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A robust depolymerization route for polysiloxanes

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A versatile, robust, and stable Tetrabutylammonium Difluorotriphenylsilicate (TBAT) catalyst has been deployed for efficient depolymerization of silicones. This catalyst is soluble in a variety of organic solvents and is stable up to 170 °C, enabling a wide range of reaction conditions under which F^--catalysed siloxane bond cleavage can be initiated. This effort offers significant advancement overcoming the traditional limitations of silicone depolymerization, such as high catalyst loading, storage and handling, and few viable reaction media.

The ecological accumulation of polymeric materials has spurred serious concerns about the way we deal with post-consumer discarded waste.[1,2] Mechanical, biological, or chemical routes to transform plastic waste are being proposed as not only methods to divert plastics away from waste streams, but also towards the generation of potential value-added chemicals as a means of recycling them.[3] Chemical depolymerization routes have one major advantage over other waste-management routes in that they have potential to be selective in dealing with mixed waste streams.[4] This is, however, provided that versatile and robust reactions can be easily and cheaply deployed for post-processing of mixed polymer waste streams. Here, we report a potential method for chemically breaking down linear and cross-linked polysiloxanes where a change the polymer-catalyst pair expands the possibility of chemical recycling by overcoming the drawbacks of similar, previously reported depolymerization examples.

Poly(dimethylsiloxane) (PDMS) is a common type of organosilicon polymer containing alternating silicon and oxygen atoms (siloxane linkage). PDMS materials in the market currently follows the same linear-economy trajectory as other polymeric materials where after its use, it ends up accumulating in a landfill and/or leaks into the environment. While the environmental impact of organosiloxane or the industry-specific reviews of the function, persistence, and effects of these materials are available, a clear rationale can be drawn: if these valuable materials can be diverted from landfills with an efficient conversion to value-added chemicals, a significant advancement towards the goal of zero-waste can be achieved.[5-11]

The most effective strategy for PDMS depolymerization involves cleaving the Si-O bond by strong electrophiles or nucleophiles with catalytic or non-catalytic reaction conditions and temperatures ranging from ambient conditions to 350 °C. Thermal depolymerization and radical chain-scission can also take place at higher temperatures (350-500 °C) often with a penalty of uncontrolled reaction pathways.[12-15] Some of the reported routes of depolymerization include the use of Bronsted acids or bases[16] or Lewis acids,[17-20] organic catalysts,[21, 22] highly toxic hydrogen-fluoride,[23, 24] amines,[25] alcohols,[26] organotin catalysts,[27] and halides.[28] These situations often demand harsh reaction conditions with inefficient or incomplete conversions. A notable improvement came from two recent reports[29, 30] where the authors reported an efficient room-temperature catalytic fluoride-based depolymerization. Despite the significant advantages, their catalyst – tetrabutylammonium fluoride (TBAF) – needs special storage and handling procols,[31,32] and the reaction condition is limited to a single solvent. For example, Dehydrating TBAF results in decomposition via Hofmann elimination, leading to significant bifluoride (HF2-) and tributylamine contamination.[33]

Inspired by the call for earth-friendly solvents or diverse reaction conditions,[34] we explored a new catalytic system based on Tetrabutylammonium Difluorotriphenylsilicate (TBAT)[35] that can be applied to a broad class of PDMS polymers and where its applicability won’t be constrained by the solvent choices, temperature, hygroscopic properties, or shelf-life stability. Our pursuit led to TBAT which was initially introduced as a replacement for tetraalkylammonium fluoride for nucleophilic fluorination. As reported elsewhere,[35] TBAT is less nucleophilic and less basic compared to tetrabutylammonium fluoride. The

