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## Selective oxidative devulcanization of hydrosilylation-cured silicone elastomers: Enhanced circularity

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Table S1 Shore OO Hardness of cured elastomers.

	Shore OO Hardness
Homemade	74
GE Silicones	66
Homemade	29
Sylgard 184	80
SilPlus 40 HT	40
	Homemade GE Silicones Homemade Sylgard 184 SilPlus 40 HT

Table S2 Experimental of degradation comparisons between hydrosilylated and RTV elastomers in different solvents.<sup>a</sup>

Elastomer (g)	Br2 (volume of 1M solution) [in solvent]	Time for degradation (no solids remain)	% yield recovered by weight
Hydrosilylation cure	(homemade)		
1.0424	5 mL [CDCl₃/DCM]	90 min	86%
0.4575	2.5 mL [H <sub>2</sub> O]	No reaction	N/A
1.1076	5 mL [IPA]	No reaction	N/A
HTV Elastomer			
0.5065	5 mL [CDCl₃/DCM]	150 min	88%
0.4908	2.5 mL [H <sub>2</sub> O]	No reaction	N/A
0.4374	2.5 mL [IPA]	No reaction	N/A
RTV cured elastome	er (homemade)		
0.7910	5 mL [CDCl₃/DCM]	24 h	87%
0.4439	2.5 mL [H <sub>2</sub> O]	No reaction	N/A
0.3375	2.5 mL [IPA]	No reaction	N/A

<sup>a</sup> This includes data presented in Table 1 of the manuscript.

1 M Br <sub>2</sub>	Trial 2	Average				
Homemade RTV	36	37	36	35	32	35.2
GE Silicones RTV	18ª	18	18	18	18	18
Homemade Pt-cure	0.35	0.4	0.33	0.37	0.35	0.36
Sylgard-184	0.5	0.53	0.57	0.5	0.53	0.526
0.22 M Br <sub>2</sub>						
Homemade RTV	48	48	48	48		48
GE Silicones RTV	18	16	18	18		17.5
Homemade Pt-cure	0.42	0.38	0.42	0.37		0.3975
Sylgard-184	0.66	0.66	0.66	0.66		0.66

<sup>a</sup> All occurred overnight, at least 18 hours.

Table S4 GPC res	ults of degraded	l hvdrosilvlated	and RTV	cured silicones
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	Hydrosilylated elastomer							RTV elastomer <sup>b</sup>			
	A (Vi-PDMS- Vi + Pt)	B (Vi-PDMS- Vi + PDMS-		A + B +Br			3r RTV (S32 + RTV +			Br <sub>2</sub> (24	
			70 min			90 min		MTMS)	hou	ırs)	
		H)									
			High <sup>a</sup>	$\rightarrow$	Low	High	Low		High	Low	
			63%	19%	18%	61%	39%		19%	81%	
Mn	17548	12464	19182	1887	640	8396	571	32171	1600	627	
Mw	31522	30290	38628	2178	659	15521	586	69283	1766	659	
Ðм	1.80	2.43	2.01	1.15	1.03	1.85	1.03	2.15	1.10	1.05	

<sup>a</sup> The products had a trimodal molar mass distribution, the relative abundance (%) is shown for each component.<sup>b</sup> Using tin catalysis.

Table S5 Shore OO comparison of Pt-cured elastomers and RTV elastomers made from bromine degraded Pt-cured elastomers.

Materials	Initial Shore Hardness OO	Curing time
Pt-cured (original preparation)	29	Overnight
RTV (MTMS + HO-PDMS-OH, original preparation)	74	24 h
Recovered silicone oils after bromination of Pt-cure	d elastomers, cured using RT	V conditions
RTV (Pt-cured + MTMS)	18	1 week

Table S6 Experimental set-up for  $\mathsf{Br}_2$  reaction with  $\boldsymbol{2},$  to study radical behavior.

Molar ratio (2:Br <sub>2</sub> )	Conditions	Model Compound 2	1M Br <sub>2</sub> in CDCl <sub>3</sub>	NMR
	Dark	101.2 mg	25.5 μL	Figure S6, Figure S7
(1:0.1)	UV ~254 nm	104.3 mg	26.3 μL	Figure S6, Figure S8
	Light	101.7 mg	25.6 μL	Figure S6, Figure S9

Table S7 Quantities for kinetics study.

Molar ratio (2:Br <sub>2</sub> )	Model Compound <b>2</b>	$1M Br_2$ in $CDCl_3$	NMR
(1:1)	65.1 mg	164 μL	Figure S15
(1:0.5)	45.9 mg	57.8 μL	Figure S16
(1:0.25)	63.9 mg	45.2 μL	Figure S17
(1:0.1)	38.4 mg	9.7 μL	Figure S18
Molar ratio ( <b>3</b> :Br <sub>2</sub> )	Model Compound <b>3</b>	$1M Br_2$ in $CDCl_3$	
(1:1)	82.3 mg	265 μL	Figure S19
Molar ratio ( <b>1</b> :Br <sub>2</sub> )	Model Compound <b>1</b>	1M Br <sub>2</sub> in CDCl <sub>3</sub>	
(1:1)	40.1 mg	85 μL	Figure S14



S4



Figure S2. ESI scan of A: hydrosilylated (Pt-cured) elastomer reacted with Br<sub>2</sub> after 90 minutes; B: RTV-cured silicone elastomer + Br<sub>2</sub>, after overnight. In both cases the masses are separated by 74 mass units (Me<sub>2</sub>SiO).



