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Entropy-Driven Depolymerization of Poly(dimethylsiloxane)

Jordan L. Torgunrud, Aracelee M. Reverón Pérez, Emily B. Spitzberg, and Stephen A. Miller*

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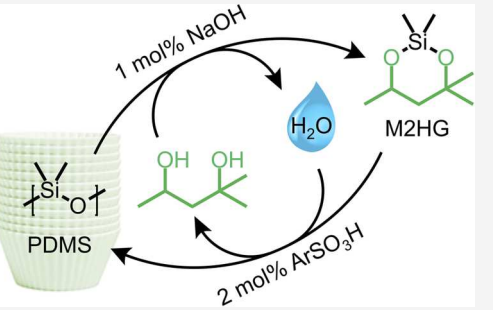
ABSTRACT: Poly(dimethylsiloxanes) (PDMSs) are widely used because of their unique properties but require a highly polluting and energy-intensive synthesis starting from silica. Chemical recycling offers an opportunity to regenerate new materials with comparable properties while avoiding the inefficiencies of the *de novo* synthesis. Herein, we report computational and experimental results of depolymerizing PDMS with diols. Computationally, depolymerization with methanol is always endergonic, while depolymerization with 2-methyl-2,4-pentanediol (hexylene glycol, HG) is exergonic over a wide temperature range. Acid-catalyzed exchange reactions between $SiMe_2(OMe)_2$ and hexylene glycol show silicon's thermodynamic preference for the diol due to entropically favorable chelation. An optimized procedure for depolymerizing PDMS with hexylene glycol to a cyclic monomer, M2HG, was developed and applied to a variety of commercial PDMS sources. Cyclic siloxanes are byproducts early in the reaction, requiring a two-step process to obtain highly pure M2HG. The procedure is selective for PDMS even in complex reaction mixtures and gives good yields (38−78%) regardless of the starting material used. Polymerizing M2HG back to PDMS proved challenging but feasible. Ring-opening polymerization of M2HG was catalyzed by trifluoromethanesulfonic acid or *p*-toluenesulfonic acid to yield low-molecular-weight polysilicon acetals (M_n up to 1500) or high-molecular-weight PDMS ($M_n \sim 39{,}900$), respectively. Terpolymerizations of M2HG with vinyl ethers and aldehydes also yielded low-molecular-weight material (M_n up to 5000). PDMS was successfully reconstituted from M2HG under cationic emulsion polymerization conditions, affording high molecular weights up to M_n = 49,000.



INTRODUCTION

Synthetic polymers find utility in many aspects of everyday life, including packaging, consumer products, textiles, electronics, transportation, machinery, and building materials, among other things.[1] Most polymers are hydrocarbon-based and made from fossil fuels, a finite resource. Polysiloxanes, while containing hydrocarbon moieties, possess a backbone of silicon and oxygen, the two most abundant elements in the Earth's crust.[2] The silicon in all commercial polysiloxanes originates from the most abundant material proximal to humans, silica (SiO_2).[3] Silica is heated to high temperatures in the presence of coke to reduce silicon(IV) to silicon(0). The elemental silicon is then subjected to another high-temperature process, the Müller−Rochow synthesis that yields chloromethylsilanes of formula $SiMe_xCl_{4-x}$.[4,5] The most commonly produced polysiloxane is poly(dimethylsiloxane) (PDMS), which is generally made by hydrolyzing dichlorodimethylsilane into linear or cyclic oligomeric siloxanes that are further converted to high-molecular-weight polymers by polycondensation or ring-opening polymerization, respectively.[6−9] PDMS is known to have a low glass-transition temperature, high conformational flexibility, hydrophobicity, low surface tension, high gas permeability, low flammability, biocompatibility, and high chemical, thermal, and UV stability.[10−15] These properties make PDMS useful for many applications, such as hydraulic fluids, lubricants, sealants, adhesives, anti-foaming agents, coatings, biomedical devices, and elastomers.[6,15−18] Because of these diverse applications, silicones have an annual market value of $3.33 billion as of 2022; this number is projected to rise to $3.77 billion by 2025, according to Statista.[19]

Like other commodity materials, polysiloxanes face several possible end-of-life scenarios: mechanical recycling, incineration for energy, landfilling, or loss to the open environment.[1] Mechanical recycling results in lower quality products that eventually add to the waste stream. Incineration to produce energy (thermal recycling) is not a viable option for polysiloxanes because of their high thermal and oxidative stability.[13] Upon entry into the environment via landfilling or littering, PDMS degrades both biotically (minor) and abiotically (major), albeit slowly, due to its stability. In soil, PDMS degrades into oligomers and volatile cyclics, which are further degraded radically in the upper atmosphere to water, carbon dioxide, and silica.[11,20,21] Although polysiloxanes degrade into benign products after landfilling, it would be ideal to avoid the energy-intensive and polluting synthesis necessary to make

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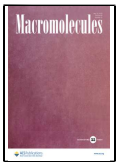

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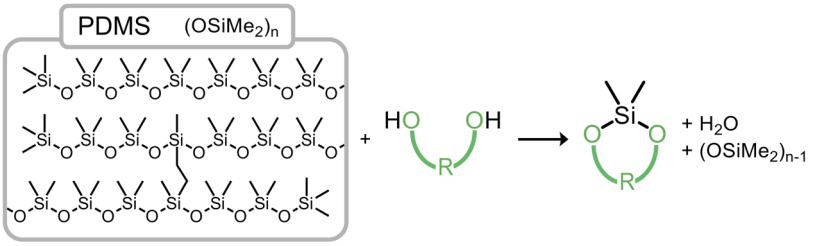

Figure 1. Depolymerization of poly(dimethylsiloxane) (PDMS) with diols yields cyclic silicon acetals and water.

