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# Carbosiloxane Bottlebrush Networks for Enhanced Performance and Recyclability

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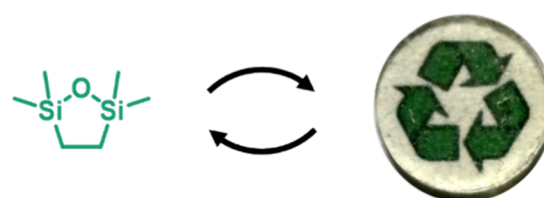
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**ABSTRACT:** Silicone bottlebrush copolymers and networks derived from cyclic carbosiloxanes are reported and shown to have enhanced properties and recyclability compared with traditional dimethylsiloxane-based materials. The preparation of these materials is enabled by the synthesis of well-defined heterotelechelic macromonomers with Si–H and norbornene chain ends via anionic ring-opening polymerization of the hybrid carbosiloxane monomer 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane. These novel heterotelechelic  $\alpha$ -Si–H/ $\omega$ -norbornene macromonomers undergo efficient ring-opening metathesis copolymerization to yield functional bottlebrush polymers with accurate control over molecular weight and functional-group density. Si–H groups retained at the ends of side-chains after ring-opening metathesis copolymerization allow for the preparation of supersoft networks via hydrosilylation with cross-linkers such as tetrakis[dimethyl(vinyl)silyl]orthosilicate. In contrast to traditional PDMS systems, the incorporation of poly(carbosiloxane)

side chains allows the resulting networks to be recycled back to the original monomer (>85% recovery) via depolymerization at elevated temperatures (250 °C) in the presence of base catalysts (potassium hydroxide and tetramethylammonium hydroxide). The recovered monomer was successfully repolymerized through anionic ring-opening polymerization with no decrease in structural fidelity or activity. In summary, this combination of unique (macro)monomer design and bottlebrush architecture creates new opportunities in sustainable practices by offering a robust, recyclable alternative to commercial silicone-based materials.

## Carbosiloxane Bottlebrush Networks



- Recyclable to Original Monomer
- Tunable, Super-Soft Modulus
- More Robust than PDMS

## INTRODUCTION

Polysiloxanes, commonly known as silicones, are ubiquitous in daily life, serving as key components in numerous commercial products.<sup>1,2</sup> The most common silicone, polydimethylsiloxane (PDMS), is readily incorporated into cross-linked networks using commercially available kits such as SYLGARD 184, which are based on linear building blocks and robust catalysts.<sup>3–5</sup> A powerful and defining feature of this and other silicone-based materials is the inorganic polymer backbone containing Si–O bonds, which creates unique physical properties such as a low glass-transition temperature ( $T_g$ ), high optical transparency, low surface tension, and good biocompatibility.<sup>6–9</sup> Consequently, silicones are used in a broad range of applications such as coatings,<sup>8,10</sup> photolithography,<sup>6–16</sup> microfluidics,<sup>17–19</sup> electronics,<sup>20–24</sup> and medical devices.<sup>25–27</sup>

One strategy to broaden the potential applicability of silicones is identifying new and/or improved properties by varying macromolecular architecture.<sup>28–32</sup> In particular, bottlebrush polymers have received significant attention due to their unique network properties that arise from a high density of polymeric side chains attached to backbone repeat units while also remaining synthetically accessible.<sup>33,34</sup> For example, the presence of such side chains suppresses entanglements and results in supersoft properties ( $G' < 100$  kPa), even in the absence of solvent.<sup>28,29,35,36</sup> Because of its ubiquity, PDMS is a

common choice for the side-chain chemistry of bottlebrushes; we and others have recently demonstrated the promise of these systems<sup>30,37–40</sup> in a variety of applications ranging from high-sensitivity capacitive sensors<sup>38</sup> to biological tissue mimics<sup>41,42</sup> and efficient dielectric actuators.<sup>43,44</sup>

