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Elastomers without Covalent Crosslinking: Concatenated Rings Giving Rise to Elasticity

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ABSTRACT: There is intense interest in making mechanically stable elastomers with properties resembling those of human muscles for use in soft robotics. Recently, a polydimethylsiloxane (PDMS) elastomer prepared without the use of crosslinking moieties from heterobifunctional PDMS macromonomers of intermediate molecular weight has been shown to exhibit surprising inherent softness and excellent stability upon both large deformation and swelling—in clear contradiction of classical rubber elasticity theories. In this work, this unexpected elasticity is shown to originate from concatenated rings.

Recently silicone elastomers have received considerable attention for their use in advanced products such as stretchable electronics,^{1–4} medical devices,^{5,6} implants and microfluidics.^{7–9} Significant research efforts have explored the preparation of silicone elastomers with softness and elasticity resembling that of human tissue.^{10–14} However, the softness of mechanically stable silicone elastomers prepared by classical means is limited by their entanglement threshold (elastic modulus of around 0.6 MPa).^{15,16} In order to circumvent this threshold and achieve even softer elastomers, strategies such as sparse crosslinking,¹⁷ addition of solvent during curing,^{18,19} development of rotaxane structures,^{20,21} and crosslinking bottle-brush type PDMS^{22,23} have all been applied, but none of the resulting elastomers possess the stable mechanical properties of human muscle upon repeated deformation. Some recover from the stretch only slowly, while some never fully recover, instead showing a permanent set that makes their use in repeated actuation strain history-dependent and thus complicated.

Recently, an extremely soft elastomer with an elongation of more than 5000% and a strain recovery of 82% after 10 cycles of deformation to 80% of maximum strain was reported by Goff et al.¹³ Unlike conventional crosslinked elastomers produced from telechelic vinyl functional silicone polymers, multifunctional hydride crosslinker and platinum catalyst, this elastomer was produced solely using near-monodisperse α -monovinyl- ω -monohydride telechelic PDMS and a platinum catalyst—i.e., without using a crosslinker.¹³ Because the degree of covalent crosslinking was below the detection level of nuclear magnetic resonance (NMR), traditional covalent crosslinking cannot account for the reported elastic behavior of this elastomer. Its combination of stable mechanical properties in the absence of chemical crosslinks departs from the classical understanding of rubber elasticity, according to which a material with virtually no crosslinks and no possibility of forming transient bonds should not possess such a high degree of elasticity or strain recovery.²⁴

From the reported reaction route, based on highly efficient Pt-catalyzed hydrosilylation with limited side reactions,²⁵ it can be

concluded that there are two possible topological structures present during curing, when macromonomers are of high purity: intermediate chain extended linear PDMS from intermolecular reaction, and cyclic PDMS from intramolecular reaction (**Figure 1a**). The linear macromolecules may either undergo an *intermolecular* reaction or an *intramolecular* reaction. Since the intermolecular reaction always results in end-functional macromolecules, the heterobifunctional ring closure reaction may happen for any intermediate linear PDMS. Due to the very high reaction efficiency and lack of NMR signals for unreacted end groups (see **Figure S1** and **Figure S2** in electronic supplementary information (ESI), where macromonomer purity is also shown), it is clear that two structures can exist in the final elastomer: namely, rings or extremely long polymer chains with unreacted end groups. This was earlier reported for a similar reaction of difunctional telechelic PDMS reacting with difunctional crosslinker^{26–28} However, this system requires crosslinkers to connect the PDMS chains, which significantly lowers the possibility of forming rings since the ring formation depends on not only the molecular weight of the PDMS, but also the ratio of crosslinker and PDMS.

In this work, we synthesize the above elastomers without silica fillers and compare these polymer-only networks to two reference samples—a conventional PDMS elastomer and an entangled PDMS melt—in order to demonstrate the unique mechanical properties of this new type of “concatenated ring network”. Materials and sample preparation are described in the ESI. Elastomer-HV15, Elastomer-HV22 and Elastomer-HV31 were prepared from α -monovinyl- ω -monohydride terminated PDMS of three chain lengths: DMS-HV15 ($\bar{M}_n \approx 4$ kDa), DMS-HV22 ($\bar{M}_n \approx 15$ kDa) and DMS-HV31 ($\bar{M}_n \approx 27$ kDa), respectively. In **Figure 1b**, the tensile properties of these elastomers are compared to a conventional crosslinked PDMS network prepared from a polymer of similar length to HV22 (DMS-V25, $\bar{M}_n \approx 15$ kDa). The concatenated networks are much softer and stretch to a much greater extent than the conventional PDMS elastomer with similar molecular weight between crosslinks. Indeed, the developed concatenated networks exhibit excellent elasticity, with maximum strain at break of 1270% and strain

