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Article

A Better Monomer Makes Superior Silicones: Synthesis, Mechanical Properties, and Recyclability of Low Defect Hemisilicone Elastomers

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ABSTRACT: The synthesis, mechanical properties, and recyclability of a novel class of elastomers composed of a hemisilicone polymer, $-(SiMe_2-O-SiMe_2-CH_2CH_2)_n-$ (PM_2E), derived from the anionic ring-opening polymerization of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (*c*-M_2E), are reported. The lower reactivity of the PM_2E backbone toward nucleophiles/bases, compared to conventional silicones, prevents undesired backbiting and chain transfer side reactions, facilitating the formation of low defect hemisilicone elastomers. These elastomers exhibit exceptional mechanical properties, with elongation exceeding 1000% without fracture, as well as minimal hysteresis under 500% strain. The tear resistance is similarly outstanding, as no crack propagation occurs from initial notches during elongation. In terms of recyclability, a base-catalyzed degradation process effectively cleaves the cross-linking junctures, yielding a liquid polymer with >97% efficiency. Subsequent distillation in the presence of KOH, followed by standard redistillation, regenerates the pure monomer in >70% yield based on the elastomer mass. The combination of superior mechanical performance and efficient recyclability highlights hemisilicone elastomers as promising, sustainable, and superior (in some respects) alternatives to conventional silicone elastomers.

INTRODUCTION

Silicones are a fascinating class of synthetic polymers that are widely used in diverse applications including cosmetics, medical devices, sealants, coatings, lubricants, insulators and electronics.[1−5] Their primary structure consists of inorganic siloxane units (−Si−O−Si−) as the polymer backbone, characterized by flexible bond angles, longer bond lengths, and lower rotational energy barriers compared to carbon−carbon bonds in conventional polymers.[6] This unique structure imparts high flexibility and exceptional resistance to environmental factors such as heat, UV irradiation, and various chemicals.[7] As a result, silicones maintain their performance across a wide temperature range and various environments. The versatility of silicones has made them integral to numerous aspects of modern life.

The chemical structure of silicones can be described by use of the common nomenclature (MDTQ),[8] as shown in Figure 1a. The most widely used and well-known silicone materials are based on polydimethylsiloxane (PDMS, shown in Figure 1b) which is composed of D units in the polymer backbone. The preparation of PDMS-based elastomers generally relies on the solvent-free hydrosilylation reaction,[9] in which difunctionalized PDMS as a prepolymer, typically divinyl- or dihydride-terminated PDMS, is mixed with a multifunctionalized (vinyl or hydride) cross-linker in the presence of a parts-per-million level platinum catalyst. Although this straightforward process is widely applied across industries, the resulting silicone elastomers often exhibit considerable brittleness, with a maximum elongation at break (E_{max}) of less than 200%, as shown in Figure 1b. To enhance the mechanical properties, fillers such as fumed silica are commonly incorporated into the elastomer formulation.[10] This strategy, however, compromises transparency, increases production costs, and poses challenges for recycling.

The mechanical properties of silicone elastomers are enhanced by using relatively monodisperse prepolymers (molecular weight dispersity index, $Đ = 1.19$), achieving E_{max} of approximately 350%, as shown in Figure 1b. The PDMS elastomers described in the figure were synthesized through the hydrosilylation of divinyl-terminated PDMS sourced from Gelest, Inc. using tetrakis(dimethylsiloxy)silane M_4^HQ (details provided in the Supporting Information). This observation highlights that a key factor contributing to the poor mechanical performance of silicone elastomers is the presence of undesired derivatives, such as cyclic oligomers, overly long or short

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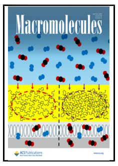