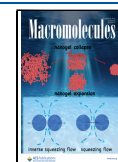
This widespread and growing prevalence of silicone-based materials contrasts with the more limited literature on silicone recycling and/or upcycling.<sup>45–47</sup> Although PDMS itself may be depolymerized with either base catalysis in the presence of heat or fluoride catalysis, this process produces a complex mixture of cyclic siloxane units (commonly referred to as  $D_4$ ,  $D_5$ , and  $D_6$ ) which are unsuitable for the anionic ring-opening polymerization of well-defined PDMS due to their low ring strains (Figure 1, top).<sup>48–53</sup> As a result, the development of novel monomers and synthesis strategies that allow for recycling or upcycling of siloxane-containing network materials, coupled with control over macromolecular architecture and properties,

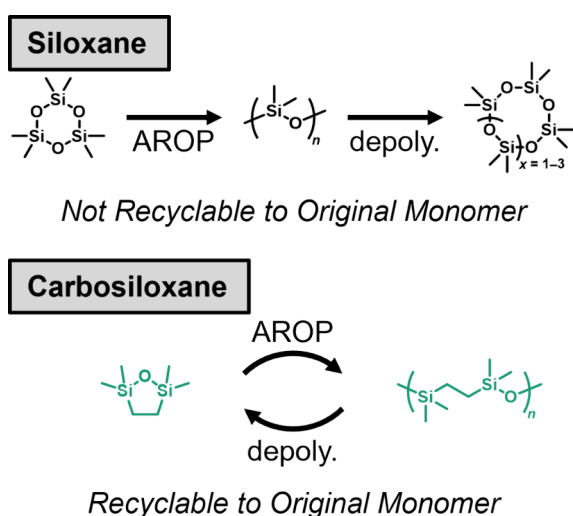
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**Figure 1.** Comparison of the recycling potential of the siloxane PDMS (top) and the cyclic carbosiloxane PTMOSC (bottom). PTMOSC is recyclable to the original monomer, while the depolymerization of PDMS results in a mixture of less reactive cyclic oligomers ( $D_4$ ,  $D_5$ , and  $D_6$ ) that are not suitable for anionic ring-opening polymerization (AROP).

represents a significant opportunity for creating sustainable silicone-based systems.

To investigate alternatives to PDMS, researchers have focused on the polymer derived from a known but under-explored cyclic carbosiloxane: poly(2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane) (PTMOSC).<sup>54</sup> PTMOSC was first reported in the 1960s by Merker et al. in a series of papers<sup>55–57</sup> with the polymer being synthesized through a hydrosilylation reaction between divinyltetramethyldisiloxane and tetramethyldisiloxane. Significantly, Merker was able to show that this parent polymer could be depolymerized under high temperatures with a base catalyst to recover the five-membered ring monomer, 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (TMOSC).<sup>55,57</sup> Subsequent work by various groups demonstrated that this monomer can be subjected to different ring-opening polymerization methods (acid-catalyzed, base-catalyzed, anionic, and cationic) to yield PTMOSC (Figure 1, bottom).<sup>58–62</sup> Like PDMS, this alternative carbosiloxane polymer exhibits a low glass-transition temperature ( $T_g$ ), high optical transparency, low surface tension, and

good biocompatibility.<sup>63–65</sup> In a seminal 2022 paper, Bian and McCarthy prepared networks based on linear PTMOSC and demonstrated that these cross-linked materials are efficiently recyclable to the cyclic carbosiloxane monomer in high yield.<sup>54</sup>