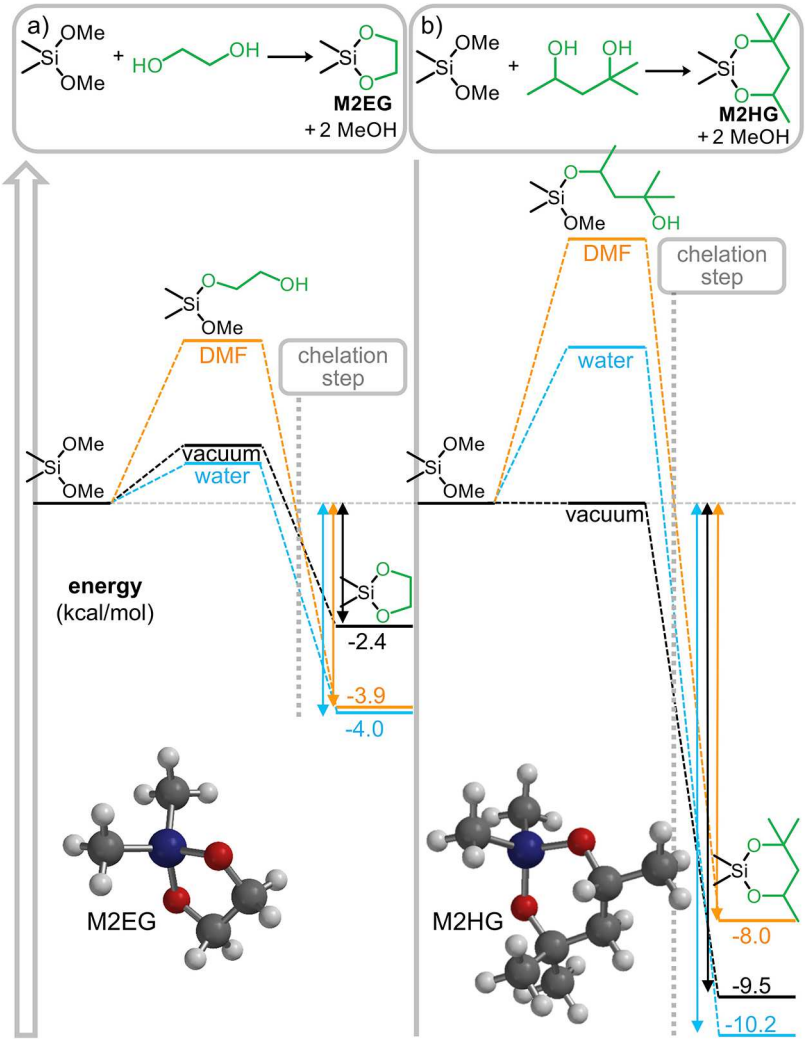

Figure 2. Calculated (DFT/B3LYP/6-31+G*) thermodynamics (Gibbs free energy @298 K) for the conversion of $SiMe_2(OMe)_2$ to cyclic $SiMe_2[OR'O]$ via (a) ethylene glycol (EG) or (b) hexylene glycol (HG).

them from raw materials.[22] An alternative end-of-life mechanism is chemical recycling, whereby a waste stream becomes a feedstock for the same or upgraded material.[23−25] The chemical recycling of polymers is an increasingly attractive option and offers an opportunity to reduce natural resource usage, greenhouse emissions, and the squandering of land for landfilling. However, previous approaches to the chemical recycling of PDMS have been largely inefficient, relying on elevated pressures, sacrificial reagents, expensive catalysts, or excess solvent.

Enthaler and co-workers employed a variety of approaches to form Si−F or Si−Cl containing monomers from polysiloxanes. In a stand-alone method, fluorine was introduced using boron trifluoride diethyl etherate.[26] In other methods, the Si−O bond was first activated with either Zn or Fe salts[27,28] and then cleaved with carboxylic acid derivatives. With benzoyl fluoride, no additional reagent was necessary; otherwise, potassium fluoride was added. Similarly, Si−Cl linkages were formed using an Fe catalyst and an acid chloride.[29] With iron catalysts, fatty alcohols or fatty acid anhydrides were used to depolymerize polysiloxanes to monomers, which could then be used to resynthesize polysiloxanes.[30,31] Okamoto *et al.* depolymerized PDMS to $SiMe_2(OMe)_2$ using methanol, metal halide salts, and dimethyl carbonate; the carbonate served as a water scavenger and was necessary to drive the reaction to completion.[32] In the same

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vein, Enthaler *et al.* coupled the depolymerization of polycarbonates and polysiloxanes, exploiting the liberated carbon dioxide to drive the reaction.[29] Chang *et al.* implemented a base-driven aminolysis at room temperature to form cyclic and linear siloxanes with the D4 cyclic siloxane (*cyclic*-$[OSiMe_2]_4$) as the major product.[33] Similar results were obtained by Oku *et al.* when conducting a KOH-catalyzed depolymerization with vulcanized silicone rubbers, which showed improved yields of cyclic siloxanes with the addition of an acid buffer.[34] Laine and co-workers reprocessed silicone resins with mixed phenyl and methyl functionality at room temperature in a TBAF/THF solution; over 100 cycles of recycling were achieved with no loss of fidelity.[13] Furgal *et al.* expanded this approach, isolating D4, D5, and D6 from high-swelling organic solvents and varying loadings of TBAF.[22]

Recently, we demonstrated that chelating diols—unlike monoalcohols—provide a thermodynamic driving force for silica depolymerization[35] and now reason that similar chelation strategies should apply to PDMS depolymerization. Laine *et al.* depolymerized silica using hindered diols to obtain spirocyclic alkylorthosilicate products.[36] Our group previously demonstrated that $SiMe_2(OMe)_2$ and diols (HOR′OH) exchanged to form bis-silicon acetals $(MeO)Me_2SiOR'OSiMe_2(OMe)$, which were subjected to silicon acetal metathesis polymerization (SAMP), forming polysilicon acetals with a repeat unit of $-[SiMe_2OR'O]-$ and new properties (e.g., T_m = 40−105 °C) not possessed by PDMS.[15] We envisaged taking advantage of the entropic benefits of chelation to depolymerize PDMS, yielding cyclic silicon acetals ($SiMe_2[OR'O]$, Figure 1), which could then be used to resynthesize PDMS via hydrolysis or to synthesize new polymers via SAMP. The method we propose herein is successful at ambient pressures with near-stoichiometric equivalents of reagent, inexpensive catalysts, and no excess solvent—effectively solving the challenges faced by other methods.

RESULTS AND DISCUSSION

Exchange of Silicon Acetals with Diols. Figure 2 describes the thermodynamics (Gibbs free energy) of exchanging the −OMe groups of dimethoxydimethylsilane ($SiMe_2(OMe)_2$) for the −OR groups of ethylene glycol (EG) or 2-methyl-2,4-pentanediol (hexylene glycol, HG). $SiMe_2(OMe)_2$ was chosen because acyclic silicon acetals are common target monomers in previously established depolymerization protocols, and it is the simplest silicon acetal. For ethylene glycol (EG), the overall thermodynamics of producing the corresponding cyclic acetal M2EG (Figure 2a) are similar in each medium. In vacuum at 298 K, ΔH = −0.4 kcal/mol for the first step and is slightly favorable but cannot compensate for the penalizing ΔS of −5.0 cal/(mol K), resulting in an overall endergonic ΔG_{rxn} = 1.1 kcal/mol. For the chelation step, the ΔH = 6.2 kcal/mol and is quite penalizing, but the highly favorable entropy (ΔS = 32.3 cal/(mol K)) overwhelms the enthalpy for an overall exergonic process with ΔG_{rxn} = −2.4 kcal/mol. The pattern holds in polar solvents (DMF and water). Compared to vacuum, the addition step enthalpy is comparable in both solvents: ΔH = 0.9 kcal/mol in DMF and ΔH = −0.1 kcal/mol in water. The chelation step enthalpy is less penalizing than in vacuum: ΔH = 2.6 kcal/mol in DMF and ΔH = 3.6 kcal/mol in water. The entropy of chelation in both DMF and water is similar to that in vacuum: ΔS = 32.1 cal/(mol K) in DMF and ΔS = 28.1 cal/(mol K) in water. Hence, in polar solvents, production of M2EG is considerably exergonic: ΔG_{rxn} = −3.9 kcal/mol in DMF and ΔG_{rxn} = −4.0 kcal/mol in water.

