sept)	5.8 (³ J _{HF}) (¹ J _{SiF}) 276.9		
²⁹ Si{ ¹ H}	−2.4		n.d.		−10.4, −20.9, −21.3, −21.4, −21.9	

^a¹H, ¹⁹F, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra were recorded on a Bruker Avance 200 MHz (¹H, 200.13 MHz; ¹³C, 50.32 MHz; ¹⁹F, 188.31 MHz; ²⁹Si, 39.71 MHz) in CDCl₃ at 298 K. ^bMultiplicity s, singlet; d, doublet; t, triplet; sept, septet.

bonds. On the other hand, a colorless liquid that was continuously distilled off from the reaction mixture was observed in the cooled collection flask due to the low boiling points of the products [3 (bp = 3 °C) and 4 (bp = 71–72 °C)]. After 1 h, the products were obtained in sufficient yield (63–72% student and 90% advisor yield) and purity for characterization by ¹H, ¹³C{¹H}, ¹⁹F, and ²⁹Si{¹H} NMR spectroscopy. Depending on the NMR instrumentation available or cost of NMR time, suitable characterization can be done with ¹H and ¹⁹F NMR data, especially the coupling between ¹H and ¹⁹F, as well as ²⁹Si, allows students to learn new tools about characterization of chemicals. For instance, 3³⁰ and 4³¹ can be easily distinguished by the different coupling pattern (Table 1).

The reaction setup allowed the isolation of a mixture of 3 and 4, which is advantageous for the next reaction step (polymerization). Importantly, the temperature of the flask should not rise above 0 °C during the distillation or in preparation for the polymerization experiment. After analysis, the second part of the experiment was started.^{42,43} In order to demonstrate the recycling process (Scheme 3), the cooled mixture of 3 and 4 in the collecting flask of the depolymerization process was cooled to −78 °C, an aqueous solution of potassium hydroxide was added, and the mixture was slowly warmed to room temperature and heated to 100 °C. After the reaction was finished (25–51% student and 63% advisor yield), analysis of the cyclic poly(dimethylsiloxane)s by GC–MS showed a M_n of ~500 g/mol and a M_w of ~521 g/mol. In general, students noticed the similarity of the polymerization to the well-established industrial polysiloxane synthesis starting from dichlorodimethylsilane. Overall, the combination of both processes (depolymerization and polymerization) allowed a recycling of poly(dimethylsiloxane)s under mild reaction conditions and in short reaction times.

The practical and technical aspects of the recycling of end-of-life silicones via iron-catalyzed depolymerization and polymerization were assessed via a lab report, quiz questions, and discussions revealing the successful achievement of the pedagogic aims. The questions required students to identify problems with the current handling of resources, state-of-the-art recycling technologies, state-of-the-art synthesis and application of poly(dimethylsiloxane)s, advantages of catalysis, application of cheap and abundant metals, depolymerizations, polymerizations, and different tools (e.g., NMR spectroscopy) for characterization of chemicals.

SUMMARY

An inexpensive and operationally simple procedure for introducing a recycling concept for poly(dimethylsiloxane)s

into an undergraduate inorganic chemistry laboratory course was described. End-of-life poly(dimethylsiloxane)s were depolymerized with benzoyl fluoride as depolymerization reagent and cheap, abundant iron(III) chloride as catalyst. The major products difluorodimethylsilane and 1,3-difluoro-1,1,3,3-tetramethyldisiloxane were isolated and reacted in a second step with aqueous potassium hydroxide to form new poly(dimethylsiloxane)s, and overall a recycling of silicones. The exercise introduced the principles of chemical recycling via depolymerization and polymerization to students.

ASSOCIATED CONTENT

Supporting Information

Descriptions and experimental procedure, spectroscopic data, instructor notes, and pre-lab questions can be found in the Supporting Information. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stephan.enthaler@tu-berlin.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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

