# Back-to-cyclic-monomers: chemical recycling of silicone wastes using a [polydentate ligand-potassium silanolate] complex

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Silicones are ubiquitous materials owing to their exceptional mechanical and thermal stability as well as low toxicity. Recycling them has become a seducing target for Circular Economy purposes. Conventional chemical recycling processes of polysiloxanes allow for the recovery of valuable cyclic monomers. Unfortunately, they lack efficiency and still require high operating temperatures thus yielding detrimental by-products. We introduce an efficient method for the solvent-free depolymerisation of linear polydimethylsiloxanes using a [polydentate ligand-silanolate] complex as a catalyst, that promote chemical recycling of silicones into cyclic monomers from many industrial substrates including actual waste materials. Our method only requires a small amount of catalyst (0.1 mol%) and proceeds over a wide range of temperature (60°C-170°C) to efficiently yield of a mixture of cyclosiloxanes (up to 98-99% yield) from up to a 100g scale of waste silicone oils. Moreover, the recyclability of this catalyst was demonstrated over five runs without loss of activity.

## Introduction

Silicone polymers are widely used in applications ranging from lubricants, construction & automotive materials, electronics, medical formulations & engineered materials.[1,2] In 2020, the world's production of silicones was over 8 million tons, representing a market value at 15.1 billion USD.[3] Silicone polymers consist of Si-O-Si bound highly resistant backbones. Si-O bonds are longer than C-O bonds and the bond angle for Si-O-Si is wider than that in carbon analogues. These materials are thus thermally stable, mostly chemically inert (except to strong acids and bases) and highly flexible.[3] Recycling of these high-value inorganic polymers has become strategic for both environmental and economic reasons.

Polydimethylsiloxanes (PDMS) is one of the most important silicone products. Most of them are produced through the hydrolysis of chlorosilanes that are prepared *via* "Rochow direct process",[4,5,6] then the associated production of cyclics (mainly $D_3$ and $D_4$) that are subsequently polymerized in the presence of a based catalyst.[7] Although Silicon (Si) is an abundant elemental in the earth, the production of the Si metal grade necessary for the "Direct Process" is highly energy-intensive requiring extremely high temperature (>1400°C).[8] Moreover, it also releases a substantial amount of greenhouse gases detrimental to our environment.[9] Recycling of out-of-specs or end-of-life polydimethylsiloxanes to value-added compounds such as cyclic monomers or functional oligomers thus emerges as a highly desirable and potentially sustainable solution.

The recycling of silicone polymers and materials remains limited and principally involves downcycling through mechanical processing (powdered waste elastomers for instance) or limited chemical recycling.[10,11] Most of the chemical recycling methods and associated industrial processes rely on a rather high "catalytic" amount (thus questioning the efficient catalysis) of alkaline hydroxides,[11] or strong organic and inorganic acids[12,13] and the reaction conditions as well as separation steps of the processes mandate high temperatures and low pressures, to recover valuable cyclic monomers.[11] There is thus a dire need of catalysis upgrading to allow for a wider implementation of silicone chemical recycling.

The chemical recycling of waste silicones has been widely studied for over 80 years.[10] Initially, the decomposition of polysiloxanes was carried out at very high temperature (600°C) under inert condition or in air (300°C).[14] On the one hand, the reaction at 600°C gives a mixture of cyclosiloxanes ($D_3$-$D_8$) favouring small cycles. On the other hand, $CO_2$ and silica are observed as the major products for the thermal cracking in air at 300°C. Besides, steam could be used as an agent for the conversion of the polysiloxanes at high temperature to (oligo)silanols.[15] However, most of these methods require high temperature and give a moderate yield of a mixture of products such as cyclic siloxanes, but also silanols, silica, etc. Recycling to recover PDMS-based cyclics, the shortest cycle within the silicone industry, remains highly desirable, and lacks very competitive catalyts to become viable on very large scales.

In 1997, Allandrieu and Cardinaud have found that strong alkaline hydroxides or quaternary ammonium-based hydroxide could be used as an efficient catalyst for the depolymerisation of silanol-terminated PDMS.[11] The reaction was carried out at 140°C to yield approximately 90% of a mixture of cyclosiloxanes. Later, GE Bayer Silicones claimed that mono or diester of phosphoric acid $(RO)_x(HO)_{3-x}PO$ (x= 1 or 2) could be used as an activator for the depolymerisation of both the uncrosslinked & crosslinked polysiloxanes.[16] After 77-184 hours at room temperature, the viscosity of siloxane oils decreased from 2.7 to 4.3 times in comparison with in the absence of activator, indicating the potential applications on the functionalization of polysiloxanes into oligosiloxanes derivatives. Interestingly, when anionic processes are employed cyclics from $D_3$ to $D_5$ are obtained, whereas when acid-catalysed cationic processes are utilized, larger cyclics (up to D6 or even larger) devoid of $D_3$ are produced.[12]

Additionally, Tremco, Inc. reported a method for the depolymerisation of silicone rubber wastes to produce cyclosiloxanes. This process occurs in diethylene glycol monobutyl ether at 150-180°C in the presence of 2.5wt% of $H_2SO_4$ then 3.5wt% KOH at 80-115°C under reduced pressure of 16-24 mbar.[17]

Furthermore, numerous reports focus on thermal cracking of polysiloxanes. For example, alcoholysis of siloxane polymers was extensively studied.[18,19] Okamoto and Petrus used dimethyl carbonate and methanol in the presence of KF at 150°C or an heterobimetallic aryloxide of Mg-K with the support of a methylsalicylato ligand at 220°C as the catalysts. The observed produced alkoxy(oligo)siloxanes could be further derivatised to polysiloxanes by hydrolysis.