For production of M2HG from hexylene glycol, the ΔG_{rxn} values are very similar regardless of medium, and each net process is more favorable (Figure 2b) than that for the corresponding M2EG (Figure 2a). The origin of this difference is the comparatively more favorable enthalpy of the chelation step: ΔH = −1.9 kcal/mol in vacuum, ΔH = −2.0 kcal/mol in DMF, and ΔH = −2.0 kcal/mol in water. Possibly because of steric effects, the first addition step for M2HG is unfavorable in all media. Nonetheless, the overall ΔG_{rxn} for production of M2HG from $SiMe_2(OMe)_2$ is more exergonic than for M2EG in all media: ΔG_{rxn} = −9.5 kcal/mol in vacuum, ΔG_{rxn} = −8.0 kcal/mol in DMF, and ΔG_{rxn} = −10.2 kcal/mol in water. Overall, the entropic benefit of chelation is clear. For production of the cyclic species from $SiMe_2(OMe)_2$, the entropy is positive since the overall reaction generates three molecules from two: 24.9−27.4 cal/(mol K) for M2EG (Figure 2a) and 22.6−30.8 cal/(mol K) for M2HG (Figure 2b). Because this is an equilibrium, forming $SiMe_2(OMe)_2$ from either cyclic species would be substantially endergonic, with an overall negative entropy component.

We previously demonstrated a silicon acetal metathesis[15] reaction between $SiMe_2(OMe)_2$ and $SiMe_2(OEt)_2$. While this metathesis is very slow without added catalyst, the addition of a Brønsted acid, such as *p*-toluenesulfonic acid (*p*-TSA), allows equilibration within 5 h at room temperature, yielding the statistically expected amount of $SiMe_2(OMe)(OEt)$. Here, we employ a related exchange strategy to investigate the relative thermodynamic stability of $SiMe_2(OMe)_2$ and M2HG. Figure 3 describes the fate of the two species when equilibrium is

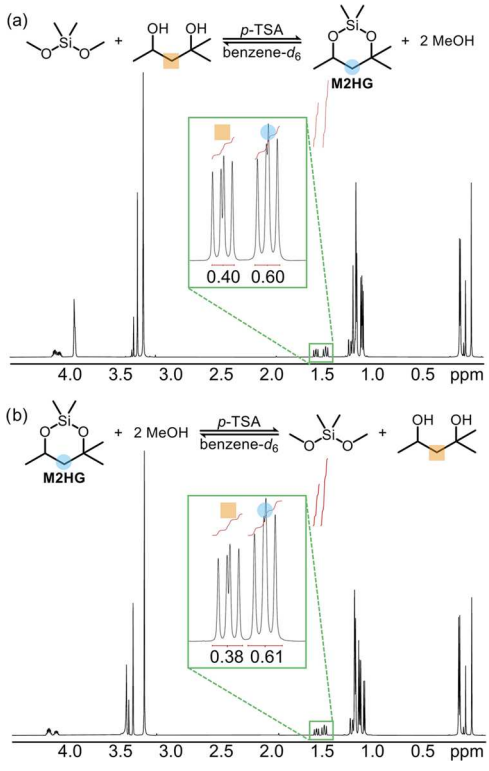

Figure 3. (a) With an acid catalyst, $SiMe_2(OMe)_2$ exchanges with hexylene glycol (HG, orange square) to produce M2HG (blue circle) and methanol. (b) With an acid catalyst, the reverse reaction occurs, yielding the same product distribution.

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approached from either direction using *p*-TSA as a catalyst in benzene-d_6 at room temperature. Figure 3a shows the outcome of combining $SiMe_2(OMe)_2$ with 1.00 equivalent of hexylene glycol (orange square) to form M2HG (blue circle) and methanol. Figure 3b shows the outcome of combining M2HG with 1.98 equiv of methanol to form $SiMe_2(OMe)_2$ and hexylene glycol. Equilibrium is established rapidly, and the final distribution is 60% M2HG and 40% $SiMe_2(OMe)_2$, for a K_{eq} of 1.5 in favor of M2HG. Conversion to M2HG is above 50%, indicating greater thermodynamic stability compared to $SiMe_2(OMe)_2$, as rationalized by the entropically favored chelation steps computed in Figure 2. Although the computational study suggests a K_{eq} of about 10^7 in favor of M2HG, it seems that intramolecular hydrogen bonding of free hexylene glycol in the experimental benzene medium pushes the equilibrium in the opposite direction.

PDMS Depolymerization Model. The net depolymerization thermodynamics of PDMS with methanol, ethylene glycol, or hexylene glycol to yield $SiMe_2(OMe)_2$, M2EG, or M2HG, respectively, can be approximated computationally. The idealized reactions with PDMS are:

$$(OSiMe_2)_n + 2n\ MeOH \rightarrow n\ SiMe_2(OMe)_2 + n\ H_2O$$

$$(OSiMe_2)_n + n\ HOCH_2CH_2OH \rightarrow n\ SiMe_2[OCH_2CH_2O] + n\ H_2O$$

$$(OSiMe_2)_n + n\ HOC(CH_3)_2CH_2CH(CH_3)OH \rightarrow n\ SiMe_2[OC(CH_3)_2CH_2CH(CH_3)O] + n\ H_2O$$

Importantly, the methanol reaction converts $2n + 1$ molecules to $2n$ molecules, but the diol reactions convert $n + 1$ molecules to $2n$ molecules. The entropy parameters demand the depolymerization model matches this stoichiometry. The eight-membered siloxane ring (*cyclic*-$[OSiMe_2]_4$) is reported to be free of ring strain;[3,37,38] hence, a viable model reaction involves depolymerizing the D4 cyclic siloxane:

$$cyclic\text{-}[OSiMe_2]_4 + 8\ ROH \rightarrow 4\ SiMe_2(OR)_2 + 4\ H_2O$$

Figure 4 shows the model reaction of the eight-membered D4 with methanol, ethylene glycol, or hexylene glycol. The computed reaction enthalpies (ΔH), entropies (ΔS), and free energies (ΔG) at both 25 and 100 °C are listed in Table 1 (DFT/B3LYP/6-31+G*/C-PCM solvent correction model). The ΔG of each reaction is plotted against temperature in vacuum (dotted lines), dimethylformamide (dashed lines), or water (solid lines) as the computational solvent medium. With all alcohols, the reaction enthalpy is positive: 22.4−25.2 kcal/mol for methanol, 36.4−48.5 kcal/mol for ethylene glycol, and 16.8−24.2 kcal/mol for hexylene glycol. With a positive enthalpy, the reaction with methanol is never exergonic because the reaction entropy is negative (−15.6 to −32.3 cal/(mol K)), as indicated by the stoichiometry (9 molecules to 8 molecules). However, the reactions with diols have temperatures above which the reaction is exergonic because they have positive entropies (77.1−84.6 cal/(mol K) for ethylene glycol and 75.0−101.8 cal/(mol K) for hexylene glycol). For ethylene glycol, the thermoneutral temperature ($\Delta G = 0$) is nearly the same when either water or DMF is the computational solvent: 157 °C in water (Figure 4, solid blue line) or 163 °C in DMF (Figure 4, dashed blue line). These temperatures are attainable in a laboratory setting. The