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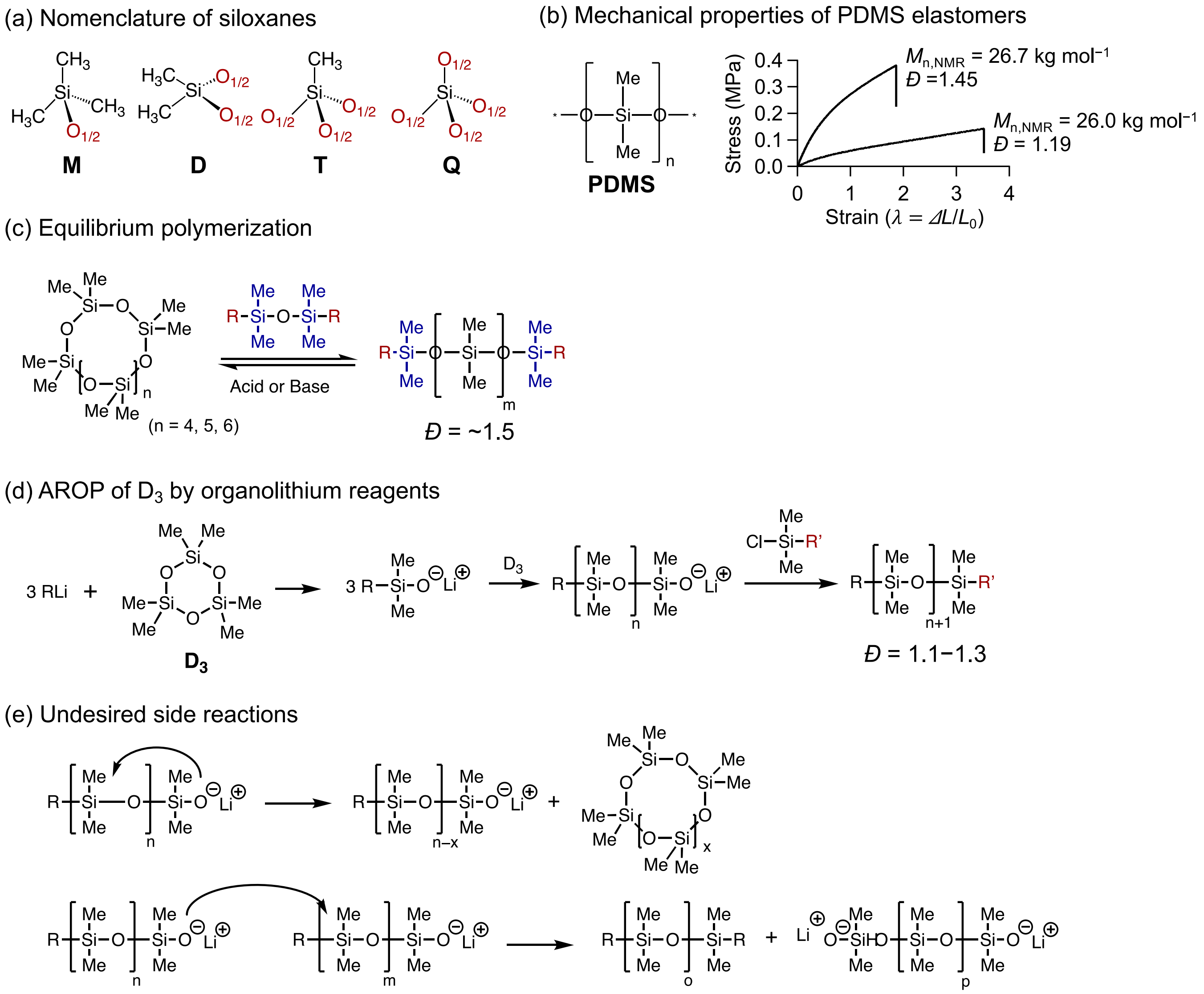


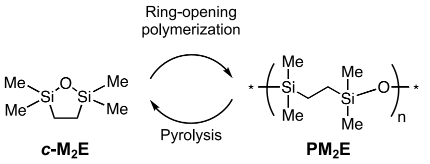
Figure 1. (a) Nomenclature of siloxanes. (b) Chemical structures and mechanical properties of polydimethylsiloxane (PDMS) elastomers prepared using divinyl-terminated PDMS with different molecular weight distributions sourced from Gelest Inc. (c) Chemical scheme of equilibrium polymerization of cyclic siloxanes, (d) AROP of D_3 by organolithium reagents, and (e) undesired side reactions during those polymerization processes.

chains, and monofunctionalized chains in the prepolymer, which introduce heterogeneity into the network structure.

PDMS prepolymers are typically synthesized via acid- or base-catalyzed equilibrium polymerization of cyclic siloxanes (D_4, D_5, D_6), a process that produces 13−15% cyclic oligomers and results in broad molecular weight distributions (Figure 1c).[11] Monodisperse PDMS, by contrast, can be synthesized via anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) using organolithium reagents (Figure 1d).[12,13] In this approach, 3 equiv of an organolithium reagent (RLi) react with D_3 to generate lithium silanolate species (3 RMe_2SiOLi), which then propagate chain growth through sequential additions of D_3. The polymerization is typically terminated using chlorosilane chemistry to introduce the desired functional end groups.

Although AROP yields relatively monodisperse PDMS, the D-based backbone remains reactive toward lithium silanolate at the chain ends, potentially leading to undesired side reactions, including backbiting and chain transfer, during polymerization (Figure 1e).[14] Due to the intrinsic instability of the D-based backbone (every silicon is bonded to two oxygens), complete removal of the formation of the undesired chain structures in PDMS products may be practically unattainable.