More recently, Hoge and his colleagues reported the first example of isolated silanol-silanolated anions [Si-O…H-O-Si].[20,21] These counter-anions exist in combination with weakly coordinating phosphazenium counter-cations. These anions are thus strong nucleophiles and could be utilised as catalysts for the depolymerisation of silicone oils. However, only 38% yield of cyclosiloxanes was observed under reaction condition (90°C, 7 mbar). Moreover, these silanolate salts start to decompose at 90°C in *vacuo* and rapid decomposition occurs above 100°C, therefore limiting their application as chemical recycling catalysts. As such, there is still a dire need for more robust and very efficient catalysts for the chemical depolymerization of PDMS-based oils into valuable cyclic monomers and industrial intermediates (such as D5).

In this paper, we developed an efficient and straightforward method for the thermal cracking of linear PMDS (both virgin and waste oils of various viscosities and functionalities) to a mixture of cyclosiloxanes: D3, D4 & D5, all desirable industrial monomers/raw materials. Potassium silanolate in combination with a polydentate complexing agent of K+, such as crown ether or polyethylene glycol dimethyl ether, was efficiently used as a catalyst for this reaction.

## Results and discussion

### Catalysts synthesis and corresponding characterisations

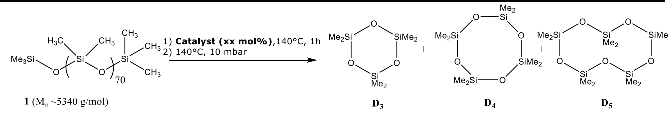
As we mentioned above, alkaline hydroxides such as KOH, CsOH, etc can be used as efficient catalysts for the depolymerisation of silanol-terminated (Si-OH) PDMS into mainly cyclic monomers.[11,17,22] It is a relatively efficient method that suffers from the unavoidable introduction of water into the recycling process, lowering the overall efficiency and limiting the types of waste that this chemistry can recycle. Si-H containing waste, for instance, becomes a hazard in the presence of water and base. Moreover, the use of an alkaline hydroxide can lead to the demethylation of a dimethylsiloxane moiety ($(CH_3)_2SiO$), which subsequently leads to formation of T (or even Q) moieties, "non-recyclable", accumulating inside the reaction media.[23] This detrimental demethylation reaction preferentially occurs at a terminal –SiMe2-OH moiety and further condensation reactions then promote other T and Q motifs, when further demethylation proceeds. Terminal –Si-OH moieties are linked to the overall water content of the reaction medium as well as initial functionalities of the silicone waste materials to be recycled. [23] Thus one should minimize the [OH] content to favour maximal yields in cyclic monomers.

In order to solve this problem and increase the effectiveness of the thermal cracking process, an "OH-free" new catalyst system comprising of potassium silanolate and a complexing agent (such as crown ether-18-6, PEG derivatives), could prove more efficient already than the existing KOH-catalyzed cracking process. We hoped to limit the side reactions, thus getting improved yields. We envisioned that the benefit could be threefold: 1) the ligand could dissociate the ion pair and improve the nucleophilicity of counter-anions then enhance the kinetics of the depolymerisation reaction (or lower the required catalytic amount); 2) the [crown ether-potassium cation] could act as a Lewis acid to activate the Si-O-Si bond, resulting in the same effect (Figure S1); 3) this complex could additionally limit the demethylation pathway, which involves the K+ cation with its key intermediate. [23]

We reckoned the more dissociated silanolate anions could behave as enhanced active species to cleave effectively the siloxane chains. The cyclosiloxanes would be released through more efficient back-biting reactions. We synthesized this new catalyst following a procedure described by Schultz *et al.*[24] In the $^1$H-NMR spectrum (Figure S2a), one can easily determine the chemical shift of characteristic protons of the crown ether in the complex at 3.60 ppm, which is a similar chemical shift compared to one in the free crown ether ( $\delta$ =3.57 ppm) . Moreover, a new signal ascribed to silanolate appears at -0.13 ppm that is different to those in HMDS or $KOSiMe_3$ ( $\delta$ =0.07 ppm), indicating the formation of the complex [**$KOSiMe_3$-Crown-ether-18-6**]. In addition, the $^{29}$Si-NMR and $^{13}$C-NMR spectrum of [**$KOSiMe_3$-Crown-ether-18-6**] show a singlet at -13.6 ppm and 4.8 ppm that are different from those displayed in HMDS ( $\delta$ =7.6 ppm and 1.8 ppm) (Figure S2b, S2c), further evidencing the formation of the desired complex.

First, we tested the depolymerisation reaction under solvent-free condition using trimethylsilyl-capped silicone oil **1** as a model substrate. The reaction was carried out at 140°C under reduced pressure (10 mbar) to displace the equilibrium balance between cyclic siloxanes and polysiloxanes. Unfortunately, a low yield of cyclic siloxanes was observed when KOH (0.1 mol%) or $KOSiMe_3$ (0.1 mol%) were used as the catalyst (Table 1, entries 1-2). A similar condition (KOH 4mol%, 140°C) that was reported in US patent No. 5,670,689, was also evaluated for this model substrate but cyclic siloxanes was obtained at a low yield (15%; Table 1, entry 3). However, 97% of cyclic siloxanes could be obtained after the reactive distillation when a combination of $KOSiMe_3$ (0.1 mol%) and crown ether-18-6 (0.1 mol%) was used as a catalyst for this depolymerisation reaction (Table 1, entry 4). It seems to be a proof of concept that [$KOSiMe_3$+18C6] could be a promising catalyst for the depolymerisation reaction. Moreover, a blank test using only 18C6 do not lead to the formation of the desired products (Table 1, entry 5), implying the crucial role of complexing agent in the improvement of basic thermal cracking of siloxane oil.

Table 1: Initial screening of catalyst for thermal cracking of siloxane oil.