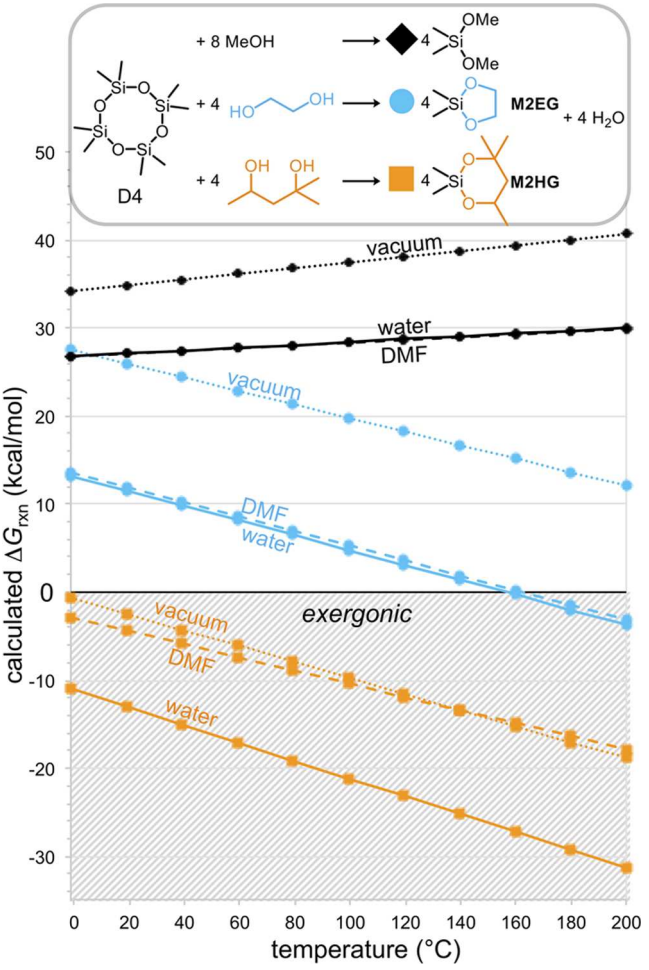

Figure 4. Calculated (DFT/B3LYP/6-31+G*) poly(dimethylsiloxane) depolymerization thermodynamics as a function of temperature, as modeled by alcoholysis of *cyclic*-$[OSiMe_2]_4$. Reactions with monoalcohols (such as methanol, black diamonds) are never thermodynamically viable since ΔH_{rxn} is positive and ΔS_{rxn} is negative. Reactions with diols (such as ethylene glycol, blue circles, or hexylene glycol, orange squares) have an exergonic temperature range since ΔH_{rxn} and ΔS_{rxn} are both positive. With hexylene glycol, the depolymerization of PDMS is calculated to be exergonic above 0 °C in any medium.

thermoneutral temperature for hexylene glycol is considerably lower because of the greater thermodynamic stability of the 6-membered ring versus the 5-membered ring, which is formed from ethylene glycol. The reaction is exergonic above −107 °C in water (Figure 4, solid orange line) and −38 °C in DMF (Figure 4, dashed orange line). Compared to methanol, the corresponding reaction of D4 with bulky isopropanol, forming $SiMe_2(OiPr)_2$, is even less favorable, probably because of sterics (Table 1).

PDMS Depolymerization with Hexylene Glycol. Confident that the thermodynamics were favorable, we began our depolymerization work with commercial, hydroxy-terminated, PDMS (M_n = 6800; DP = 92; $Đ$ = 1.3), the most industrially relevant polysiloxane,[7] with varying alcohol and catalyst loadings. Hexylene glycol (HG) was the selected diol because our computations suggested a strong thermodynamic preference for depolymerization and because HG can derive from acetone, an inexpensive and increasingly bio-based feedstock.[39] Sodium hydroxide was the selected catalyst

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Table 1. Calculated Thermodynamic Parameters for PDMS Depolymerization Modeled by the Alcoholysis of D4 (*Cyclic*-$[OSiMe_2]_4$) According to the Reactions of Figure 4[a]

alcohol	medium	ΔH (kcal/mol)	ΔS (cal/mol K)	$\Delta G_{25\,°C}$ (kcal/mol)	$\Delta G_{100\,°C}$ (kcal/mol)
methanol	vacuum	+25.3	−32.3	+35.0	+37.4
	DMF	+22.5	−15.6	+27.2	+28.3
	water	+22.5	−15.9	+27.2	+28.4
ethylene glycol	vacuum	+48.5	+77.1	+25.6	+19.8
	DMF	+36.6	+83.8	+11.6	+5.3
	water	+36.4	+84.6	+11.1	+4.8
hexylene glycol	vacuum	+24.2	+91.0	−2.9	−9.7
	DMF	+17.6	+75.0	−4.7	−10.4
	water	+16.8	+101.8	−13.5	−21.1
isopropanol	vacuum	+42.4	−80.9	+66.6	+72.6

[a]DFT/B3LYP/6-31+G*/C-PCM solvent correction model.

because it has been used with HG to depolymerize silica to form spirocyclic alkylorthosilicates[36] somewhat analogous in structure to our target molecule, M2HG.

We decided to follow a reaction stoichiometry similar to that used to depolymerize silica:[36] 1 equiv PDMS with 7 equiv hexylene glycol and 10 mol % sodium hydroxide (Table 2, entry 1). The reaction was heated to 175 °C, slowly yielding a distillate containing a mixture of M2HG (bp 146 °C)[40] and D3, D4, and D5 cyclic siloxanes (*cyclic*-$[OSiMe_2]_n$; bp 135,[41] 176,[42] and 210 °C,[43] respectively). The reaction was then heated to 200 °C, more rapidly yielding a second distillate that was mostly pure M2HG. A simple water wash successfully removed unreacted hexylene glycol and other polar impurities. The overall yield of M2HG was 67%, but since the first distillate was a mixture of products, the pure M2HG yield was 50%.