Kantor reported that the reactivity of hexamethyldisiloxane (MM) with tetramethylammonium hydroxide is significantly lower than that of D-containing siloxanes.[15] Frye studied the reactivity of siloxanes with organolithium reagents and found similar trends to Kantor's observations.[12] These studies suggest that M-based silicones with main chains containing silicon bonded to only one oxygen could mitigate side reactions, resulting in more well-controlled polymer structure. Piccoli et al. developed a siloxane polymer with an M-based backbone, polymerized from the highly strained five-membered ring monomer 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (c-M_2E), as shown in eq 1.[16] This monomer undergoes AROP initiated by lithium silanolates, producing PM_2E with a relatively narrow molecular weight dispersity.[17,18] Despite the potential of PM_2E as an alternative to PDMS, this polymer has been overshadowed by the more extensively researched PDMS. There are several reports concerning this polymer's properties,



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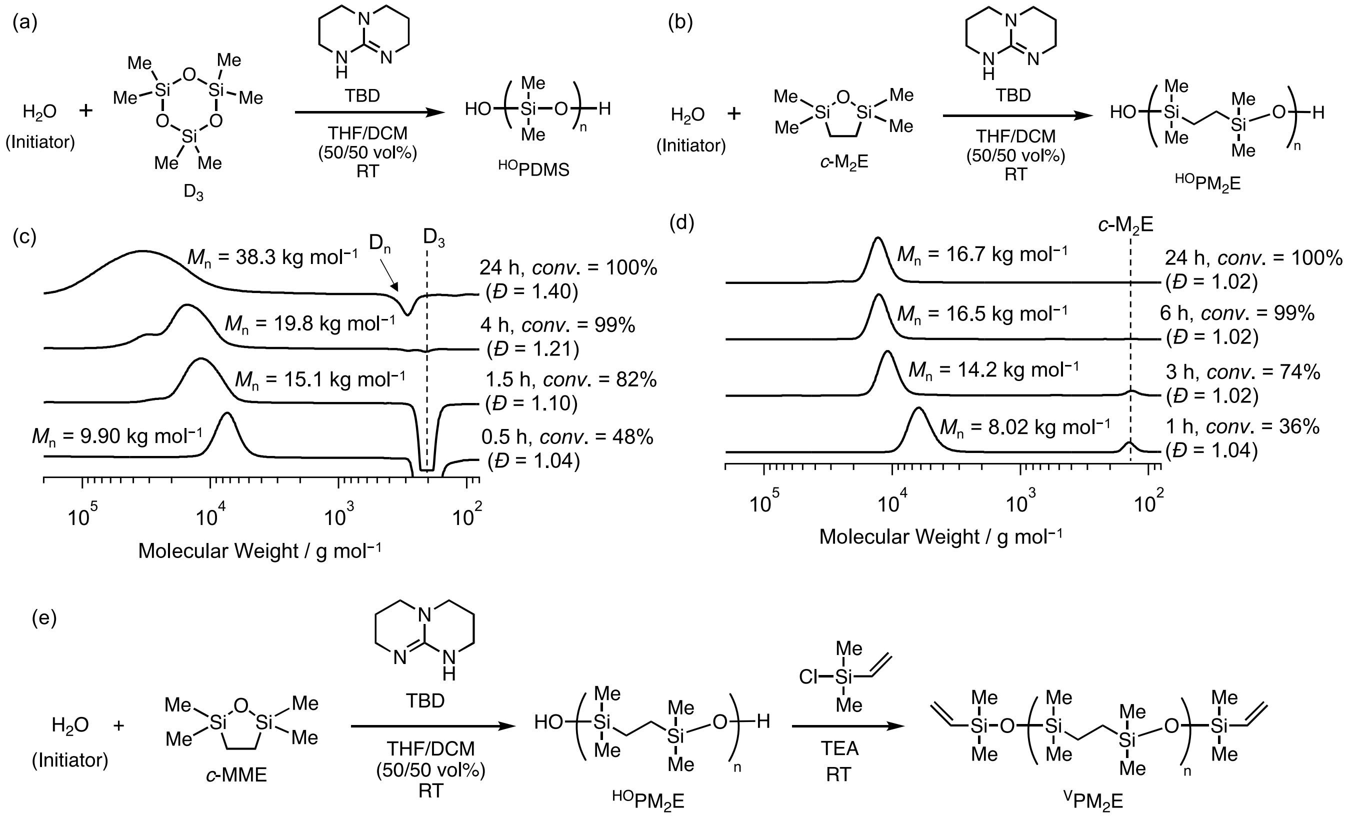
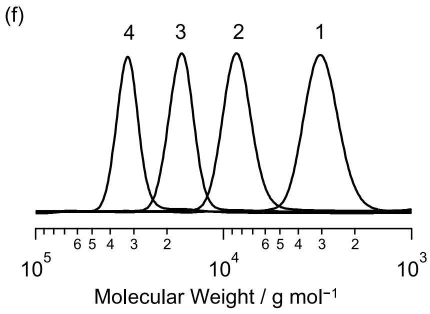
which unveiled promising characteristics including a notably low glass transition temperature (T_g = −88∼−95 °C)[19,20] and comparable (to PDMS) thermal stability under nitrogen conditions. PM$_2$E does not exhibit any toxicity when applied as a drug carrier for a transdermal drug delivery system, promising high biocompatibility similar to that of PDMS.[21−23] Furthermore, we demonstrated that the most efficient method for preparing the monomer *c*-M$_2$E is through the recycling of PM$_2$E polymers, aligning with the current demand for sustainable material development.[20]