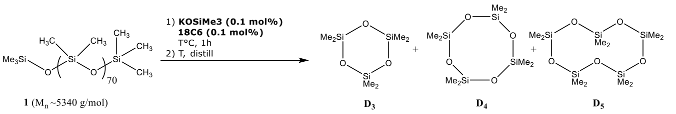
| Entry | Catalyst (mol%) | Yield of cyclo-siloxanes (%)[b] | Ratio[c] D3/D4/D5/ others[d] | Mass balance (%)[e] |
|---|---|---|---|---|
| 1 | KOH (0.1) | 16 | 7/79/13/1 | 98 |
| 2 | $KOSiMe_3$ (0.1) | 15 | 8/81/11/2 | 98 |
| 3[f] | KOH (4) | 16 | 7/78/13/2 | 98 |
| 4 | $KOSiMe_3$ (0.1)+ 18C6 (0.1) | 97 | 6/80/11/3 | 98 |
| 5 | 18C6 (0.1) | 0 | nd | 100 |

[a]Reaction conditions: **1** (10 ml, 120 mmol $SiMe_2$-O unit), **catalyst** (0.1 or 4 mol%), solvent-free. [b]Yield of siloxanes was determined by the ratio between the mass of distillated fraction and the mass of silicone oil. [c]The ratio of cyclic siloxanes was determined by the ratio of each compound in $^{29}$Si-NMR. [d]Others = HMDSO + D6. [e]Mass balance was calculated by ratio between (mass of residue and distillated fraction) and mass of silicone oil. [f] A mixture of 9.5 g silicone oil **1** and 1 g cyclic siloxanes $D_n$ was used, as described in US Patent 5,670,689.

### Variation of depolymerisation conditions and catalyst composition

First, we have investigated the depolymerisation of silicone oil **1** (viscosity = 100 cSt, $M_n$= 5340 g/mol) in the presence of $KOSiMe_3$ (0.1 mol%) and 18C6 (0.1 mol%) under a wide range of temperature from 60°C to 170°C (Table 2). 60°C was necessary to adapt the required vacuum or reduced pressure of our process to achieve distillation of the high boiling-point (at $P^0$) products such as $D_4$ and $D_5$ (Table 2, entry 1). However, the depolymerisation reaction afforded a 91% yield of a mixture of cyclosiloxanes when the temperature reached 60°C (Table 2, entry 1, P~0.1 mbar). Within this mixture, $D_4$ is the major cyclic product (with 68% produced) whereas $D_3$, $D_5$ and others (minute amounts of HMDSO and $D_6$) represent 2%, 27% and 3%, respectively. When the temperature was continuously raised to 70, 90, 110° and the pressure was kept at 0.1 mbar, good yields of distillate products were afforded (94-95%) with a good mass balance (95-97%) and a similar ratio between each cyclic siloxanes (Table 2, entries 2-4). However, taking into account that reduced pressure below 10 mbar are hard to achieve industrially, the condition for depolymerisation reaction was adjusted to 140°C, 10 mbar (Table 2, entry 5). An excellent yield of cyclic siloxanes (97%) was observed after 30 minutes with a higher proportion of $D_4$ inside this mixture (80%). The purity of this mixture of cyclics is remarkable (see SI, Figure S3) and further separative distillation could advantageously yield pure products. A similar result was also obtained at 170°C (Table 2, entry 6), indicating that the catalyst system ($KOSiMe_3$ +18C6) could function within a wide range of temperatures, and that selectivity can be slightly adjusted with temperature. To balance between reduced pressure of distillation and heating transfer considerations, we chose 140°C and 10 mbar of pressure as standard conditions for further optimisation.

Table 2: Temperature screening for the depolymerisation of the PDMS

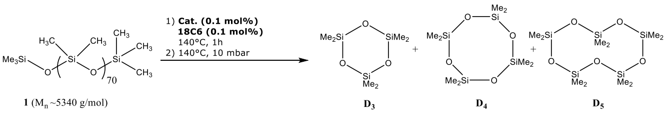


| Entry | T (°C) | P (mbar) | Yield of Cyclo-siloxanes (%)[b] | Ratio[c] D3/D4/D5/others[d] | Mass balance[e] (%) |
|---|---|---|---|---|---|
| 1 | 60 | 0.1 | 91 | 2/68/27/3 | 93 |
| 2 | 70 | 0.1 | 95 | 2/74/22/2 | 97 |
| 3 | 90 | 0.1 | 94 | 2/68/28/2 | 95 |
| 4 | 110 | 0.1 | 94 | 2/66/28/4 | 95 |
| 5 | 140 | 10 | 97 | 6/80/11/3 | 98 |
| 6 | 170 | 35 | 96 | 8/76/14/2 | 98 |

[a]Reaction conditions: **1** (10 ml, 120 mmol Si-O), $KOSiMe_3$ (0.1mol%), solvent-free. [b]Yield of siloxanes was determined by the ratio between the mass of distillated fraction and the mass of silicone oil. [c]The ratio of cyclic siloxanes was determined by the ratio of each compound in $^{29}$Si-NMR. [d]Others = HMDSO + D6. [e]Mass balance was calculated by ratio between (mass of residue and distillated fraction) and mass of silicone oil.

Next, a series of salts in a combination with 18C6 were investigated for the depolymerisation of silicone oil **1**. When trimethylsilanolate potassium and dimethylvinyl silanolate potassium were used, ~96% yield of the cyclic siloxanes was observed with an excellent mass balance (98%), indicating minimal volatile products (D3, HMDSO) were lost during the distillation process (traces on glassware & vacuum trap, Table 3, entries 1-2). Similar results were also observed when KOH and *t*-BuOK were evaluated for this reaction, giving high yields of cyclosiloxanes at 95% and 97%, respectively (Table 3, entries 3-4). More importantly, this experiment shows far superior yield compared to the sole use of KOH as a catalyst for depolymerisation reaction/reactive distillation (Table 1, entry 1). Moreover, the composition of the siloxane mixture seems independent on the counter-anions, suggesting that once the active chain end, or silanolate, is obtained then it drives the depolymerization. $D_4$ is always the major component of the cyclic siloxane mixture, approximately 80% while $D_5$, $D_3$ and others often represent around 11%, 7% and 2%, respectively. Otherwise, the potassium acetate or halogenated potassium salts K-X (X = F, Cl, Br, I) were also tested under the same conditions (Table 3, entry 5). However, no reactivity was observed, due to the lack of nucleophilicity of the anions, thus unable to generate the required active silanolate.