We proceeded to optimize this procedure by reducing the mol % of catalyst (NaOH) and diol equivalents (Table 2, entries 2−9). The reactions proceeded similarly with decreasing equivalents of diol, giving pure M2HG product in the second distillate until near-stoichiometric equivalents were used. Two equivalents of diol appeared optimal (Table 2, entry 4). Note that the excess diol was not necessarily discarded; the reaction is similarly effective when additional PDMS is combined with the diol leftover from a previous reaction. Hence, this depolymerization protocol should be amenable to a continuous process method. Regarding the catalyst loading, 1 mol % of sodium hydroxide appeared optimal and afforded a maximum yield of 58% pure M2HG (Table 2, entries 2 and 4). After reaction completion, only 0.16 g of unreacted PDMS remained, corresponding to a conversion of 99.6%.[44] Interestingly, the depolymerization also proceeds without a catalyst but only with hydroxy-terminated PDMS; however, a mixture of products is obtained for both distillation steps (see Figures S8 and S9).

Previous studies indicate that the hydrolysis of PDMS is influenced by both pH and counterion identity.[12] So, we tested other metal hydroxides, organic bases, and organic and inorganic acid catalysts (Table 2, entries 10−17). The base catalysts resulted in a mixture of products for both distillation steps, and the acid catalysts afforded low yields and minimal M2HG selectivity. Interestingly, the counterion present does indeed influence the outcome, as potassium and calcium hydroxides gave mixtures of the desired product and cyclic siloxanes, while sodium hydroxide afforded the pure product. Because of the prevalence of fluoride-containing catalysts in previous studies,[13,22,26−28,32] we also tested potassium fluoride and tetrabutylammonium fluoride (Table 2, entries 14 and 15). Potassium fluoride afforded nearly pure M2HG in the second distillation step but still lower purity versus sodium hydroxide. Tetrabutylammonium fluoride produced low yields and complex mixtures in both distillation steps. Thus, sodium hydroxide (1 mol %) was the optimal catalyst for this process. Note that with the exception of TBAF, M2HG was the predominant product in both distillates regardless of the catalyst used.

Once we established optimized conditions for depolymerizing hydroxy-terminated PDMS, we tested the applicability of the method toward PDMS bearing other end groups, specifically vinyl (Table 2, entry 20) and trimethylsiloxy (Table 2, entry 21). We did not observe any impurities resulting from the end groups by ^{1}H NMR (see Figures S26−S29), indicating the end groups remained in the reaction mixture, were removed during workup, or were of too low concentration to observe. For the vinyl-terminated polymer having M_n = 22,000, DP = 297, and $Đ$ = 1.6, the end-group concentration is 0.7%. For the trimethylsiloxy polymer having M_n = 43,400, DP = 586, and $Đ$ = 1.8, the end-group concentration is 0.3%. Note that comparable depolymerization success was found regardless of end-group identity or PDMS molecular weight, which varied from 6800 (hydroxy-terminated) to 43,400 (trimethylsiloxy-terminated).

Because the optimized procedure produced a mixture of products in the first distillation step, we sought to concentrate M2HG via an iterative process. First, commercial D4 cyclic siloxane was subjected to the optimized conditions (Table 2, entry 22), resulting in 95% conversion to M2HG in the second distillate. Confident that the cyclics would convert to M2HG, we subjected a mixed feed of M2HG (41 Si mol %), D3 (14 Si mol %), D4 (38 Si mol %), and D5 (7 Si mol %) to the optimized conditions (Table 2, entry 23). The distillate obtained was 93% pure M2HG, suggesting that an iterative process can, indeed, improve the purity.

Mechanism for Base-Catalyzed Depolymerization. The depolymerization proceeds without a catalyst only if the PDMS is hydroxy-terminated, suggesting there are different mechanisms for PDMS with different end groups. Herein, we propose the base-catalyzed depolymerization mechanism applicable to PDMS with any end group (Scheme 1). Without a catalyst, hexylene glycol (HG) is a poor nucleophile, but upon deprotonation with base, HG becomes an excellent nucleophile and can attack any silicon at the chain ends or in the main chain—forming a pentavalent silicate anion. This is followed by heterolytic Si−O bond cleavage (leaving group

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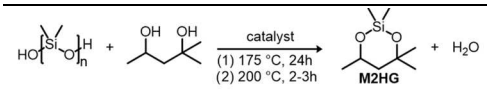
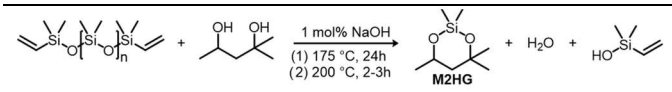
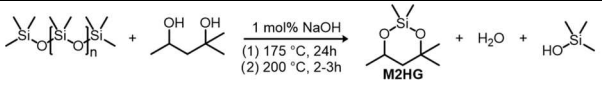
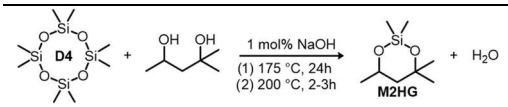
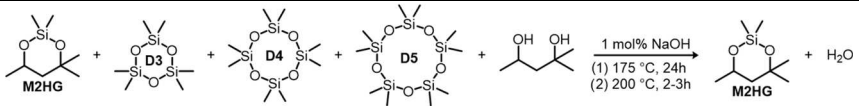
Table 2. Conditions for the Depolymerization of PDMS with Varying Diol Equivalents and Catalysts[a]

Entry	Diol equiv.	Catalyst	Catalyst (mol%)	1st distillate			2nd distillate			M2HG yield[b]	
				yield (g)	%M2HG[b]	%D3, D4, D5[b]	yield (g)	%M2HG[b]	%D3, D4, D5[b]	Overall (%)	Pure[c] (%)
											
1	7	NaOH	10	12.66	76	10, 14, 1	28.86	100	0, 0, 0	67	50
2	7	NaOH	1	12.61	76	11, 12, 1	33.34	100	0, 0, 0	75	58
3	4	NaOH	1	15.42	72	9, 17, 1	26.19	100	0, 0, 0	65	45
4	2	NaOH	1	24.00	67	8, 23, 3	50.52	100	0, 0, 0	77	58
5	1.2	NaOH	1	16.84	63	12, 23, 3	70.78	78	2, 16, 3	57	-
6	2	-	0	10.44	60	26, 13, 1	43.34	78	8, 12, 2	46	-
7	2	NaOH	10	16.67	67	9, 22, 2	45.46	98	0, 2, 0	64	52
8	2	NaOH	5	25.17	75	6, 17, 2	48.79	100	0, 0, 0	78	56
9	2	NaOH	0.1	21.79	63	9, 25, 3	50.07	88	1, 8, 3	67	-
10	2	TBD	1	14.78	50	10, 35, 6	35.71	84	1, 12, 3	43	-
11	2	DBU	1	9.18	71	19, 10, 0	24.63	68	9, 21, 1	27	-
12	2	KOH	1	18.48	69	10, 19, 2	52.42	93	1, 5, 1	71	-
13	2	$Ca(OH)_2$	1	17.36	68	10, 21, 1	51.81	79	1, 15, 6	61	-
14	2	KF	1	28.48	68	9, 20, 3	43.97	92	0, 6, 2	69	-
15	2	TBAF	1	2.74	30	29, 27, 2	4.71	52	16, 30, 3	4	-
16	2	HCl	1	0.0	0	0, 0, 0	58.80	0	10, 83, 7	-	-
17	2	H_3PO_4	1	19.14	86	14, 0, 0	48.13	41	2, 2, 2	42	-
18	2	malic	1	0.0	0	0, 0, 0	0.0	0	0, 0, 0	-	-
19	2	acetic	1	0.0	0	0, 0, 0	0.0	0	0, 0, 0	-	-
											