Here, we present a synthesis of monodisperse PM$_2$E for the preparation of elastomers with well-defined structures, enhanced mechanical properties, and their efficient recycling process from the elastomer to the monomer. The base stability of PM$_2$E eliminates side reactions during the AROP of *c*-M$_2$E, enabling the direct synthesis of elastomers from *c*-M$_2$E without requiring intermediate prepolymer isolation. This clean polymerization process allows precise control over the prepolymer molecular weight, facilitating control of the elastomer moduli by adjusting the molecular weight between cross-links (M_c). During tensile tests, the elastomers exhibit remarkable elasticity, effortlessly reverting to their original shape even when elongated beyond 1000%, with no signs of rupture. The hysteresis of tension was nearly negligible at 500% elongation or below. Furthermore, the elastomers demonstrate excellent tear resistance. Finally, we demonstrated that the synthesized elastomers can be treated with a basic solution, yielding a high recovery (∼97%) of transparent liquid





Sample	[cM$_2$E]/[H$_2$O] (MW: kg mol^{-1})	$M_{n,NMR}$ (kg mol^{-1})	$M_{n,GPC}$ (kg mol^{-1})	$M_{w,GPC}$ (kg mol^{-1})	Đ
^{V}PM$_2$E-1	20 (3.20)	3.36	4.75	5.22	1.05
^{V}PM$_2$E-2	50 (8.01)	7.48	8.82	9.09	1.03
^{V}PM$_2$E-3	100 (16.0)	16.1	17.7	18.1	1.02
^{V}PM$_2$E-4	200 (32.0)	31.6	34.3	35.1	1.02

Figure 2. Synthesis of (a) ^{HO}PDMS and (b) ^{HO}PM$_2$E via TBD-catalyzed AROP. GPC traces of (c) ^{HO}PDMS and (d) ^{HO}PM$_2$E at different reaction time. (e) Synthesis of divinyl-terminated PM$_2$E (^{V}PM$_2$E) via TBD-catalyzed ring-opening polymerization utilizing water as the initiator. (f) GPC chromatograms of ^{V}PM$_2$Es with varying molecular weights and a table summarizing molecular weight values determined by both ^{1}H NMR and GPC based on polystyrene standards.

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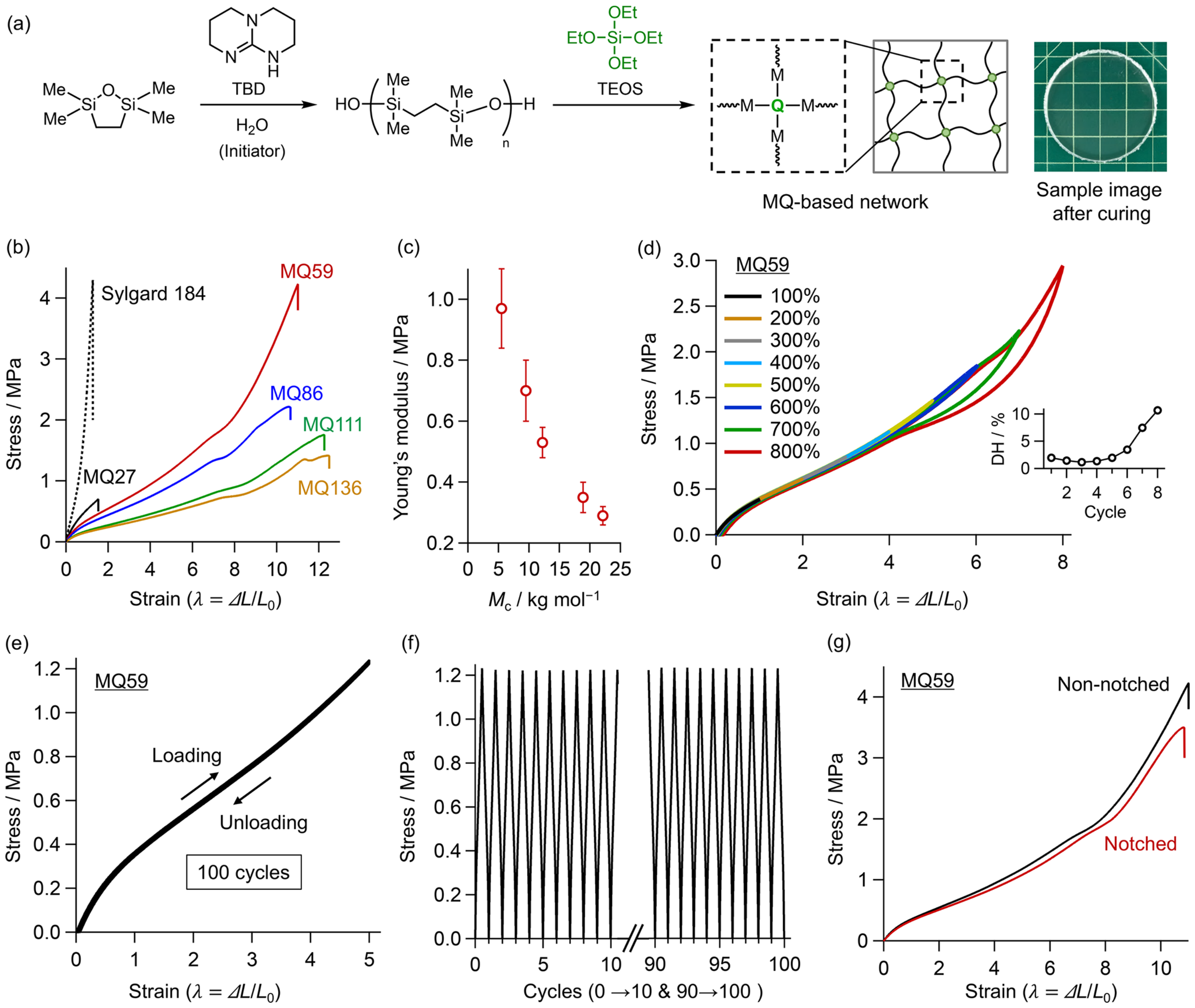