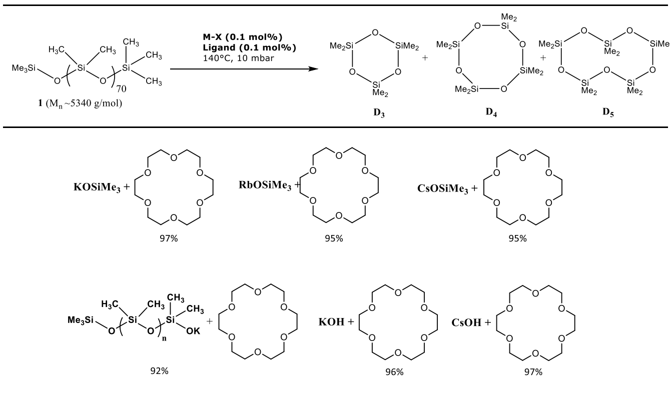
Table 3: Anion screening in the catalyst for the depolymerisation of the PDMS



| Entry | Anion | Yield of Cyclo-siloxanes (%)[b] | Ratio[c] D3/D4/D5/others[d] | Mass balance (%)[e] |
|---|---|---|---|---|
| 1 | $OSiMe_3$ | 97 | 6/80/11/3 | 98 |
| 2 | $OSiMe_2Vi$ | 96 | 8/83/8/1 | 98 |
| 3 | OH | 95 | 7/78/14/1 | 97 |
| 4 | O-*t*Bu | 97 | 5/78/14/3 | 98 |
| 5 | F, Cl, Br, I | 0 | nd | nd |

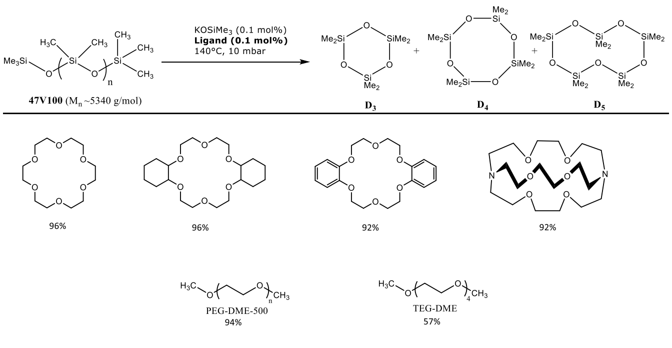
[a]Reaction conditions: **1** (10 ml, 120 mmol Si-O), catalyst (**K-X**, 0.1mol%), solvent-free. [b]Yield of siloxanes was determined by the ratio between the mass of distilled fraction and the mass of silicone oil. [c]The ratio of cyclic siloxanes was determinated by the ratio of each compound in $^{29}$Si-NMR. [d]Others = HMDSO + D6. [e]Mass balance was calculated by ratio between (mass of residue and distilled fraction) and mass of silicone oil.

Next, we turned our attention to the role of the cation. First, a series of silanolate salts were examined as the catalyst for the depolymerisation of the PDMS (Scheme 1). We selected K and bigger alkali cations (Rb, Cs) to maximize charge separation for the anion/cation pair and thus enhance reactivity of the corresponding counter-anions.[25] The potassium salt provided a good yield of desired products (97%). Moreover, the caesium silanolate and rubidium silanolate were also tested under standard condition and desired products were afforded at 95% yield. Additionally, siloxanes' oligomer-based trimethylsilanolate potassium that is used as catalyst for industrially R.O.P of cyclic siloxanes,[4,7] was tested as active species for depolymerisation reaction, then giving 92% yield of desired products. A series of alkaline hydroxides were also evaluated as standard catalysts for base cracking of PDMS for a better comparison. KOH and CsOH also gave an excellent yield of cyclic siloxanes. Finally, we selected a mixture of $KOSiMe_3$ and 18C6 as the optimised catalyst for this reaction, combining best yield and enhanced solubility without resorting to additional diluent (in particular water).



Scheme 1: Cation screening for the depolymerisation of the silicone oil.

Having established that $KOSiMe_3$/18C6 is a good catalyst for the depolymerisation of PDMS, we have subsequently evaluated the role of the ligand for the reactivity (Scheme 2). First, a series of (substituted)-crown ether-18-6 was used as the ligand. On the one hand, 18C6 gave 96% yield of cyclic siloxanes. On the other hand, 96% and 92% yield of cyclic siloxane were provided when dicyclohexyl and dibenzo substituted crown ether 18-6 were used as the ligands. Moreover, Kryptofix®-2,2,2 was also tested for this reaction giving also 92% yield of desired products. However, as potent complexing agents, these crown ethers and cryptands are hazardous chemicals that could damage the body's ion balance (due to high affinity to potassium cation).[26] In order to find another alternative for these macrocyclic polyethers, a series of cheap (and safer) polyethylene glycol derivatives were tested as the ligand for the complexation. First, PEG dimethyl ether (PEG-DME; $M_n$=500 g/mol) gave an excellent yield of cyclosiloxanes (94%). We used methylated PEG to avoid detrimental hydrogen bonding with silanolate anions, thus decreasing the nucleophilicity of the active species.[27] Next, we evaluated several PEG-DMEs under the same reaction conditions. When tetraethylene glycol dimethyl ether was used, a yield of desired products dropped to 57%. Even though crown ether-18-6 and PEG-DME ($M_n$=500 g/mol) showed a similar performance, a crown ether 18-6 was selected as a ligand for further optimisations because of its faster distillation (4 times in compared to one with PEG-DME). Nonetheless, methylated PEGs provide an interesting cheap and safer alternative as efficient complexing agents.