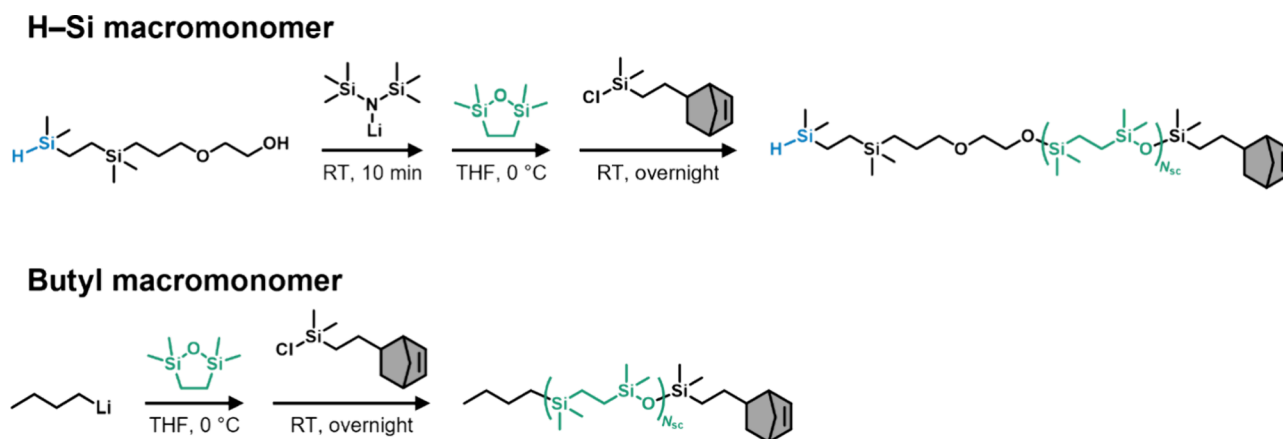
Here, inspired by the recyclability of PTMOSC and the unique mechanical properties of bottlebrush networks, we report a facile synthetic method for preparing PTMOSC bottlebrush networks. As expected, these tailorable materials were supersoft with plateau moduli ranging from 3 to 40 kPa, but unlike PDMS analogues, PTMOSC networks are mechanically robust and easily recycled back to monomer in high yield (>85%). Recycled TMOSC is readily repolymerized into well-defined, linear PTMOSC building blocks. In summary, we explore herein the significant potential of carbosiloxane-based PTMOSC derivatives as easily recyclable alternatives to PDMS for use in architecturally complex materials such as bottlebrush networks.

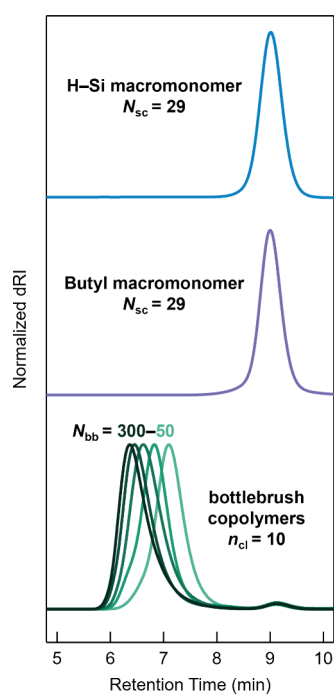
## RESULTS AND DISCUSSION

**Network Design and Synthesis.** PTMOSC bottlebrush networks were fabricated via a stepwise synthesis strategy that allows for precise control over and rigorous characterization of key bottlebrush parameters. Well-defined, linear PTMOSC macromonomers were synthesized by anionic ring-opening polymerization of the cyclic carbosiloxane initiated from either *n*-butyl lithium or a novel silyl hydride (Si–H) initiator (Scheme 1). Both polymerizations were terminated with a norbornene chlorosilane to yield heterotelechelic macromonomers compatible with ring-opening metathesis polymerization, adapting a previously published method.<sup>37</sup> These macromonomers were characterized via nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectroscopy and size-exclusion chromatography (SEC) to determine their degree of polymerization ( $N_{sc}$ ) and dispersity ( $\mathcal{D}$ ) (Figure 2) with the macromonomer  $N_{sc}$  being accurately controlled by varying the ratio of monomer to initiator. <sup>1</sup>H NMR and SEC confirmed that both heterotelechelic and monofunctional macromonomers were prepared with  $N_{sc} = 8, 16,$  and  $29$  repeating units and  $\mathcal{D} < 1.2$  (Figures S1–S8).