Figure 3. (a) Direct synthesis of PM_2E elastomers via the condensation reaction of $^{HO}PM_2E$ with TEOS, resulting in the formation of MQ-based network structures. (b) Stress−strain curves for MQ elastomers with dashed lines representing Sylgard 184 as the control. (c) Relationship between Young's modulus and M_c for PM_2E elastomers. (d) Loading and unloading tensile curves for MQ59 at different strains, with the inset showing the degree of hysteresis (DH) for each cycle. (e) Stress−strain curves for MQ59 during the 100-cycle test. (f) Stress fluctuation during the first 0−10 cycles and the last 90−100 cycles of the 100-cycle test. (g) Stress−strain curves for MQ59 with (red) and without (black) a prenotch.

PM_2E that can be efficiently converted back to the starting material, c-M_2E, with a yield of approximately 71%. Overall, this study demonstrates a highly efficient methodology for synthesizing PM_2E elastomers while precisely controlling their mechanical properties. Moreover, it highlights the successful conversion of the elastomers back to the monomer, rendering them viable materials with a wide range of potential applications.

■ RESULTS AND DISCUSSION

AROP for c-M_2E and D_3. Lohmeijer et al. demonstrated that PM_2E with a remarkably narrow polydispersity can be achieved through 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyzed AROP, wherein alcohols are utilized as initiators.[24] Strong organic bases like TBD are well-suited for catalyzing the AROP of siloxane-based cyclic monomers. Fuchise et al. successfully synthesized difunctionalized PDMS with narrow polydispersity using such base catalysts.[25] In their reaction setup, water played a crucial role as the initiator, leading to the formation of disilanol-terminated PDMS as an intermediate product. Subsequently, they functionalized the end groups using functional chlorosilanes.

Inspired by the aforementioned works, we monitored the AROP process for D_3 and c-M_2E using TBD as the catalyst and water as the initiator. The synthesis procedure is illustrated in Figure 2a,b. Initially, we mixed D_3 or c-M_2E and water in a solvent mixture comprising tetrahydrofuran (THF) and dichloromethane (DCM) in a 50/50 vol % ratio. The polymerization was initiated by adding TBD to the mixture at room temperature, leading to the formation of disilanol terminated PM_2E ($^{HO}PM_2E$) or PDMS (^{HO}PDMS). As shown in Figure S1, the rate constant for D_3 propagation is higher than that of c-M_2E ($k_{D3} = 1.19\ h^{-1}$ and $k_{c\text{-}M2E} = 0.456\ h^{-1}$). We note that this is an example of a polymerization where the more strained ring polymerizes more slowly. In the PDMS system, the dispersity index ($Đ$), determined by gel permeation

Table 1. Summary of Molecular Weight of Prepolymer ($^{HO}PM_2E$) before Curing, Molecular Weight between Crosslinks, and Young's Modulus

sample	M_n (kg mol^{-1})[a]	M_w (kg mol^{-1})[a]	$Đ$[a]	$M_{c,swelling}$ (kg mol^{-1})[b]	$M_{c,tensile}$ (kg mol^{-1})[c]	E (MPa)[d]
MQ27	4.38 (DP = 27)	4.57	1.04	5.50	6.94	0.97
MQ59	9.41 (DP = 59)	9.69	1.03	9.48	9.62	0.70
MQ86	13.7 (DP = 86)	14.1	1.02	12.2	12.7	0.53
MQ111	17.8 (DP = 111)	18.2	1.02	18.8	19.2	0.35
MQ136	21.8 (DP = 136)	22.4	1.02	22.1	23.2	0.29