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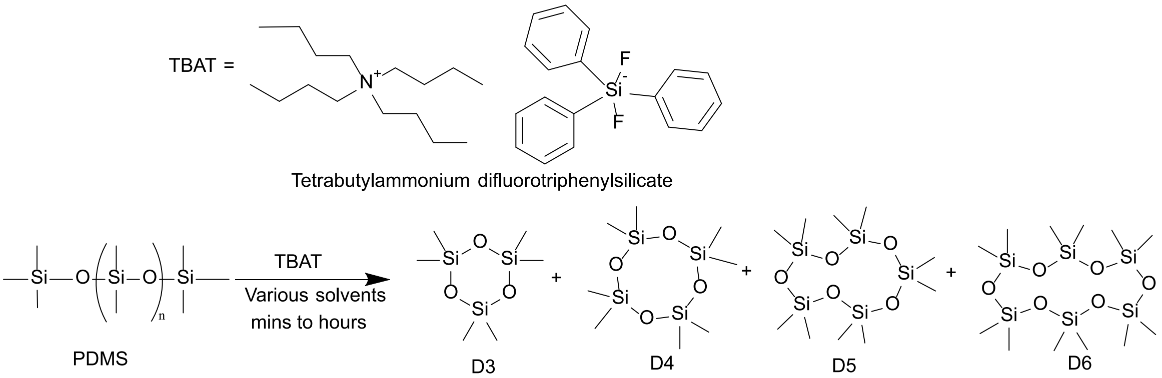
[b] *Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x*



Scheme 1. Depolymerization of PDMS with TBAT as a catalytic fluoride source and the formation of cyclic products

exceptional thermal stability of TBAT (figure S1, S2, and S3 in the ESI) combined with its solubility in many organic solvents make TBAT an excellent candidate to catalyse depolymerization of PDMS (Scheme 1). We chose a high molecular weight linear PDMS substrate called DMS T56 for two reasons. First, its molecular weight is sufficiently high (260 kDa) to allow for disentanglement to occur during depolymerization.[36] Second, Its gel permeation chromatography (GPC) trace will be distinctly different from small molecule and oligomeric products formed post-depolymerization. To narrow down the solvent selection, we primarily used Pfizer's solvent selection guide, avoiding undesirable solvents based on toxicity and environmental risk. [37]

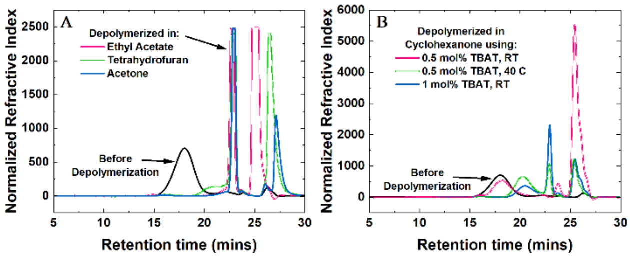


Figure 1. Depolymerization of linear PDMS (DMS T56) tracked by GPC. Two distinct outcomes can be observed based on the solvent choice. **A.** Complete depolymerization of DMS T56 with ethyl acetate, acetone, and THF (0.5 mol% TBAT, room temperature). **B.** Partial depolymerization with cyclohexanone (CHN) as solvent. The depolymerization efficiency can be enhanced by raising the reaction temperature or the catalyst level.

Our attempts to characterize the depolymerization (see SI for experimental details) by ^{1}H NMR proved to be ineffective because of the overlapping signals of depolymerized species and starting silicone (figure S17). The depolymerization products were then characterized using GPC, shown in Figure 1. Two distinct behaviours emerged from different solvents. The solvents where PDMS and catalyst both were soluble (THF, acetone, ethyl acetate) required 0.5 mol% catalyst loading and room temperature for complete depolymerization (Figure 1A). In the other set of solvents (cyclohexanone, ethanol, and isopropanol) where only the catalyst was soluble, a heterogeneous reaction was observed with a significant slowdown in the reaction progress. (Figure S13) Even with an increase in temperature or catalyst loading, complete depolymerization did not occur (Figure 1B).