Ring-opening metathesis copolymerization of the heterotelechelic and monofunctional macromonomers yielded bottlebrush copolymers with controlled backbone degrees of polymerization ( $N_{bb}$ ) and numbers of Si–H cross-linking sites ( $n_{cb}$ , i.e., the number of Si–H side chains per bottlebrush

**Scheme 1.** Synthesis of Heterotelechelic PTMOSC (H–Si Macromonomer) (Top) and Monofunctional PTMOSC (Butyl Macromonomer) (Bottom) Macromonomers via Anionic Ring-Opening Polymerization



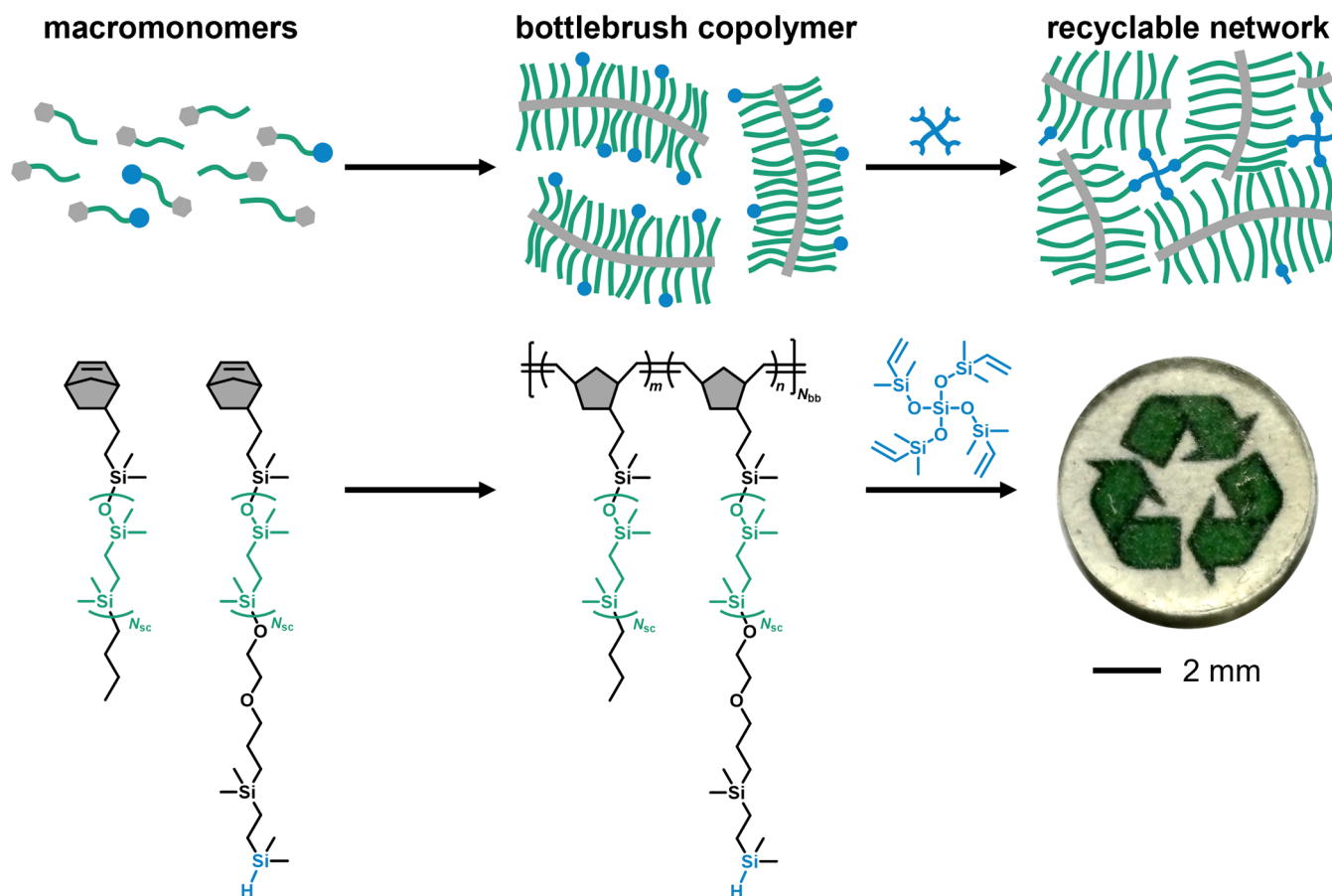


**Figure 2.** Normalized SEC traces of bottlebrush copolymers with varied  $N_{bb}$  and a constant number of cross-linking sites ( $n_{cl} = 10$ ) prepared from macromonomers with  $N_{sc} = 29$ .