REFERENCES

- (1) Barnes, D. K. A.; Galgani, F.; Thompson, R. C. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. London, Ser. B* **2009**, 364 (1526), 1985–1998.
- (2) Newborough, M.; Highgate, D.; Vaughan, P. Thermal depolymerisation of scrap polymers. *Appl. Therm. Eng.* **2002**, 22 (17), 1875–1883.
- (3) Kaminsky, W.; Hartmann, F. New Pathways in Plastics Recycling. *Angew. Chem., Int. Ed.* **2000**, 39 (2), 331–333; Neue Wege im Kunststoffrecycling. *Angew. Chem.* **2000**, 112 (2), 339–341.
- (4) Brandrup, J. *Recycling and Recovery of Plastics*; Hanser/Gardner: München, 1996.
- (5) Hopewell, J.; Dvorak, R.; Kosior, E. Plastics recycling: challenges and opportunities. *Philos. Trans. R. Soc. London, Ser. B* **2009**, 364 (1526), 2115–2126.
- (6) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*; Wiley-VCH: Weinheim, 2004.
- (7) Cornils, B.; Herrmann, W. A.; Horváth, I. T.; Leitner, W.; Mecking, S.; Olivier-Bourbigou, H.; Vogt, D. *Multiphase Homogeneous Catalysis*; Wiley-VCH: Weinheim, 2005.