[a] Determined by GPC data which was corrected by the correction factor determined based on the correlation in between the $M_{n,NMR}$ and $M_{n,GPC}$ for $^{V}PM_2E$. [b] Estimated by swelling experiments based on Flory−Rehner theory[29,30] (details are shown in Supporting Information). [c] Estimated from the stress−strain curves (details are shown in Supporting Information). [d] Young's modulus estimated from the initial linear region of the stress−strain curves.

chromatography (GPC), was relatively low ($Đ < 1.10$, shown in Figure 2c) at conversions below 50%, it gradually increased throughout the polymerization process, and eventually reached significant polydispersity after 24 h ($Đ \sim 1.40$). At 82% conversion, a shoulder, which increased in intensity at later stages, appeared in the GPC chromatogram corresponding to approximately double the molecular weight of the main peak. This observation suggests that TBD can catalyze a condensation reaction between ^{HO}PDMS molecules, as previously reported in the literature.[25,26] Notably, oligocyclic siloxanes exhibit a lower refractive index compared to THF, resulting in a negative signal in the refractive index (RI) detector. As shown in the GPC profile, a negative peak emerged at a slightly larger molecular weight than D_3 after 24 h, indicating the formation of larger oligocyclic siloxanes (D_n, where $n > 3$) due to the backbiting reaction. These findings confirm the occurrence of side reactions during PDMS polymerization, attributed to the high reactivity of the D-based backbone toward the basic end group.

In contrast, the PM_2E system maintained a more narrow molecular weight distribution ($Đ < 1.05$) throughout the polymerization process and even at 100% conversion (Figure 2d). No peaks corresponding to larger cyclic oligomers were observed in the lower molecular weight region. These results strongly suggest that the absence of side reactions during the AROP of c-M_2E is due to the lower reactivity of the M-based backbone in PM_2E. We note that TBD-catalyzed condensation to form dimeric polymers begins to become competitive between 99% and 100% conversion (6 and 24 h reaction time).

The silanol end group can be functionalized through a termination reaction based on chlorosilane chemistry. We synthesized divinyl-terminated PM_2E ($^{V}PM_2E$) with different molecular weights by the TBD-catalyzed AROP and termination with vinyldimethylchlorosilane in the presence of triethylamine (TEA) (Figure 2e). Figure 2f illustrates the GPC profile of $^{V}PM_2E$ prepared with varying molar ratios of the monomer to water ($[c\text{-}M_2E]/[H_2O]$ = 20, 50, 100, or 200), along with a summary of their number-average, weight-average molecular weights ($M_{n,GPC}$, and $M_{w,GPC}$, respectively), and $Đ$ determined by polystyrene standards. Additionally, the ^{1}H NMR-based molecular weight ($M_{n,NMR}$) was estimated by comparing the proton integration values of the vinyl groups and the main chain (Figures S2−S5), and the results are summarized in Figure 2f. The correlation between the molecular weight values determined by ^{1}H NMR and GPC was used to establish a correction factor (Figure S6), which was applied to estimate the molecular weight of PM_2E utilized for elastomer preparation in the following section.

Synthesis and Mechanical Properties of PM_2E Elastomers. The TBD-catalyzed AROP of c-M_2E yields well-defined $^{HO}PM_2E$ containing end group silanols that are activated by TBD. These $^{HO}PM_2E$ samples serve as prepolymers for the subsequent fabrication of PM_2E elastomers. Figure 3a illustrates the synthesis scheme of PM_2E elastomers by mixing $^{HO}PM_2E$ with tetraethyl orthosilicate (TEOS), which produces MQ (tetra-functional) based network structures. During the synthesis of PM_2E elastomers, the procedure mirrored the polymerization method described in Figure 2e, up until the midpoint of the process. At the stage of $^{HO}PM_2E$ formation, instead of utilizing chlorosilane in the final step, the cross-linking agent was introduced, which initiated the formation of a network structure. The resulting mixture was then carefully transferred to an aluminum mold and left to cure at room temperature for 18 h, then at 60 °C for 1 day, and then at 100 °C for another day. These procedures were conducted under a nitrogen atmosphere. All the cured materials exhibit remarkable transparency as shown in Figure 3a. The residual TBD catalyst was efficiently removed by swelling (extraction) the samples with chloroform. The gel fraction of all prepared elastomers, determined by the sample mass before and after the extraction process, was over 99%.