molecule, Scheme 2). This allows  $N_{bb}$  to be tuned by simply varying the ratio of macromonomer to Grubbs catalyst ( $N_{bb} = 50\text{--}300$ ), while  $n_{cl}$  was modulated by varying the molar ratio of the two macromonomers in the starting bottlebrush reaction ( $n_{cl} = 10\text{--}30$ ).  $^1\text{H}$  NMR and SEC (Figures 2 and S9–S13) were used to determine  $N_{bb}$  and  $\mathcal{D}$ , with  $n_{cl}$  being determined by integrating the distinctive Si–H and butyl end groups observed at 3.8 and 0.9 ppm, respectively, in the  $^1\text{H}$  NMR spectrum (Figures S14 and S15). It should be noted that the functional bottlebrush polymers were prepared on multigram scales and are stable to storage under ambient conditions for extended periods of time.

From these bottlebrush copolymers, networks were prepared by a simple hydrosilylation reaction. Si–H moieties attached to the PTMOSC bottlebrush side chains were reacted with commercially available tetrakis[dimethyl(vinyl)silyl]orthosilicate (a 4-arm vinyl cross-linker) in the presence of Karstedt's catalyst with dimethyl maleate added as an inhibitor to prevent immediate curing of the material. This allows the formulation to be mixed well and degassed prior to curing.<sup>66</sup> To establish proper curing conditions for network formation, a bottlebrush network was cured in situ on an oscillatory rheometer. A mixture of functionalized bottlebrush, tetrafunctional cross-linker, Karstedt's catalyst, and dimethyl maleate was loaded onto the rheometer at room temperature. As expected, the mixture was a flowable liquid, as evidenced by the storage modulus being less than the loss modulus ( $G' < G''$ ).

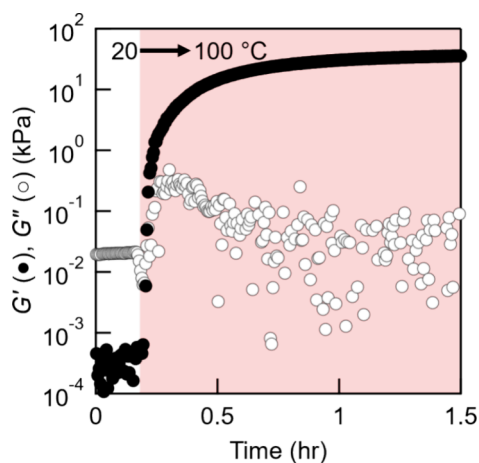
**Scheme 2.** Synthesis of Bottlebrush Copolymers via Ring-Opening Metathesis Copolymerization and Network Formation via Hydrosilylation (Top); Corresponding Chemical Structures of Macromonomers, Bottlebrush Copolymer, 4-Arm Vinyl Crosslinker, and an Optical Image of the Resulting Bottlebrush Network (Bottom)



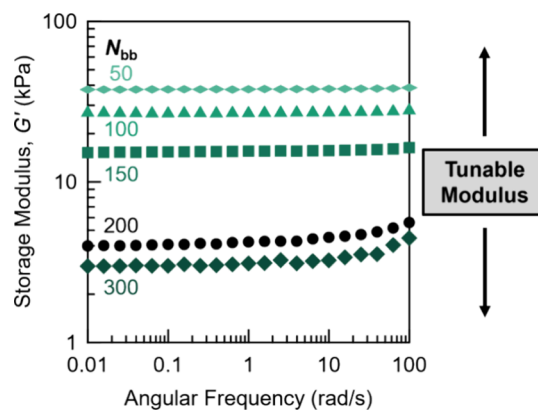
Subsequent rapid heating of the solution to 100 °C yielded an immediate increase in  $G'$  and solidification ( $G' > G''$ ), followed by a plateau in  $G'$  within approximately 1.5 h (Figures 3 and S18). To ensure complete cross-linking, all subsequent networks were cured at 100 °C overnight.