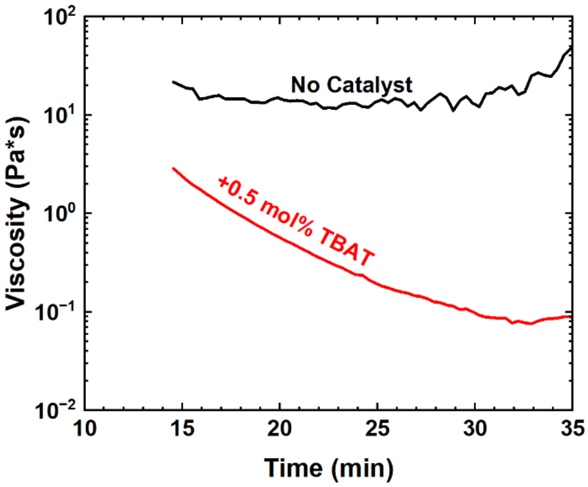


Figure 2. Depolymerization of linear PDMS (DMS T56) in acetone at room temperature monitored by measuring viscosity over time using cone-plate rheology.

We further confirmed our GPC observations by monitoring the room temperature viscosity of two different DMS T56 solutions in acetone overtime, with and without 0.5 mol% TBAT using cone plate rheology. (details of the experimental conditions can be found in the ESI) The viscosity of a solution was, of course, dictated by the molecular weight of the dissolved species. Thus, these results show that the depolymerization of linear DMS T56 in acetone occurred within approximately 30-35 minutes (Figure 2). With acetone as the solvent, faster depolymerization kinetics were supported further by GPC studies where 30 min was sufficient with a stirring condition (figure S13) or less than 10 mins in a Thinky® Mixer (figure S14), a planetary centrifugal bubble-free mixer. Cyclomethicone was used as a reference for depolymerized species for both rheology and GPC (figure S11 and S15).

We utilized GC/MS (details of the experimental conditions can be found in the ESI) to analyse the depolymerized products. The product distribution from the depolymerization followed the previous observations of silsesquioxane cage equilibration[38] using TBAF. A clear mixture of cyclic siloxane was observed for non-nucleophilic solvents whereas a complicated product formation mixtures containing silanols and linear oligomeric components were observed for nucleophilic solvents such as ethanol and isopropanol (figure S4-S8). While reference standards would be required to quantify these compounds, the peak areas can be compared as a rough way to compare composition between samples, as these are similar molecules and should have similar response factors. Thermodynamically controlled product distribution further demonstrates the significant upcycling potential of these reactions where a clean reaction pathway can be recognised with clean, earth-friendly solvents. Although not shown here, a possible repolymerization routes of cyclic siloxanes can be adopted based on documented ring opening polymerization reactions and group-transfer polymerization (GTP).[39-42]

We assumed the mechanism of depolymerization is similar to the backbiting mechanism[30] with TBAF where fluoride can initiate the depolymerization followed by backbiting to form cyclic species or breakdown to smaller units that then rearrange to achieve thermodynamic equilibrium. To test our hypothesis, we chose tetrabutylammonium difluorotriphenylstannate, a structural analogue of TBAT, where silicon is replaced by tin as the fluoride carrier. We did not see any significant depolymerization (see figure S15 in the ESI) with the catalytic amount of Sn analogue. One possible reason is that the Si-F bond is more thermodynamically stable compared to the Sn-F bond, as their bond dissociation energies are 565 and 414 kJ/mol respectively. That is, when the Sn-F bond is broken during the catalytic cycle, (see figure S18 in the ESI), there is no thermodynamic incentive for catalyst regeneration to occur. Thus, very little depolymerization occurs as a result.