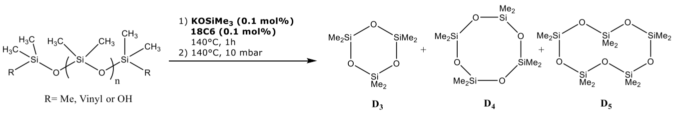


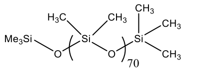
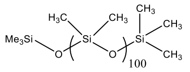
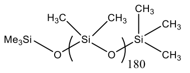
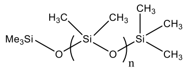
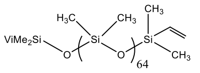
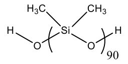
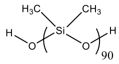
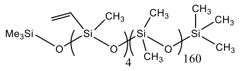
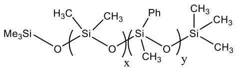
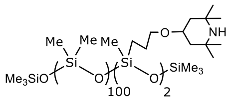
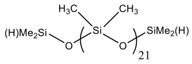
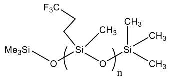
Scheme 2: Ligand screening for depolymerisation of the PDMS

### From simple PDMS to in-chain and chain-end functionalized silicone oils and even crosslinked elastomers

After optimising the conditions for the thermal cracking of the linear PMDS (140°C, 0.1 mol% $KOSiMe_3$ +18C6), we have applied these conditions to the depolymerization of a series of the silicone oils. Several trimethylsilyl-terminated polysiloxanes with different viscosity from 100 cSt, 350 cSt to 1000 cSt (silicone oil **1**, **2 (waste thermostatic-bath oil)** and **3**) were first investigated (Table 4, entries 1-3). Interestingly, all of those gave an excellent yield of cyclosiloxanes (95-97%), indicating that the molar masses of the linear PDMS do not affect the efficiency of the depolymerization method. More interestingly, waste **2** depolymerization afforded similar chemical recycling yields as virgin oils. Moreover, silicone gum **4** that is an extremely high molar-mass polysiloxanes ($M_n$=0.5-100.10$^6$) with very high viscosity, was also evaluated under optimised conditions but almost no cyclic products was obtained, due to extremely high viscosity medium, which rendered stirring impossible during the depolymerisation process. To circumvent this issue, a mixture of silicone gum **4** and silicone oil **1** (mass ratio 1:1) was considered. Interestingly, a homogeneous mixture of manageable viscosity was obtained after 30-minute stirring (Table 4, entry 4). The depolymerisation then proceeded straightforwardly, giving 96 % of cyclic siloxane monomers. D$_4$ remains the major product, accounting for 80% of the cyclic mixture. Then, the polysiloxanes containing vinyl-moiety **5** were also investigated under optimised conditions (Table 4, entry 5). Once again, a good yield (94%) of cyclosiloxanes were isolated after the distillation. Additionally, OH-terminated silicone oils **6** was tested under this set of conditions (Table 4, entry 6). Unfortunately, cyclic siloxanes were isolated in lower yield (75%). This lower efficiency could be explained by reversible condensation reaction. At elevated temperature (140°C), silanol condensation is more favoured than depolymerisation reaction.[28] In order to solve this issue, silicone oil **1** (10-90% mass) was introduced to avoid the condensation (Table 4, entry 7). Notably, the overall yield of cyclic siloxane was increased up to 98%. Next to those simple silicone oils, in chain and chain-end funtionalized silicone oils or even crosslinked silicone elastomers were also subjected to depolymerization under standard conditions (Table 4 , entries 8-10). On the one hand, the reaction with vinylmethyl-siloxane-*co*-PDMS **7**, phenylmethyl-siloxane-*co*-PDMS **8** and amino-pendent polysiloxanes **9** gave 93%, 79% and 68% yield of cyclosiloxanes, respectively. More interestingly, a small amount of D$_4^{vi}$ - which is also a valuable monomer to recover - was observed (indicating by singlet peak at -18.6 ppm) since copolymers **7** was used as a substrate for the depolymerisation reaction. On the other hand, up to 95% of cyclic products were afforded when a low Si-H content silicone oil such as **11** or the part containing Si-H moieties of a RTV2 formulation were used as the model substrates (Table 4, entries 11 and 12). We suspect a prerequisite reaction of the terminal Si-H with Si-OH (combined use of oils **1** and **6** as diluents) and then conventional back-biting. Additionally, the RTV2 crosslinked elastomer itself (product of platinum catalyzed crosslinking), was tested under optimised conditions, providing 95% of the desired product, from the long linear PDMS chains in between crosslinking knots (Table 4, entry 13). Finally, the fluorosilicone oil **12** was depolymerized (Table 4, entry 14). Interestingly, 92% yield of fluorinated cyclosiloxanes was afforded. All of these results indicate a high robustness and chemo-compatibility of this catalyst for the depolymerisation of linear PDMS chains.