**Mechanical Characterization.** To demonstrate control over the material properties of PTMOSC bottlebrush networks, rheometry experiments were performed on three separate series of samples. Specifically, the low-frequency plateau modulus  $G_x$ —which we define as the measured value of  $G'$  at a frequency of 0.01 rad/s—was found to be tunable between 3 and 40 kPa by varying several key design parameters. Consistent with existing bottlebrush literature,<sup>67,68</sup> increasing the  $N_{bb}$  of PTMOSC bottlebrushes resulted in a decreasing  $G_x$  (Figures 4 and S19). As  $N_{bb}$  increases at constant  $n_{cl}$ ,  $G_x$  decreases due to a reduction in cross-linking density. A similar result was observed by decreasing  $n_{cl}$  (Figure S20) and increasing  $N_{sc}$  (Figure S21). We note that one sample ( $N_{bb} = 200$ ,  $n_{cl} = 10$ ,  $N_{sc} = 29$ )—denoted by the black circles in Figure 4—is present in all three series of networks, serving as a convenient point of comparison. Thus, the bottlebrush network architecture offers three design features for easily tuning the plateau modulus of these materials.

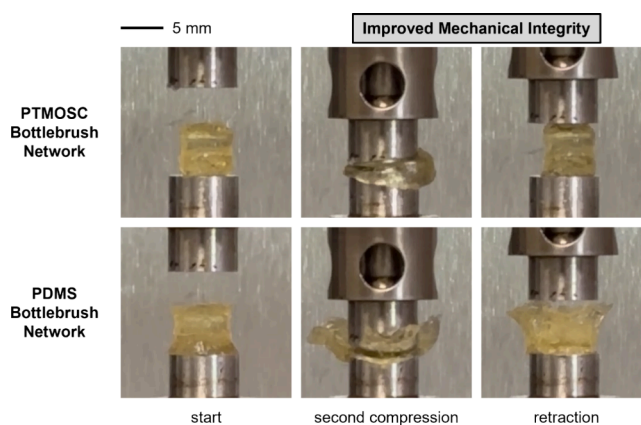
Surprisingly, PTMOSC bottlebrush networks are considerably more mechanically robust compared to PDMS analogues. This effect is immediately evident upon qualitatively handling the samples and was further quantified by cyclic compression testing. For comparison purposes, we prepared similar PDMS bottlebrush networks ( $N_{BB} = 200$ ,  $n_{cl} = 10$ ,  $N_{sc} = 64$ ) using methods described in our prior work (Figures S22–S25).<sup>37</sup> It should be noted that these PDMS bottlebrush networks have the same side-chain molecular weight as the PTMOSC bottlebrush networks ( $N_{bb} = 200$ ,  $n_{cl} = 10$ ,  $N_{sc} = 29$ ). Furthermore, the plateau modulus of the PDMS network ( $G_x = 6$  kPa) is comparable to that of the PTMOSC network ( $G_x = 4$  kPa) (Figure S26). To highlight the improved mechanical properties of PTMOSC-based materials, networks were subjected to three cycles of compression (to a gap of 1 mm between rheometer plates) and retraction. The PTMOSC bottlebrush network remained intact after three compressions with no indication of damage (Figure 5, top). Conversely, the PDMS bottlebrush fractured during the first compression, a distinction that becomes more visually apparent during the second compression



**Figure 3.** Curing profile of a PTMOSC bottlebrush network via hydrosilylation. Oscillatory rheometry indicates complete curing within 1.5 h after heating to 100 °C.