In the elastomer synthesis, the molar ratio of the monomer to water was varied as follows: $[c\text{-}M_2E]/[\text{water}]$ = 25, 50, 75, 100, 125. The molecular weight of the prepolymer $^{HO}PM_2E$ was estimated by GPC using the correction factor determined above before the addition of the cross-linker (Figure S7), and the results are summarized in Table 1. The resulting elastomers, possessing MQ-based cross-links, are systematically labeled as follows: MQ#, where the "#" represents the degree of polymerization estimated from the corrected $M_{n,GPC}$ value.

Figure 3b displays stress−strain curves of the PM_2E elastomers. Additionally, we conducted a tensile test for Sylgard 184,[27,28] and the result is shown in the figure as a dashed line. All samples, except for MQ27, exhibited highly stretchable properties, far surpassing that of Sylgard 184. To determine M_c, we conducted a solvent swelling experiment based on the Flory−Rehner theory[29] for all samples, and the corresponding values ($M_{c,swelling}$) are summarized in Table 1. We also estimated M_c based on the stress−strain curves and summarize the values ($M_{c,tensile}$) in Table 1 as well. Notably, the M_c values show a clear correlation with the M_n of the prepolymers, suggesting the formation of nearly defect free network structures in the elastomers. The cross-linking reaction used for PM_2E elastomers should statistically form dangling loops in the network, which could increase the M_c beyond the expected value. While the possibility of such

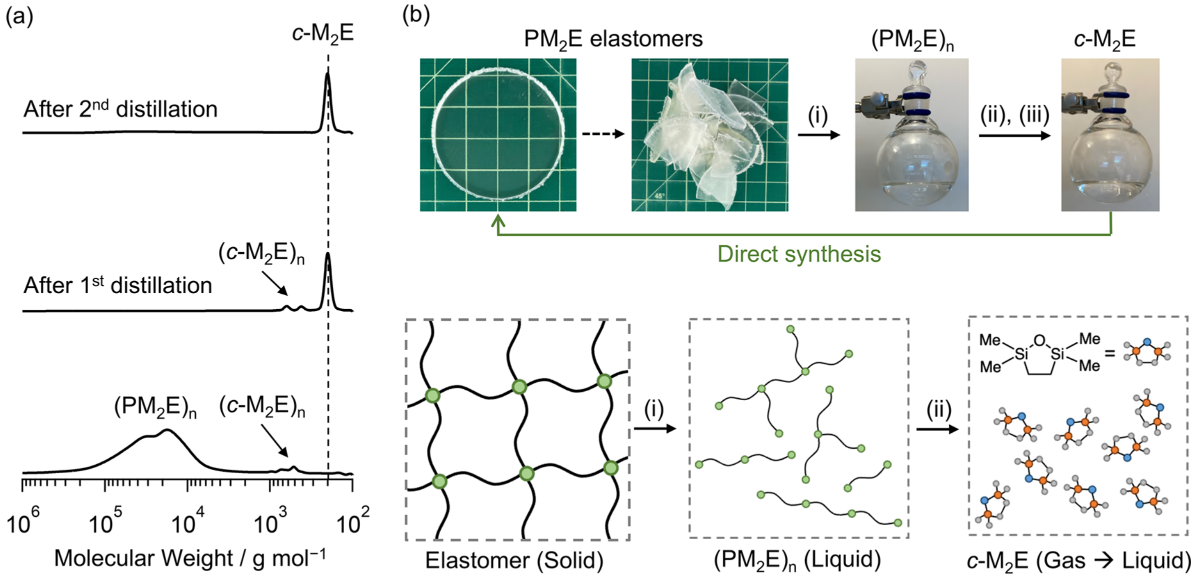

Figure 4. (a) GPC chromatograms illustrating the product at each step. (b) Photographic images and schematic illustrations depicting each step in the degradation process. Reaction conditions: (i) 0.3 M MeONa, THF/Methanol (50/50 vol %), room temperature, 18 h (yield: 97%); (ii) distillation from KOH at 200 °C under 30 Torr (yield: 89%); (iii) subsequent redistillation at 90 °C under 60 Torr (yield: 82%).

defects cannot be ruled out, the nearly 100% gel fraction and the consistency between the prepolymer molecular weight and the calculated M_c values indicate that the amount of dangling loop formation is likely minimal.

The Young's modulus of PM_2E elastomers exhibits a dependency on $M_{c,swelling}$ as illustrated in Figure 3c. During the tensile test, all specimens, except for MQ27, slipped out of the clamps of the instrument with no observable structural failure within the dog-bone midsection, as visually exhibited with photographs shown in Figure S8. Figure 3d presents the elastic hysteresis behavior of MQ59 subjected to varying levels of strain. This demonstrates nearly negligible hysteresis up to 500% strain (degree of hysteresis (DH) < 2%, discussed in Supporting Information) as illustrated in the inset of Figure 3d. Beyond 600% strain, the DH parameter exhibits an increasing trend, reaching approximately 10% at 800% strain. We conducted a cyclic loading−unloading experiment for MQ59, where the sample was stretched from 0 to 500% and then returned to 0% for 100 cycles without any interval pause. The stress−strain curves revealed no significant differences throughout the cycling test (Figure 3e). As shown in Figures 3f and S9, the ultimate stress at 500% elongation remained nearly constant over all 100 cycles.