Table 4: Scope of silanolate-crown ether catalyzed depolymerisation of silicone oils



| Entry | Substrate | Yield of cyclo-siloxanes (%)[b] | Ratio[c] D3/D4/D5/others[d] |
|---|---|---|---|
| 1 |  **1** ($M_n$ ~ 5340 g/mol) | 97 | 6/80/11/3 |
| 2 |  **2** ($M_n$ ~7560 g/mol) | 97 | 7/81/11/1 |
| 3 |  **3** ($M_n$ ~ 13500 g/mol) | 95 | 9/80/10/1 |
| 4[e] |  + **1**<br>**4** ($M_n$ ~ 0.5-100. 10^6 g/mol) | 96 | 7/78/13/1 |
| 5 |  **5** ($M_n$ ~ 5000 g/mol) | 94 | 10/74/13/3 |
| 6 |  **6** ($M_n$ ~ 6700 g/mol) | 75 | 10/82/8/0 |
| 7[f] |  + **1**<br>**6** (Mn= 6700 g/mol) | 98 | 4/82/14/0 |
| 8 |  **7** ($M_n$ ~ 12400 g/mol) | 93 | 1/73/22/4[m] |
| 9[g] |  + **1**<br>**8** (PDMS-5%Ph) | 79 | 8/77/13/2 |
| 10 |  **9** | 68 | 7/78/14/1 |
| 11[h] |  + **1** + **6**<br>**10** (Mn= 1700 g/mol) | 95 | 13/79/8/0 |
| 12[i] | the part containing Si-H moieties (6% mol) of a RTV2 formulation (**11**) | 96 | 10/80/10/0 |
| 13[j] | crosslinked gel RTV2 + **1** | 95 | 8/79/11/2 |
| 14[k] |  **12** ($M_n$ ~ 14000 g/mol) | 92[h] | nd |

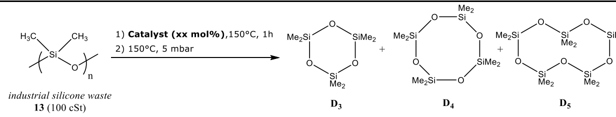
a) Reaction conditions: Silicone oil (10 ml, 120 mmol Si-O), catalyst ($KOSiMe_3$+18C6) (0.1mol%), solvent-free, 140°C, 10mbar; b) Yield of siloxanes was determined by the ratio between the mass of distillated fraction and the mass of silicone oil; c)The ratio of cyclic siloxanes was determinated by the ratio of each compound in $^{29}$Si-NMR; d) Others = HMDSO + D6. e) a mixture of 1:1 of silicone gum and silicone oil was used; f) a mixture of **6** and **1** at a mass ratio of 1:1 was used. g) a mixture of **8** and **1** at a mass ratio of 1:1 was used; h) a mixture of **10** (6 g), **1** (3 g) **and 6** (3 g) at a mass ratio of 2:1:1 was used; i) RTV2 formulation is a mixture containing 94% of vinyl terminated silicone oil (viscosity around 40000 cSt) and

6% of short chain Si-H oil; j) a mixture of **crosslinked gel RTV2** (3 g) and **1** (9 g) was used; k) distillation condition is 160°C, 0.1 mbar; l) the mainly products are $D4^F$ and $D5^F$; m) traces of $D4^{Vi}$ observed at -18.6 ppm by $^{29}$Si NMR spectroscopy (see SI, Figure S14).

### Depolymerisation of industrial silicone waste

An actual high volume industrial silicone waste was provided by Elkem Silicones©. It is a poly(dimethysiloxanes) with a viscosity of 100 cSt, containing mainly D moiety with a variety of impurities such as Si-H, $H_2O$, HCl, $AlCl_3$, etc. First, we have studied the depolymerisation of this industrial waste in our standard conditions (150°C, 5 mbar) in the presence of a low amount of catalytic system (0.1 mol%). Unfortunately, no cyclic siloxanes were observed after a certain time of distillation. Moreover, the desired products ($D_n$) could only be obtained at a 10% yield when catalyst loading was increased to 0.5 mol%. However, the rate of distillation was very slow and a viscous gel residue was afforded after completing the distillation. This phenomenon could be explained by the formation of T moieties through dehydrogeno-condensation reactions between Si-H and Si-OH (arising from the former, in the presence of $H_2O$) in the presence of a basic catalytic system. In order to avoid the formation of these detrimental T moieties, which contribute to an unmanageable viscosity, either a diluent is required to reduce the viscosity of the reaction medium or improved kinetics have to be targeted in order to favour cyclisation over T-motif formation. Firstly, the reaction was performed in the presence of $KOSiMe_3$ (0.5 mol%) and PEG-DME 500 (2mol%), which was used as a ligand & a diluent for the depolymerisation reaction. Interestingly, the yield of cyclic siloxanes increased to 75%. Secondly, other high-boiling-point diluents (with low mass ratio) have been used to facilitate the depolymerisation and the best result was obtained in the presence of n-octadecanol (10wt%), giving 75% yield of cyclosiloxanes (ESI-Table S1). It is likely that the preferential T motifs formed from the condensation of this long-chain alcohol and the residual Si-H moieties yield manageable viscosities. Further study at 170°C, 5 mbar provided a better 84% overall yield, in which $D_4$ mainly accounted for 80% of this mixture. This result is very promising to convert an industrial waste back to valuable monomer products.

Table 5: Depolymerization of industrial silicone waste.



| Entry | Catalyst (mol%) | Diluent | Yield of cyclo-siloxanes (%)[b] | Ratio[c] D3/D4/D5/ others[d] |
|---|---|---|---|---|
| 1 | $KOSiMe_3$ (0.1)<br>18C6 (0.1) | - | 0 | nd |
| 2 | $KOSiMe_3$ (0.5)<br>18C6 (0.5) | - | 10 | 19/78/2/1 |
| 3 | $KOSiMe_3$ (0.5)<br>PEG-DME 500 (2) | - | 75 | 13/79/8/0 |
| 4 | $KOSiMe_3$ (0.5)<br>18C6 (0.5) | $C_{18}H_{37}OH$ (10 wt%) | 75 | 7/80/12/1 |
| 5[e] | $KOSiMe_3$ (0.5)<br>18C6 (0.5) | $C_{18}H_{37}OH$ (10 wt%) | 84 | 8/80/11/1 |

[a] Reaction conditions: industrial silicone waste (10 mL, 9.5g), catalyst (xx mol%), diluent (10%wt, if necessary). [b]Yield of siloxanes was determined by the ratio between the mass of distillated fraction and the mass of silicone oil. [c]The ratio of cyclic siloxanes was determinated by the ratio of each compound in $^{29}$Si-NMR. [d]Others = HMDS + D6. [e]the distillation condition was performed at 170°C, 5 mbar.