- (8) Moretto, H.-H.; Schulze, M.; Wagner, G. Silicones. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2005; pp 675–712.
- (9) Kalchauer, W.; Pachaly, B. Müller–Rochow Synthesis: The Direct Process to Methylchlorosilanes. In *Handbook of Heterogeneous Catalysis*, 2nd ed.; Ertl, G., Knozinger, H., Schuth, F., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, 2008; pp 2635–2647.
- (10) Farooq, O. Fluoridative degradation of cyclosiloxanes with alkali metal salt of perfluorinated complex anion. Part 5. *J. Organomet. Chem.* **2000**, 613 (2), 239–243.
- (11) Sommer, L. H.; Ansul, G. R. Hybrid Paraffin-siloxanes Containing the 1,6-Disilaheptane Grouping. *J. Am. Chem. Soc.* **1955**, 77 (9), 2482–2485.
- (12) Alexander, M. R.; Mair, F. S.; Pritchard, R. G.; Warren, J. E. Mild depolymerization of silicone grease using aluminum(III)chloride: high-yield synthesis and crystal structure of $[\{\text{ClSiMe}_2\text{OAlCl}_2\}_2]$, and its controlled hydrolysis on aluminum surfaces. *Appl. Organomet. Chem.* **2003**, 17 (9), 730–734.
- (13) Aishima, I.; Sakurai, H.; Takashi, Y.; Monita, H.; Hirotsu, Y.; Hamada, T. Catalysts for producing ethylene polymers and ethylene copolymers. U. S. Patent 3,661,878, 1972.
- (14) Appleby, A. W.; Barron, A. R. Cleavage of poly-(diorganosiloxanes) by trimethylaluminum. *Organometallics* **1990**, 9 (7), 2137–2141.
- (15) Mulhaupt, R.; Calabrese, J.; Ittel, S. D. (Trialkylsiloxy)-dialkylaluminum dimers. *Organometallics* **1991**, 10 (9), 3403–3406.
- (16) McMahon, C. N.; Bott, S. G.; Alemany, L. B.; Roesky, H. W.; Barron, A. R. Cleavage of Cyclo-dimethylsiloxanes by Dialkylaluminum Hydrides and the Nature of the Siloxaluminum Products. *Organometallics* **1999**, 18 (25), 5395–5408.
- (17) Brook, M. A.; Zhao, S.; Liu, L.; Chen, Y. Surface etching of silicone elastomers by depolymerization. *Can. J. Chem.* **2012**, 90 (1), 153–160.
- (18) Okamoto, M.; Suzuki, S.; Suzuki, E. Polysiloxane depolymerization with dimethyl carbonate using alkali metal halide catalysts. *Appl. Catal., A* **2004**, 261 (2), 239–245.
- (19) Pappas, P. S.; Just, R. L. Aminolysis of crosslinked polysiloxanes: Tautomeric catalysis by 2-pyridone. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, 18 (2), 527–531.
- (20) Chang, C.-L.; Lee, H. S.-J.; Chen, C.-K. Nucleophilic Cleavage of Crosslinked Polysiloxanes to Cyclic Siloxane Monomers: Mild Catalysis by a Designed Polar Solvent System. *J. Polym. Res.* **2005**, 12 (6), 433–438.
- (21) Chang, C. L.; Lin, Y. K. Competition of aminolysis and alcoholysis in nucleophilic cleavage of a model compound for polysiloxane networks. *Polym. Degrad. Stab.* **2005**, 87 (1), 207–211.
- (22) Okamoto, M.; Miyazaki, K.; Kado, A.; Suzuki, S.; Suzuki, E. Deoligomerization of Cyclooligosiloxanes with Dimethyl Carbonate Over Solid-Base Catalysts. *Catal. Lett.* **2003**, 88 (3–4), 115–118.
- (23) Okamoto, M.; Miyazaki, K.; Kado, A.; Suzuki, E. Deoligomerization of siloxanes with dimethyl carbonate over solid-base catalysts. *Chem. Commun.* **2001**, No. 18, 1838–1839.
- (24) Schimmel, K. H. Polysiloxane. 3. Aminolytische Spaltung von Polysiloxan-Modellverbindungen. *Acta Polym.* **1987**, 38 (8), 495–498.
- (25) Fouquet, T.; Bour, J.; Toniazzo, V.; Ruch, D.; Charles, L. Characterization of ethanolysis products of poly(dimethylsiloxane) species by electrospray ionization tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, 26 (17), 2057–2067.
- (26) Chang, C. L.; Lee, H. S.; Chen, C. K. Aminolysis of cured siloxane polymers. *Polym. Degrad. Stab.* **1999**, 65 (1), 1–4.
- (27) Schimmel, K. H.; Schulz, J. Polysiloxane. 4. Zum Verhalten linearer Poly(dimethylsiloxane) in Diethylamine. *Acta Polym.* **1987**, 38 (9), 536–538.
- (28) Schimmel, K. H.; Schroeder, E.; Schulz, J.; Souvimonh, T. Polysiloxane. 5. Netzwerkspaltung durch Amine. *Acta Polym.* **1988**, 39 (6), 310–314.
- (29) Savelle, R.; Zawartka, W.; Leino, R. Iron-Catalyzed Chlorination of Silanes. *Organometallics* **2012**, 31 (8), 3199–3206.
- (30) Enthaler, S. Zinc-Catalyzed Depolymerization of End-of-Life Polysiloxanes. *Angew. Chem., Int. Ed.* **2014**, 53 (10), 2716–2721. et al. *Angew. Chem.* **2014**, 126 (10), 2754–2759.
- (31) Enthaler, S.; Kretschmer, R. Low-Temperature Depolymerization of Polysiloxanes with Iron Catalysis. *ChemSusChem* **2014**, 7 (7), 2030–2036.
- (32) Kamber, N. E.; Tsujii, Y.; Keets, K.; Waymouth, R. M.; Pratt, R. C.; Gregory, W.; Nyce, G. W.; Hedrick, J. L. The Depolymerization of Poly(ethylene terephthalate) (PET) Using N-Heterocyclic Carbenes from Ionic Liquids. *J. Chem. Educ.* **2010**, 87 (5), 519–521.
- (33) Kaufman, D.; Wright, G.; Kroemer, R.; Engel, J. “New” Compounds from Old Plastics: Recycling PET Plastics via Depolymerization. An Activity for the Undergraduate Organic Lab. *J. Chem. Educ.* **1999**, 76 (11), 1525–1526.
- (34) Campbell, D. J.; Wright, E. A.; Dayisi, M. O.; Hoehn, M. R.; Kennedy, B. F.; Maxfield, B. M. Classroom Illustrations of Acidic Air Pollution Using Nylon Fabric. *J. Chem. Educ.* **2011**, 88 (4), 387–391.
- (35) Donahue, C. J.; Exline, J. A.; Warner, C. Chemical Recycling of Pop Bottles: The Synthesis of Dibenzyl Terephthalate from the Plastic Polyethylene Terephthalate. *J. Chem. Educ.* **2003**, 80 (1), 79–82.
- (36) Meadows, D. H.; Meadows, D.; Randers, J. *Limits to Growth: The 30-Year Update*; Chelsea Green Publishing Co.: White River Junction, VT, 2004.
- (37) Lancaster, M. *Green Chemistry: An Introductory Text*, 2nd ed.; Royal Society of Chemistry: Cambridge, 2010.
- (38) Steinborn, D. *Fundamentals of Organometallic Catalysis*; Wiley-VCH: Weinheim, 2012.
- (39) Platinum Today. <http://www.platinum.matthey.com/> (accessed May 2014).
- (40) Binder, H. H. *Lexikon der chemischen Elemente*; S. Hirzel Verlag: Stuttgart, 1999.
- (41) European Medicines Agency. <http://www.ema.europa.eu/ema/> (accessed May 2014).
- (42) Sowerby, D. B.; Audrieth, L. F. Inorganic polymerization reactions: I. Condensation polymerization. *J. Chem. Educ.* **1960**, 37 (1), 2–10.
- (43) Scott, E. S.; Audrieth, L. F. Inorganic polymerization reactions. *J. Chem. Educ.* **1954**, 31 (4), 168–175.