20	2	NaOH	1	25.50	80	7, 12, 0.8	46.48	100	0, 0, 0	77	54
											
21	2	NaOH	1	20.96	71	11, 16, 1	51.31	95	1, 3, 1	74	56
											
22	2	NaOH	1	16.86	70	8, 19, 2	55.19	95	1, 3, 1	71	-
											
23	2	NaOH	1	0.0	0	0, 0, 0	45.51	93	1, 5, 1	61	-

[a]Starting mass of PDMS was ~25 g for reactions with 7 or 4 diol equiv, ~36 g with 2 diol equiv, and ~49 g with 1.2 diol equiv. [b]Determined by quantitative ^{29}Si NMR. [c]Pure yields were taken from distillates with 100% M2HG product.

loss), proton transfer, intramolecular nucleophilic attack (ring-closure), and a second heterolytic Si−O bond cleavage. Because each step of the mechanism is in equilibrium, the product must be removed from the reaction via distillation to avoid repolymerization.

PDMS Depolymerization with Monoalcohols. To test our hypothesis that a chelating diol is necessary for successful depolymerization, we adapted the optimized method to monoalcohols methanol and isopropanol—used in greater excess and at a lower starting temperature to account for volatilization. Conversion to $SiMe_2(OMe)_2$ with methanol was 3% (see Figure S33). Conversion to $SiMe_2(OiPr)_2$ with isopropanol could not be confirmed by NMR, although 10% conversion to a mixture of products was observed (see Figure

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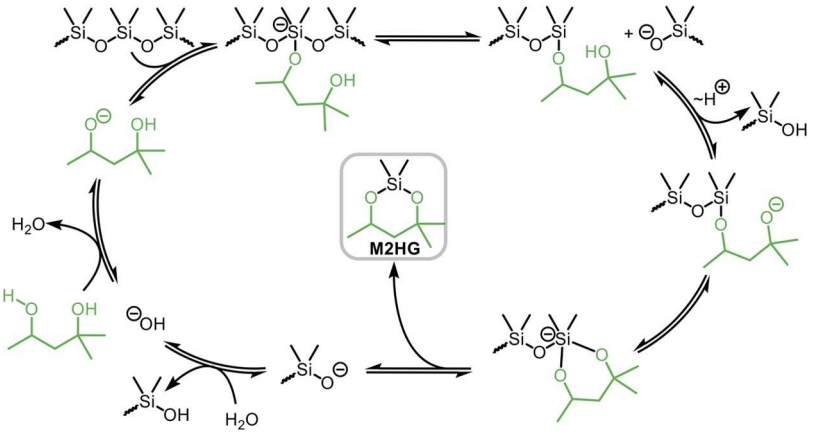
Scheme 1. Proposed Mechanism for the Base-Catalyzed Depolymerization of Poly(dimethylsiloxane) with Hexylene Glycol



S37). While our depolymerization methods operated exclusively at 1 atm, it is possible that elevated pressures could improve the obtained yields because higher temperatures would be feasible.

PDMS Depolymerization with Other Diols. After optimizing the depolymerization protocol with hexylene glycol, the next goal was to test it with other diols that would form reasonably sized rings. Shown in Figure 5 are the results for computing the ring strain of the different target molecules that could be synthesized from PDMS and commercially available diols. Ring strain was computed using an isodesmic reaction model with the target silicon acetal and dimethoxydimethylsilane combining to form the open chain analogue. Dimethoxydimethylsilane avoids hydrogen bonding and possible complications with the equilibrium. A release in ring strain gives a negative ΔH_{rxn}, whereas a minimally strained ring gives a near-zero or positive ΔH_{rxn}. Addition of methyl substituents at the α-carbon results in a decrease in ring strain for a given ring size. This is likely due to the Thorpe−Ingold effect, which favors cyclization by compressing the O−C−C bond angle and

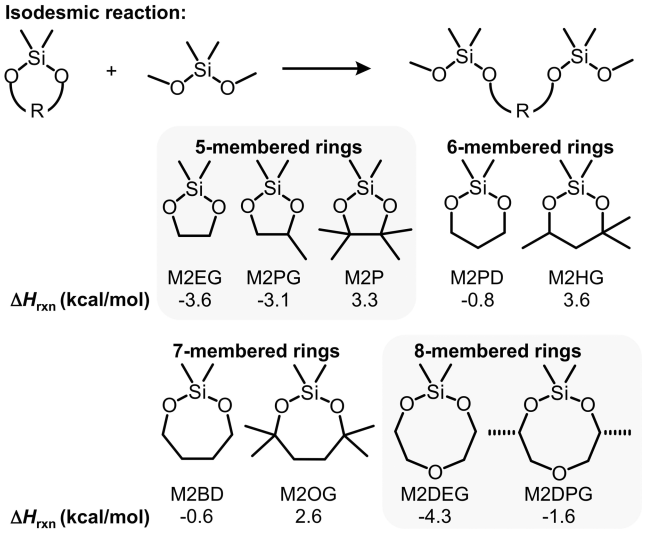


Figure 5. Calculations (DFT/B3LYP/6-31+G*) of ring strain via computational isodesmic reaction of various silicon acetal rings with dimethoxydimethylsilane, by employing a water medium according to the C-PCM solvent correction model. Note that other stereo- and regioisomers of M2DPG computed to $\Delta H_{rxn} = -1.6 \pm 1.5$ kcal/mol.

by minimizing the conformational degrees of freedom—an entropic benefit.[45] Based on this computational data, we expected pinacol, hexylene glycol, 2,5-dimethyl-2,5-hexanediol, and dipropylene glycol to yield the most stable rings for each possible ring size, as they have the most positive (or greatest) enthalpy of ring-opening.

Table 3 compares these calculations with the experiment. Depolymerization of PDMS with ethylene glycol (EG) or 1,4-butanediol (BD) generated product distributions consisting predominantly of the desired M2EG and M2BD products, respectively. Depolymerizations with 1,2-propanediol (PG), pinacol (P), 1,3-propanediol (PD), diethylene glycol (DEG), and dipropylene glycol (DPG) gave mostly the D3, D4, and D5 cyclic siloxanes with the minimal desired product. Under these basic conditions, more substituted alcohols (PG, P) might dehydrate via favorable E2 elimination faster than they can cyclize. DEG and DPG are apparently slow to form the less stable eight-membered rings. PD could make a favorable six-membered ring, but its yield is routinely poor versus hexylene glycol. Finally, attempts to use 2,5-dimethyl-2,5-hexanediol (OG) were unsuccessful because it quickly collected in the distillation apparatus upon heating.