### Recyclability of the catalyst

The recyclability of the catalyst has been studied using our optimised conditions (140°C, 1 hour then distillate under a pressure of 10mbar) (Figure 1). The first run was performed using $KOSiMe_3$ +18C6 (0.1 mol%) and an excellent yield (96%) of a mixture of cyclosiloxanes was obtained. This result is very similar to the one previously obtained (Table 4, entry 1), indicating the reproducibility of this method. After removing the volatile products, the "catalyst" remains as a residue within small amount of the PDMS (to avoid the thermal decomposition of the catalyst). It is very likely that the catalyst is an altered version of the original silanolate: after each back-biting reactions, a new silanolate is generated, thus regenerating the active species (ESI-Figure S1). Then, the flask with catalyst was refilled with the silicone oil and was kept stirring at 140°C for 1 hour before distilling again under the reduced pressure. Interestingly, no reactivity was lost over the next 4 runs, showing the recyclability of the catalyst (or at least of the active silanolate species) under our reaction conditions. Moreover, a $^{29}$Si-NMR of the residue after 5 runs was also analysed and only the signal of the remained polysiloxanes (or oligosiloxanes) was detected (ESI-Figure S4).

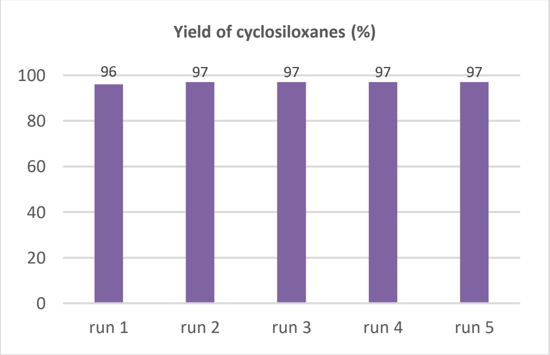
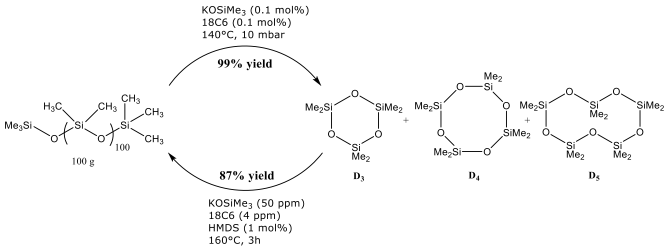


Figure 1: The recyclability of the catalyst over 5 runs

### Depolymerization-Repolymerization coupling using a single catalyst ($KOSiMe_3$ +18C6)

After optimising the conditions for the depolymerisation of the silicone oils, we have carried out the scale-up of this reaction using *waste silicone oil* **2** (100 g) as a standard substrate (Scheme 3). First, *waste silicone oil* **2** that was used over a several-year period in the lab for heating thermostatic bath, was introduced into a flask in the presence of $KOSiMe_3$ (0.1 mol%) and 18C6 (0.1mol%). This mixture was heated to 140°C for 1 hour. Then, the volatile product was continuously distilled off (140°C, 10mbar). After 3 hours, 99 g of the mixture siloxanes ($D_3$, $D_4$, $D_5$, others) was collected, highlighting the high efficiency of our catalytic system. Inside this mixture, $D_4$ accounts for 82% whereas $D_3$, $D_5$ represent 7% and 8%, respectively.

With this mixture in hand, we then performed the ring-opening polymerization of cyclosiloxanes ($D_3$, $D_4$, $D_5$) following a modified procedure described by Fleury *et al.* (Scheme 3).[7] The obtained cyclic siloxanes (99 g) with HMDS (0.6 g) were introduced in the flask and heated to 160°C. Then, $KOSiMe_3$ (50ppm) and 18C6 (4 ppm) was added into this solution at this temperature and this reaction mixture was kept at 160°C during 3 hours. After that, the reaction medium was cooled down to room temperature and a neutralized agent was introduced. Then, the resulting liquid was evaporated under reduced pressure (160°C, 1 mbar, 5 hours) to give a colourless silicone oil (87 g, 87% yield). The measurement of the level of volatile cyclic siloxanes was thus assessed to between 12.6 and 13.5%, which suggests that the thermodynamic equilibrium had been reached. The resulting silicone oil was characterised by SEC (toluene) analysis ($M_n$ = 8000 g/mol, Đ~2.0, see Figures S28 & S29, SI) as well as $^1H$ & $^{29}Si$-NMR analyses, indicating the effectiveness of depolymerisation-repolymerization strategy using a “single-catalyst” (see Figures S24-S27, SI).



Scheme 3: Coupling the depolymerisation-repolymerization of of silicone oils, towards cicularity.

## Conclusion

We have developed a new protocol for the depolymerisation of silicone oil using a mixture of $KOSiMe_3$ and adequate polydentate complexing agent (such as 18C6 or the cheaper $PEG_{500}$-DME) as the original catalytic species. The reaction was performed over a wide range of temperatures (60-170°C). 140°C was then selected to achieve an efficient compromise of fast kinetics for reactive distillation without overheating. A low loading of catalyst (typically 0.1 mol%) provides an excellent yield of cyclosiloxanes (up to 99%), with excellent purity, and the strategy is extremely robust and tolerant to a wide range of functionalities. Additionally, the catalyst could be recycled over 5 runs without losing any reactivity. Moreover, the reaction was scaled-up (100 g) and the concept of depolymerisation-repolymerization using a “single” catalyst was established, indicating the potential of this process for industrial application towards circularity for silicones.