Figure S3. Photographs showing evolution of Pt-cured and RTV cured elastomer in Br<sub>2</sub> solution for 70 min. After 24 hours both elastomers would have undergone both decrosslinking and depolymerization to give an oil.



Figure S4. <sup>1</sup>H NMR of the model compounds; 1, 3, and 2 (top to bottom).







В



C Figure S6. Mechanistic study probing radicals: <sup>1</sup>H NMR of **2**: Br<sub>2</sub> (1:0.1), with timepoints a - f (10min - 24h). A: in the dark (aluminum foil-covered vials); B) in UV-light (254nm); C) in ambient (fluorescent/daylight) light on the benchtop.



Figure S7. Higher amplification of  $\mathsf{Br}_2$  study with  ${\bm 2}$  in the dark at 2 timepoints, 2h and 24h.



Figure S8. Higher amplification of  $\mathsf{Br}_2$  study with  ${\bm 2}$  using UV at 2 timepoints, 2h and 24h.



Figure S9. Higher amplification of  $Br_2$  study with **2** in room light, room temperature at 2 timepoints, 2h and 24h.









В

Figure S13. <sup>29</sup>Si NMR of model compounds 1, 3, and 2 (top to bottom), respectively, and Br<sub>2</sub> after A) 24 h and B) 72h (this is the same data as in Figure S11-Figure S10 but is consolidated.





In the reactions of **2** with Br<sub>2</sub>, peaks in the multiplet at 0.5 ppm in the <sup>1</sup>H NMR peaks indicate the loss of alkane bridge between silicon atoms and served as the rate of reaction indicator. The major product was determined from <sup>29</sup>Si NMR to be **4** (Figure 3). <sup>29</sup>Si NMR exhibited a signal ~ 28 ppm, which correlates to halogenated Si, thus Si-Br, since this peak is present in all 3 compounds (**1**, **2**, and **3**), it further signifies the presence of Si-Br in all 3 reactions (Figure S11-Figure S13).







Figure S17. Kinetics study, <sup>1</sup>H NMR of **2**: Br<sub>2</sub>(1:0.25). Representing timepoints from a - h (10min - 48h).



Figure S18. Kinetics study, <sup>1</sup>H NMR of **2**: Br<sub>2</sub> (1:0.1). Representing timepoints from a - h (10min - 48h).



Figure S19 Kinetics study, <sup>1</sup>H NMR of **3**: Br<sub>2</sub> (1:1). Representing timepoints from a - g (10min – 24h). Conversion is reported as changes in intensity and location of the CH<sub>2</sub>Si signals. The signals between 3 and 4 ppm are ascribed to brominated compounds such as **9**.

Though similar degrees of product degradation had been achieved at 72 h, the evolution of the reaction for compounds **1** and **3** was different. For compound **3**, the silicone T group's steric hindrance forces the backside attack from bromine on pentamethyldisiloxane, hence producing more brominated pentamethyldisiloxane **4** compared to compound **2**. Compound **1** led to much less **4** because of both reduced steric demand and the mechanistic availability of arylsilanes cleavage. Brominated alkyl groups are responsible for the signals between 3 and 4 ppm, e.g., **9**, **10**, **11**.



A mass spectrometric study of the early stages of bromine-induced cleavage of **2** (earlier than the <sup>29</sup>Si NMR seen in Figure S13, by which time Si-C scission was complete). Note: unlike data reported elsewhere, these reactions were not quenched, but instead injected directly into the GC/MS. These experiments permitted the capture of fragments that clearly involve bromination at carbon and prior to elimination. The spectrum from the peak at 9.8 minutes, one of several peaks in the GC trace, is shown below. Possible fragments are provided against the m/z masses found in the spectrum. Method: GC-MS runs were carried out on an Agilent 6890/5973 GC/MS system using an Agilent DB 17HT column, 30m x 0.25 mm ID, 0.15 µm film thickness and the following temperature program: Ti = 40 °C, ramp@15 °C/min to 300 °C, hold for 8 min.

Signals derived from 10 at m/z 390.92; for 11 at 313.01; and for 12 and 13 at 331.93 and 474.09, respectively.



Figure S20. Small peak (~1%) at 9.8 minutes in GC/MS spectrum of **2** 15 minutes after addition of bromine. Note: this was the only peak in which brominated compounds were detected. If the samples were quenched as per the normal described protocol, no peaks in the GC/MS showed brominated constituents.