Depolymerization of Commercial Siloxane Polymers. After confirming the facility with which these reactions proceeded with hexylene glycol, we tested the procedure on different commercial sources of polysiloxanes with varying compositions and complexities (Table 4). The overall percent yield shown is an estimation, assuming the product is 100% linear PDMS. In reality, these items contain different types of polysiloxanes, degrees of crosslinking, and additives, substantially reducing the composition of linear PDMS. Thus, we find the overall yields (38−71%) to be acceptable. For the massage ball, the first distillation gave pure M2HG. For the heating fluid, the second distillation gave pure M2HG. For the baking cups, both distillations gave pure M2HG. In all five cases, the second distillation gave M2HG in at least 91% purity. Note that the silicone caulk releases acetic acid during curing, yet the reaction still proceeded with 1 mol % of NaOH as the catalyst. In all cases, the distillates contained only products possessing the [$OSiMe_2$] moiety, indicating that the procedure selectively depolymerizes PDMS from a mixture of starting materials.

Repolymerization of M2HG. We then targeted the repolymerization of M2HG to complete the chemical recycling loop. We focused on cationic ring-opening polymerization (CROP) of M2HG and used three different methods:

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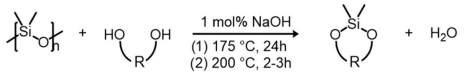
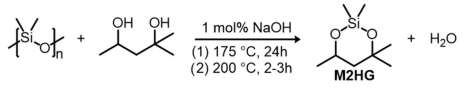
Table 3. Depolymerization of PDMS with Different Diols[a]

Entry	Diol	1st distillate			2nd distillate			Overall yield (%)
		yield (g)	%product[b]	%D3, D4, D5[b]	yield (g)	%product[b]	%D3, D4, D5[b]	
								
1	ethylene glycol	0.0	0	0, 0, 0	22.90	77	6, 13, 2	25
2	1,2-propanediol	0.0	0	0, 0, 0	10.77	9	22, 55, 6	11
3	pinacol	1.22	0	26, 70, 4	38.04	<4	16, 53, 11	45
4	1,3-propanediol	0.0	0	0, 0, 0	15.66	2	16, 63, 10	17
5	1,4-butanediol	9.82	20	48, 30, 2	63.63	76	3, 18, 2	77
6	2,5-dimethyl-2,5-hexanediol	0.0	0	0, 0, 0	0.0	0	0, 0, 0	0
7	diethylene glycol	<1.0	2	32, 62, 4	0.0	0	0, 0, 0	0
8	dipropylene glycol	0.69	1	31, 53, 13	10.10	9	33, 53, 4	11

[a]Starting mass of PDMS was ∼58 g for reactions with ethylene glycol, ∼53 g for reactions with 1,2-propanediol or 1,3-propanediol, ∼48 g for reactions with 1,4-butanediol or diethylene glycol, and ∼37 g for reactions with pinacol, 2,5-dimethyl-2,5-hexanediol, or dipropylene glycol. [b]Determined by quantitative ^{29}Si NMR.

Table 4. Depolymerization of Commercial Products Containing Polysiloxanes[a]

Entry	Polysiloxane source	1st distillate			2nd distillate			M2HG yield[b]	
		yield (g)	%M2HG[b]	%D3, D4, D5[b]	yield (g)	%M2HG[b]	% D3, D4, D5[b]	Overall (%)	Pure[c] (%)
									
1	heating fluid	26.55	80	5, 12, 1	37.93	100	0, 0, 0	71	46
2	grease	23.82	88	4, 7, 0	37.81	96	3, 1, 0	67	43
3	caulk	16.37	78	5, 15, 2	31.25	91	0, 8, 1	48	-
4	baking cups	11.80	100	0, 0, 0	21.30	100	0, 0, 0	38	38
5	massage ball	12.27	100	0, 0, 0	40.55	92	3, 3, 3	57	14

[a]Starting mass of polysiloxane material was ∼36 to 38 g. [b]Determined by quantitative ^{29}Si NMR. [c]Pure yields were taken from distillates with 100% M2HG product.

homopolymerization, terpolymerization, and emulsion polymerization. The results are summarized in Table 5.

Homopolymerizations were conducted using catalytic *p*-toluenesulfonic acid (*p*-TSA) or trifluoromethanesulfonic acid (TfOH) with both ^{1}H NMR pure M2HG (Table 5, entries 1 and 3) and M2HG dried with calcium hydride and purified via distillation (Table 5, entries 2 and 4). With ^{1}H NMR pure M2HG, these polymerizations resulted in brown, low-molecular-weight polymers having ^{1}H NMR spectra consistent with loss of the hexylene glycol moiety and having the PDMS structure. These polymers show moderate thermal stability even at low molecular weight; T_{d5} = 269 °C with *p*-TSA and 211 °C with TfOH. With CaH_2-dried M2HG, the *p*-TSA-catalyzed polymerization resulted in a brown, high-molecular-weight polymer (M_n = 39,900) having ^{1}H NMR spectra consistent with PDMS (see Figure S59) and excellent thermal stability (T_{50} > 600 °C). TfOH catalysis with CaH_2-dried M2HG once again resulted in a brown, low-molecular-weight material, at several polymerization temperatures. By ^{1}H NMR, the material appears to be polysilicon acetals (see Figure S61). Further optimization is therefore necessary to produce high-molecular-weight polysilicon acetals.

Hada *et al.* recently reported terpolymerizations of 1,3-dioxasilacycloalkanes with vinyl ethers and aldehydes using Lewis acid catalysts at low temperatures.[46] We first applied their method to ^{1}H NMR pure M2HG using ethyl vinyl ether and pivaldehyde comonomers in the presence of gallium(III) chloride as catalyst (Table 5, entry 5) and obtained a colorless, low-molecular-weight terpolymer that also contains PDMS repeat units according to ^{1}H NMR (see Figure S62). After drying M2HG, ethyl vinyl ether, and pivaldehyde with CaH_2 and isolating the starting reagents through distillation, the terpolymerization resulted in the formation of somewhat higher-molecular-weight material (M_n = 5000). Although the molecular weight improved, unreacted M2HG was present after polymerization, suggesting further optimization is still needed.