## Experimental Section

### General procedure for the depolymerisation of siloxanes oil 1 (10 g scale)

In a flask (50 mL) connecting with a short Vigreux column, siloxane oil (9.5 g, 100 mmol of siloxane unit), $KOSiMe_3$ (14 mg, 0.1 mol%), 18C6 (30 mg, 0.1 mol%) were introduced then this mixture was heated at 140°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (140°C, 10mbar) to give a mixture of cyclosiloxanes $D_3$, $D_4$, $D_5$ (9.2 g, 97% yield) as a colourless liquid.

### General procedure for the depolymerisation of siloxanes oil 1 (100 g scale)

In a flask (250 mL) connecting with a long Vigreux column, siloxane oil (100 g, 1 mol siloxane unit), $KOSiMe_3$ (142 mg, 0.1 mol%), 18C6 (300 mg, 0.1 mol%) were introduced then this mixture was heated at 140°C for 1 hour. Then, the reaction mixture was distillated under reduced pressure (140°C, 10mbar) to give a mixture of cyclosiloxanes $D_3$, $D_4$, $D_5$ (99 g, 99% yield) as a colourless liquid.

### General procedure for the polymerisation of a mixture of cyclic siloxanes oil (100 g scale)

An obtained mixture of siloxanes from the depolymerisation of silicone oil **1** (99 g) and HMDSO (0.6 g) were introduced in a three-neck round bottom flask then this mixture was heated to 160°C. At this temperature, $KOSiMe_3$ (50 ppm) and 18C6 (4 ppm) were added and the polymerisation experiment were performed at 160°C for 3 hours. Then, the reaction was cool down to room temperature and a neutralized solution containing phosphoric acid was introduced. Finally, the result mixture was evaporated under reduced pressure (170°C, 1 mbar) for 3 hours to give a silicone oil (87 g, 87% yield) as a colourless liquid.

## Author Contributions

All of experiments were conducted by N. D. V.. All the authors contributed to the preparation of this manuscript. ***Conceptualization:*** J. R. and V. M.; ***Resources*** A. B.-M; N. D. ***Writing****-Original draft, review, editing:* N. D. V., J. R., V. M.

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## References

1 H.-H. Moretto, M. Schulze, G. Wagner, *In Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000, **33**, 9–12.

2 J. E. Mark, *Acc. Chem. Res.*, **2004**, 37, 946–953.

3 Global Silicones Market (2021 to 2026) - Industry Trends, Share, Size, Growth, Opportunity and Forecasts, *https://www.globenewswire.com/news-release/2021/06/02/2240181/28124/en/Global-Silicones-Market-2021-to-2026-Industry-Trends-Share-Size-Growth-Opportunity-and-Forecasts.html*

4 T. Köhler, A. Gutacker and E. Mejía, *Org. Chem. Front.*, 2020, **7**, 4108-4120.

5 E. G. Rochow, *J. Am. Chem. Soc.*, 1945, **67**, 963–965.

6 E. G. Rochow, *US Patent*, US 2,380,995A, 1941.

7 E. Fleury, J.-M. Mas and K. Ramdani, *U.S. Patent*, US 7,776,988, Aug 17th, 2010.

8 M. Takla, N. E. Kamfjord, H. Tveit and S. Kjelstrup, *Energy* 2013, **58**, 138-146.

9 G. Saevarsdottir, T. Magnusson and H. Kvande, *J. Sustain Metall.*, 2021, **7**, 848–857.

10 B. Rupasinghe and J. C Furgal, *Polym. Int.,* 2022, **71**, 521-531, DOI 10.1002/pi.6340.

11 C. Allandrieu and D. Cardinaud, *U.S. Patent*, US 5,670,689, Sep 23rd 1997.

12 N. Okui and J. H. Magill, *Polymer*, 1977, **18**, 845–850.

13 M. A. Brook, Z. Shigui, L. Lihua, and C. Yang, *Can. J. Chem.,* 2012, **90**,153–160.

14 P. Winton and F. Wilcock Donald, J Am. Chem. Soc. 1946, 68, 358–363.

15 W. Noll, *Chemistry and Technology of Silicone Oligomers*, 1968.

16 R. Friebe, W. Weber and K.-H. Sockel, *U.S. Patent*, US 6,001,888, Dec 14th, 1999.

17 T. W. Greenlee, *U.S. Patent*, US 5,110,972, May 5, 1992.

18 M. Okamoto, S. Suzuki and E. Suzuki, *Applied Catalysis A: General,* 2004, **261**, 239–245.

19 R. Petrus, J. Utko, R. Gniłka, M. G. Fleszar, T. Lis and P. Sobota, *Macromolecules* 2021, **54**, 5, 2449–2465.

20 R. F. Weitkamp, B. Neumann, H.-G. Stammler and B. Hoge, *Angew. Chem. Int. Ed.,* 2020, **59**, 5494-5499.

21 R. F. Weitkamp, B. Neumann, H.-G. Stammler and B. Hoge, *Chem. Eur. J.*, 2021, **27**, 915-920.

22 A. Oku, W. Huang and Y. Ikeda, *Polymer* 2002, **43**, 7289–7293

23 D. Yun-qiao, L. Hai-feng, M. Qiu-hong and L. Xiao, *Polym. Degrad. Stab*., 2020, **182**, 109367.

24 K. Bläsing, R. Labbow, D. Michalik, F. Reiß, A. Schulz, A. Villinger, S. Walker, *Chem. Eur. J.* 2020, **26**, 1640-1652.

25 K. Bürglová and J. Hlaváč, *Synthesis* 2018, **50**, 1199–1208.

26 E. Weber, *In Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2007, **10**, 471-480.

27 Y. Hu, J. Steinbauer, V. Stefanow, A. Spannenberg and T. Werner, *ACS Sustainable Chem. Eng.,* 2019, **7**, 13257–13269.

28 M. E. Belowich, John M. Roberts, T. H. Peterson, E. Bellinger, K. Syverud and T. Sidle, *Macromolecules* **2020**, 53, 7487-7495.