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Short communication

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

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Abstract

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

Keywords: Catalysis; Iron; Silicones; Depolymerization; Fatty alcohols; Polymerization; Recycling

1. Introduction

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

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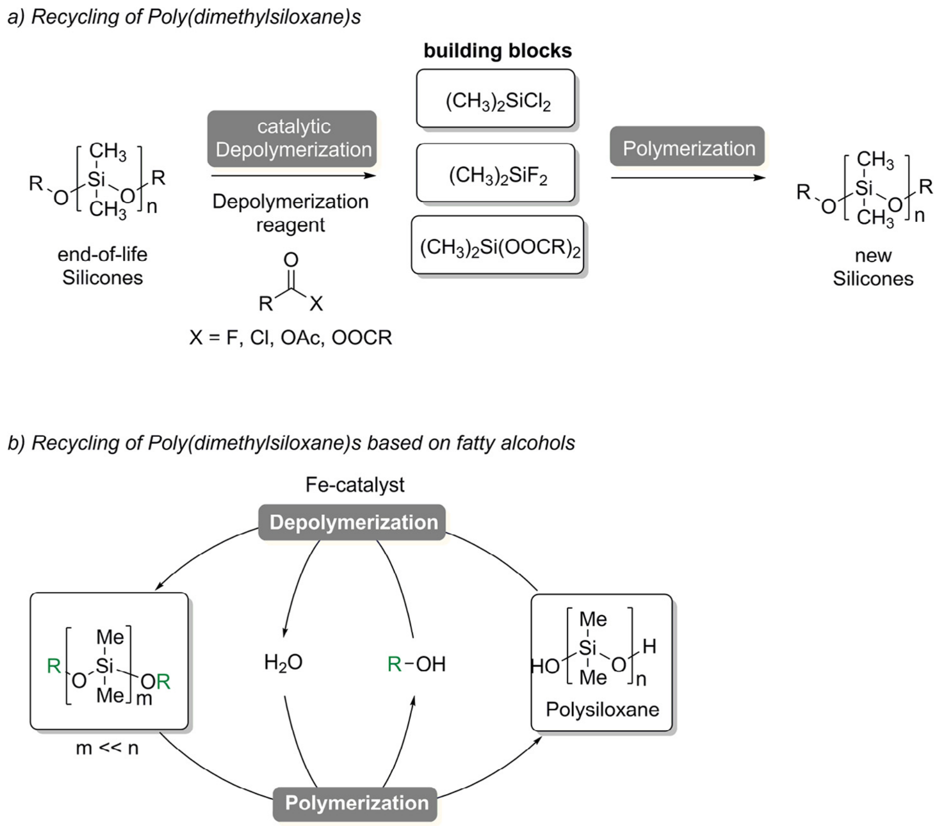

Fig. 1. Recycling of poly(dimethylsiloxane)s.

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

2. Experimental

2.1. General

Fatty alcohols, poly(dimethylsiloxane)s and iron salts were received from Sigma Aldrich, TCI and ABCR in their highest purity and were used without further purification steps. ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on a Bruker AFM 200 spectrometer (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{29}Si: 39.71 MHz) using the proton signals of the deuterated solvents as reference. GC–MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column, 40–300 °C) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

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

An open tube was charged with an appropriate amount of $FeCl_3$ (5.0 mol% with respect to the repeating unit, 0.34 mmol), the corresponding poly(dimethylsiloxane) (6.8 mmol with respect to the repeating unit) and 1-decanol (4 equiv. per repeating unit, 27.2 mmol). The reaction mixture was stirred at 200 °C for 24 hours. The mixture was cooled to room temperature and anisole (200 mg) was added as internal standard. An aliquot was dissolved in dichloromethane and subjected to