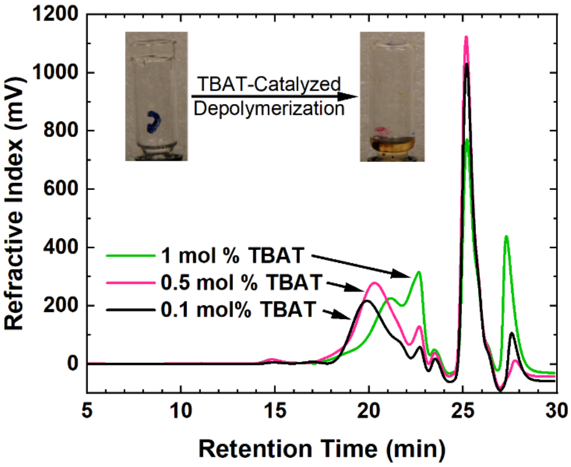


Figure 3. GPC traces of depolymerized products from Sylgard 184 (cured at room temperature) in cyclohexane at an elevated temperature using increasing TBAT loadings. (Inset diagram shows an inverted vial experiment confirming the gel to liquid transition)

Once we established the potential of TBAT in catalysing the depolymerization of high molecular weight linear polysiloxane, we turned our attention to a more challenging substrate: a moderately cross-linked Sylgard 184 silicone rubber. A curing protocol was adopted following the manufacturer's recommendation (part A and part B are mixed in a 10:1 ratio at room temperature and left for 48 hours). While room-temperature depolymerization attempts with various solvents proved to be ineffective, we took advantage of the exceptional thermal stability of TBAT paired with a high boiling solvent (cyclohexanone) to promote extensive depolymerization of the Sylgard 184 matrix at 80 °C in 12 hours (figure 3). TBAF effectively depolymerized DMS T56, as expected based on its linear structure (figure S19). However, its effectiveness significantly decreased for cross-linked Sylgard 184 (figures S20 and S21) with no de-gelation. This likely results from the competition between depolymerization and decomposition pathways of TBAF at elevated temperatures. Further investigation is needed to fully elucidate the competing mechanisms.

Given our finding that TBAT is a thermally stable catalyst, we were further curious whether the catalyst could be formulated directly into silicones for latent depolymerization. Here, we draw inspiration from the Herpes Simplex Virus, which can remain latent within healthy individuals before turning active under certain conditions.[43] We have recently explored this concept for thermally activated depolymerization of unsaturated networks, in which we have found that microencapsulation of a depolymerization catalyst (a Ru-based metathesis catalyst) is essential to control its activation profile.[44] Remarkably, we have found that TBAT can be incorporated directly into a solid, isolable silicone formulation. As shown in Figure S22, significant loadings of TBAT powder can be incorporated into the Sylgard 184 precursor mixture, after which the curing behaviour is only marginally different than a TBAT-free mixture, as evidenced by similar modulus profiles. Since the modulus of an elastomer is proportional to its crosslink density, this observation indicates that solid TBAT does not depolymerize Sylgard 184 appreciably in the absence of solvent. The cured silicone containing embedded TBAT particles remains inert until exposed to specific stressors, such as solvent vapor, triggering its controlled degradation on-demand. After 12 h exposure to cyclohexanone vapor (Figure S22), de-gelation of the TBAT-containing silicone was observed. This demonstrates the first instance of a cross-linked siloxane material that can be both activated and deactivated using external stimuli, opening exciting possibilities for novel material design and applications.

Taken altogether, TBAT stands out as a highly versatile and robust fluoride source, significantly outperforming existing PDMS depolymerization methods, particularly for cross-linked polymers. Its effectiveness stems from a unique combination of properties: remarkable shelf-life stability, low hydrophilicity, and broad solubility in common organic solvents (acetone, THF, ethyl acetate, and ethanol).[35] Rapid and full depolymerization of PDMS was possible in homogeneous reaction conditions where both catalyst and PDMS were soluble. Importantly, TBAT's solubility in high-boiling solvents (cyclohexanone) and stability at elevated temperatures (up to 170 °C) enabled rapid and complete depolymerization within cross-linked matrices, a significant challenge previously. This enhanced toolbox for PDMS breakdown directly supports the transition towards a circular economy by facilitating resource recovery, minimizing waste, and reducing environmental footprint.[45]

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

Conflicts of Interest

There are no conflicts to declare.

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