In addition to superior elongation properties, PM_2E elastomers demonstrate excellent tear resistance. Figure 3g shows the stress−strain curve of MQ59 samples with and without a precut notch. Both are almost identical curves, indicating that the elastomer did not perceive the notch while it was stretched. As displayed in Movie S1, the crack on MQ59 did not propagate at all during the elongation, and the sample slipped out of the clamp at ∼1080% elongation. The other PM_2E elastomers, except for MQ27, also exhibited similar tear resistance. This property is surprising because PDMS elastomers without fillers exhibit no tear resistance.

Recyclability of PM_2E-Based Elastomers. Finally, our endeavors extended toward the refinement of the recycling process for PM_2E-based elastomers synthesized through the direct method, converting them to the monomer c-M_2E. While the conversion of the polymer PM_2E to c-M_2E exhibited a relatively high yield (>70%),[20] the conversion of the elastomer faced challenges, yielding ∼ 40%. Eom et al.[31] addressed this issue and developed an improved method to recycle PM_2E elastomers, cross-linked with MQ structures, into c-M_2E. The process involved initially breaking down the cross-linked solid into a liquid using a base catalyst, followed by depolymerization to the monomer.

The first step leverages the difference in base stability between MM siloxane bonds in PM_2E and MQ cross-linking structures. According to Kantor's report,[15] the MM siloxane bond is much more stable than that of DD toward bases since Si in the D structure is more positively charged due to the electron-withdrawing nature of the neighboring two oxygen atoms. This observation argues that the siloxane bonds in MQ structures are more reactive toward bases than their MM counterparts and suggests that employing MQ structures as cross-linking points is advantageous for recycling. Commonly used D-based cross-linkers such as 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) and hydride-containing PDMS copolymers in hydrosilylation reactions for divinyl-terminated silicones should form elastomers that are more difficult to recycle.

A significant effort was made to optimize the decomposition conditions for PM_2E elastomers into polymer fragments. The preferred method involves immersion of the solid elastomer into a mixed solution of THF and methanol (50/50 vol %) containing 0.30 M sodium methoxide (MeONa). Over 18 h, the elastomers transition into an oily liquid, as visually illustrated in Figure S11. This liquid is washed with water and extracted with hexanes. This approach achieved an impressive yield of 97% while generating minimal cyclic oligomers, $(c\text{-}M_2E)_n$ (<1%), as confirmed by the GPC analysis shown in Figure 4a. The broad peak in the GPC profile is indicative of a polymer construct primarily composed of oligopolymers originating from prepolymers connected through MQ siloxane bonds, namely $(PM_2E)_n$.

Subsequently, the polymer liquid was converted to c-M_2E by reactive distillation with KOH. A subsequent redistillation was performed to eliminate cyclic oligomers, $(c\text{-}M_2E)_n$. Figure 4a presents the GPC profiles at each decomposition and distillation stage in the recycling process, while Figure 4b describes the recycle process from the elastomer solid to the monomer liquid. The final distilled monomer exhibited high purity based on both the GPC profile (Figure 4a) and the NMR spectra (Figures S11–S13). Notably, the cumulative yield achieved through this recycling endeavor amounted to 71%, underscoring the efficacy of the process.

■ CONCLUSIONS

In this study, we have demonstrated that the five-membered ring siloxane monomer, *c*-M_2E, undergoes TBD-catalyzed AROP without undesired side reactions, resulting in quite monodisperse silicone prepolymers for forming ideal network structures in cross-linked elastomers. The modulus of PM_2E elastomers can be well-manipulated by controlling the molecular weight of PM_2E prepolymers. The elastomers show remarkably high stretchability and low hysteresis in tensile tests as well as excellent tear resistance presumably due to the low defect network structure owing to the high purity in the PM_2E prepolymers. We note that we have not measured toughness quantitatively as the sample did not fracture, but these elastomers are certainly high toughness materials with low hysteresis.[32] We finally have demonstrated the recycling of the PM_2E elastomers by a base-catalyzed degradation process. The MM siloxane structure in PM_2E elastomers is less reactive than that of cross-links like MQ siloxane. This allows the solid elastomer to be degraded into a liquid oligopolymer of PM_2E, which can then be converted into *c*-M_2E monomer in high yield. Overall, this study demonstrates the superior properties of PM_2E elastomers compared to PDMS elastomers in both mechanical properties and recyclability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00332.

Experimental details, including polymer synthesis and characterization, and additional characterization data (PDF)

Tensile experiment of a PM2E sample (MQ59) with a precut notch (MP4)

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Author Contributions

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

Notes

The authors declare no competing financial interest.

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