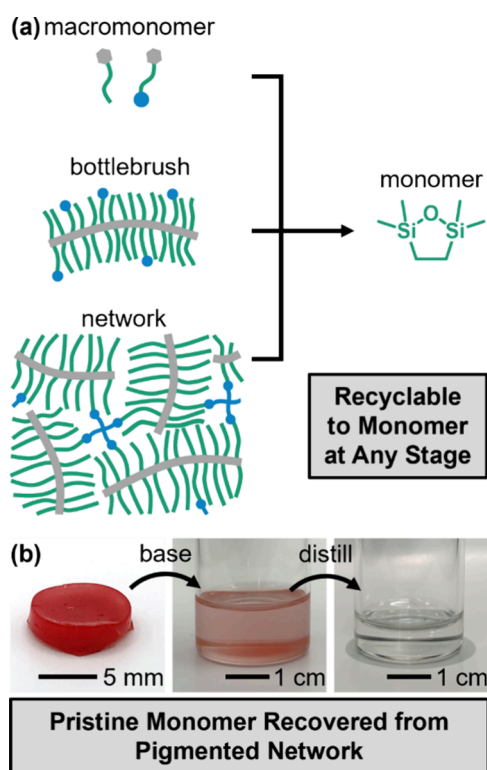
**Figure 4.** Frequency sweeps for a series of PTMOSC bottlebrush networks demonstrating the supersoft and tunable plateau moduli of these materials ( $G_x = 3$ –40 kPa). This series of networks illustrates the effect of changing the backbone degree of polymerization ( $N_{bb} = 50$ –300) while holding the side-chain degree of polymerization ( $N_{sc} = 29$ ) and number of cross-linking sites ( $n_{cl} = 10$ ) constant.



**Figure 5.** Optical images of PTMOSC bottlebrush (top) and PDMS bottlebrush (bottom) networks subjected to cyclic compression tests. The PDMS bottlebrush network fractures upon compression unlike the PTMOSC bottlebrush network, which remains intact after three compression cycles. The slight yellow tint of these materials is due to residual Karstedt's catalyst.

(Figure 5, bottom). Complete recordings of these compression experiments are available as Videos S1 and S2. In a similar manner, we also prepared a traditional network based on linear PDMS building blocks. As expected, unlike the bottlebrush networks, this linear network did not possess supersoft mechanical properties, exhibiting a plateau modulus ( $G_x = 103$  kPa) two orders of magnitude larger than the bottlebrush networks (Figure S26).

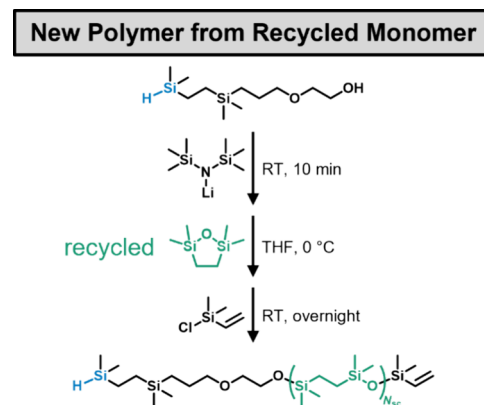
**Recycling and Repolymerization.** As envisaged, all of the PTMOSC materials (macromonomers, bottlebrushes, and networks) display significant potential as recyclable materials (Figure 6a), undergoing triggered depolymerization in the presence of heat and base to yield pure TMOSC monomer in excellent yield. Linear macromonomers and bottlebrushes were observed to cleanly degrade to monomer at 250 °C in the presence of potassium hydroxide (KOH) over 2 h. The absence of solvent in the degradation process is a major advantage and allows the cyclic carbosiloxane monomer to be directly purified by distillation in situ from the reaction mixture. As previously noted by Bian and McCarthy,<sup>54</sup> the degradation of networks



**Figure 6.** (a) All PTMOSC materials (linear macromonomers, bottlebrush copolymers, and networks) can be recycled back to TMOSEC monomer. (b) Optical images of a dyed PTMOSC bottlebrush network (left) and recovered TMOSEC (right) highlight the ability to regenerate pristine monomer even from architecturally complex materials containing additives.