Kozakiewicz *et al.* recently developed a method to polymerize the D4 cyclic siloxane to PDMS under emulsion conditions using *p*-dodecylbenzenesulfonic acid (*p*-DBSA) as an emulsifier and catalyst.[47] Adapting this method for use with M2HG, we synthesized a colorless mixture of polymers with a bimodal distribution (Table 5, entry 7) containing both high-molecular-weight (M_n = 49,000) and oligomeric (M_n < 1000)

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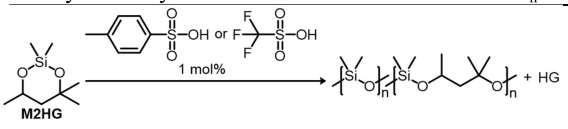
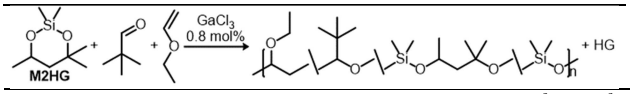
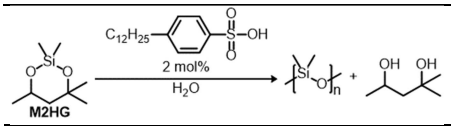
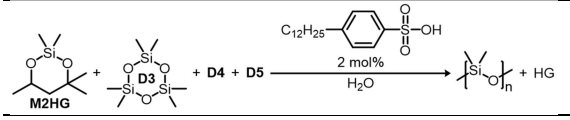
Table 5. Cationic Ring-Opening Polymerization of M2HG

Entry	Catalyst	Conditions	Yield	M_n	$Đ$
					
1	*p*-TSA	(1) 60 °C, 24h, N_2 (2) 70 °C, 24h, N_2 (3) 80 °C, 24h, N_2	67%	1,500[a]	1.2[a]
2[b]	*p*-TSA	(1) 80 °C, 24h, N_2 (2) 90 °C, 24h, N_2 (3) 100 °C, 48h, N_2	47%	39,900[c]	2.1[c]
3	TfOH, PhMe	(1) 70 °C, 24h, N_2 (2) 80 °C, 24h, N_2	39%	1,400[a]	1.2[a]
4[b]	TfOH	(1) 70 °C, 24h, N_2 (2) 80 °C, 24h, N_2 (3) 90 °C, 24h, N_2 (4) 100 °C, 48h, N_2	43%	1,100[c]	1.4[c]
					
5	$GaCl_3$	-78°C, 22h, N_2	46%	1,200[c]	1.9[c]
6[b]	$GaCl_3$	-78°C, 22h, N_2	64%	5,000[c]	1.4[c]
					
7	*p*-DBSA	(1) 88 °C, 4h, N_2 (2) 88 °C, 4h, vac	21%	49,000[c]	1.6[c]
					
8	*p*-DBSA	(1) 88 °C, 4h, N_2 (2) 88 °C, 4h, vac	42%	39,500[c]	2.2[c]

[a]Determined by HFIP GPC. [b]M2HG dried over calcium hydride and isolated by distillation prior to polymerization. [c]Determined by THF GPC.

species with a T_{50} of 500 °C, which matches the reported T_{50} of PDMS.[48] According to ^{1}H NMR, the polymer contains mostly silyl methyl groups with minimal remnant diol, indicating we synthesized the coveted PDMS and closed the chemical recycling loop. We also tested this method using a mixed feed of M2HG, D3, D4, and D5 (from Table 2, entry 4, first distillate) and achieved similar results (Table 5, entry 8). We recovered 3.2 g (60%) of the hexylene glycol liberated upon hydrolysis of M2HG during polymerization. Although further optimization is needed for these polymerization methods, the initial results indicate our overall strategy shows promise for PDMS chemical recycling.

CONCLUSIONS

The relative stabilities of various silicon acetal species formed from monoalcohols and diols were compared computationally and experimentally. Cyclic M2EG and M2HG were computationally more favorable than acyclic $SiMe_2(OMe)_2$ because of the favorable entropy term in the ring-closing step (two molecules to three). $SiMe_2(OMe)_2$ reacts with hexylene glycol to form M2HG via an acid-catalyzed exchange reaction. PDMS depolymerization with various alcohols was modeled using the D4 cyclic siloxane. Computationally, PDMS depolymerization with monoalcohols, such as methanol, is never favorable. However, PDMS depolymerization with diols can be exergonic due to the favorable entropy of chelation; the thermoneutral ($\Delta G = 0$) temperatures are −107, −38, and 0 °C in water, DMF, or vacuum, respectively. Hence PDMS depolymerization with hexylene glycol is expected to be exergonic above 0 °C in any medium. We developed a simple and selective depolymerization process for poly(dimethylsiloxane) using diols and catalytic sodium hydroxide based on these results. Hexylene glycol is the most efficient diol because of its proclivity for cyclization, largely due to the *gem*-dimethyl effect. The method can be used with a variety of commercial silicone products and shows excellent selectivity for poly(dimethylsiloxane) in complex mixtures. This method is superior to established protocols in the following ways: no elevated pressures or excess solvents are required, and all reagents are relatively inexpensive and widely available. The downfalls of this method include the necessarily elevated temperatures for isolation and the somewhat challenging repolymerization of M2HG. Attempts to form polysilicon acetals and copolymers resulted in oligomer formation, indicating more optimization is needed. The product M2HG was successfully repolymerized to PDMS by both cationic ring-opening polymerization and cationic emulsion polymerization—albeit with modest yields. Another challenge of PDMS depolymerization and repolymerization facilitated by hexylene glycol is its use in stoichiometric quantities. However, we have demonstrated that hexylene glycol can be recovered following cationic emulsion polymerization. Thus, this process appears industrially feasible and may provide a new route to reduce waste and close the recycling loop on poly(dimethylsiloxane) materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c02554.

Synthetic details and characterization data, including ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, GPC data, TGA data, DSC data, and Spartan computational data (PDF)

AUTHOR INFORMATION

Corresponding Author

Stephen A. Miller − *The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States;* orcid.org/0000-0001-7005-7537; Email: miller@chem.ufl.edu

Authors

Jordan L. Torgunrud − *The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States;* orcid.org/0000-0002-9221-1694

Aracelee M. Reverón Pérez − *The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States;* orcid.org/0000-0002-1031-4228

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Emily B. Spitzberg − *The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.2c02554

Author Contributions

J.L.T. and A.M.R.P. contributed equally.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

HG, hexylene glycol (2-methyl-2,4-pentanediol); EG, ethylene glycol; D3, hexamethylcyclotrisiloxane; D4, octamethylcyclotetrasiloxane; D5, decamethylcyclopentasiloxane; M2HG, 2,2,4,4,6-pentamethyl-1,3-dioxa-2-silacyclohexane; M2EG, 2,2-dimethyl-1,3-dioxa-2-silacyclopentane; M2PG, 2,2,4-trimethyl-1,3-dioxa-2-silacyclopentane; M2P, 2,2,4,4,5,5-hexamethyl-1,3-dioxa-2-silacyclopentane; M2PD, 2,2-dimethyl-1,3-dioxa-2-silacyclohexane; M2BD, 2,2-dimethyl-1,3-dioxa-2-silacycloheptane; M2OG, 2,2,4,4,7,7-hexamethyl-1,3-dioxa-2-silacycloheptane; M2DEG, 2,2-dimethyl-1,3,6-trioxa-2-silacyclooctane; M2DPG, 2,2,4,8-tetramethyl-1,3,6-trioxa-2-silacyclooctane; *p*-TSA, *p*-toluenesulfonic acid; TfOH, trifluoromethanesulfonic acid or triflic acid; *p*-DBSA, *p*-dodecylbenzenesulfonic acid; TBAF, tetrabutylammonium fluoride

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