(here, a bottlebrush) presents difficulties due to the limited solubility and diffusion of KOH within a tightly cross-linked structure. To address this challenge, a two-step depolymerization strategy was developed to recycle bottlebrush networks into TMOSEC monomer. In this case, cross-linked networks were initially immersed in a minimal amount of toluene, mixed with KOH and a catalytic amount of tetramethylammonium hydroxide, and heated to 120 °C. After 12 h, complete dissolution of the cross-linked gel was observed with a homogeneous solution being obtained. Analysis of this mixture by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy combined with SEC chromatography and gas chromatography–high-resolution mass spectrometry (GC–HRMS) shows primarily the formation of macrocyclic trimer of the carbosiloxane building block (Figures S27–S30). Following solvent removal via vacuum distillation, the residue was heated at 250 °C for 2 h, successfully depolymerizing the trimer into the desired TMOSEC monomer with isolated yields of >85%. To better illustrate the ability to recover pristine, usable TMOSEC monomer, we prepared a PTMOSC network containing a small amount of cadmium sulfoselenide as a red pigment (Figure 6b). Following the initial degradation of this network to give a red solution of trimers, further degradation and distillation afforded the clear and colorless cyclic carbosiloxane in high yield and purity. The purity of this recycled monomer was highlighted by repolymerization via anionic ring-opening polymerization with the same functional Si–H initiator used previously, but in this case, the linear chain was terminated with vinyl chlorosilane (Scheme 3). Significantly,  $^1\text{H}$  NMR analysis revealed distinct resonances for the Si–H ( $\alpha$ -chain end) and vinyl end groups ( $\omega$ -chain end)

### Scheme 3. Synthesis of Heterotelechelic PTMOSC from Recycled TMOSEC Monomer via Anionic Ring-Opening Polymerization<sup>a</sup>



<sup>a</sup>This polymerization was initiated with the same functional Si–H initiator but terminated with vinyl chlorosilane, showcasing the ability to use recycled TMOSEC to make new telechelic polymers.

at 3.8 and 5.7–6.2 ppm, respectively (Figures S31–S33). By varying the monomer/initiator ratio with the recycled TMOSEC monomer, heterotelechelic PTMOSC linear polymers were again successfully prepared with accurate control over experimental molar-mass dispersity ( $\mathcal{D} < 1.2$ ) and degrees of polymerization (37, 137, and 212) that compare favorably with the theoretical values of 38, 140, and 210 (Figure S34). This ability to recycle even complex cross-linked networks containing additives back to high-purity monomers clearly illustrates the recyclability and sustainability of PTMOSC-based materials.

## CONCLUSIONS

In summary, novel PTMOSC bottlebrush networks were demonstrated with enhanced properties and recyclability compared to traditional PDMS systems. The synthesis of these materials leverages a versatile cyclic carbosiloxane monomer that allows for the controlled synthesis of heterotelechelic and monofunctional macromonomers, which undergo efficient ring-opening metathesis polymerization to yield side-chain-functionalized bottlebrush copolymers. These bottlebrush building blocks containing Si–H groups can be efficiently cross-linked via hydrosilylation with tetrakis[dimethyl(vinyl)silyl]-orthosilicate as a tetrafunctional cross-linker. The plateau modulus of these networks is readily tuned by varying parameters such as  $N_{\text{bb}}$ ,  $n_{\text{cl}}$ , and  $N_{\text{sc}}$  of the starting bottlebrush copolymer with values ranging from 3 to 40 kPa being readily obtained. PTMOSC bottlebrush networks were demonstrated to be considerably more robust than PDMS analogues, showing minimal damage after repeated compression compared to the catastrophic failure and fracture observed with analogous similar PDMS systems. By virtue of using a carbosiloxane monomer, all of the PTMOSC materials—including, notably, the bottlebrush networks—were successfully recycled back to high-purity TMOSEC monomer in excellent yield. This purity was clearly illustrated by subsequent repolymerization to create well-controlled linear polymers via anionic ring-opening polymerization without any further purification. The inherent recyclability and enhanced properties of carbosiloxane-based materials like bottlebrush networks make PTMOSC a promising candidate for increasing the performance and sustainability of advanced silicones.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

Data is available free of charge from the Dryad repository at DOI: 10.5061/dryad.9s4mw6 ms2.

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.4c02147>.

Detailed experimental procedures, characterization ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR, SEC, MALDI, TGA, and DSC), and rheological measurements (PDF)

Compression experiments of PDMS bottlebrush network (MOV)

Compression experiments of PTMOSC bottlebrush network (MOV)

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### Author Contributions

<sup>#</sup>T.E. and P.T.G. contributed equally to this work. T.E., P.T.G., C.M.B., and C.J.H. designed the experiments. All authors wrote the manuscript. T.E. and P.T.G. synthesized the materials. T.E., P.T.G., and M.C. characterized the structure and properties of the materials.

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### Notes

The authors declare no competing financial interest.

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