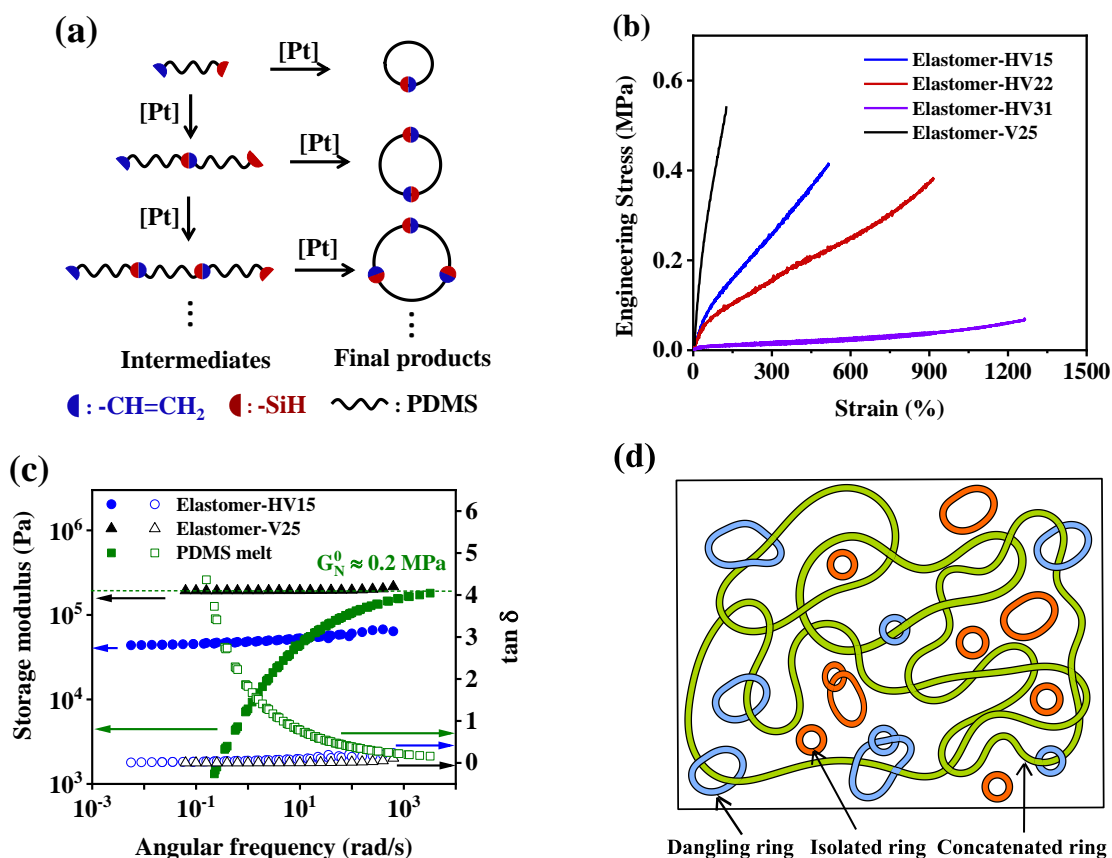


Figure 1. a) The possible reaction paths leading to ring structures of varying sizes. b) Engineering stress (force divided by initial area) of the two prepared concatenated networks compared to a traditional PDMS network with covalent bonds (black curve). c) Linear viscoelastic data for a concatenated network compared to a PDMS melt and a traditional PDMS network. d) The different ring structures forming a network and a sol. The network consists of elastically active concatenated rings as well as dangling, elastically inactive rings that are concatenated with only one other elastically active ring structure. The sol consists of rings that are not connected to the network structures.

recovery of 96% after 3 cycles (**Table S2** in ESI). The elastomers' high swelling ratios (**Figure S4** in ESI) further verify their permanent, yet very loose network structure.

To further illustrate these elastomers' peculiar rheological behavior, their linear viscoelastic responses are compared to those of the reference elastomer and an entangled polymer melt in **Figure 1c**. Both the melt and the reference network show the presence of an entanglement plateau of 0.2 MPa at high frequency. The concatenated ring networks, on the other hand, have a plateau of G' far below the entanglement threshold for all investigated frequencies. This plateau indicates only minimal relaxation, meaning that most of the network structure is elastically active and that there are only limited unreacted polymer chain ends present, as otherwise these would relax by reptation (sol molecules) or by chain end withdrawal (dangling chains). The low G' value further indicates that all the linear molecules present should be shorter than the length given by the molecular entanglement weight of PDMS and that they are not crosslinked in the traditional sense, since the plateau would then be described by a value of G' higher than the entanglement plateau.

The final feasible network structure would be a very lightly crosslinked network or infinitely long linear polymer chains

with a large fraction of fast relaxing sol molecules with molecular weight lower than that of entanglements. Since there is no trace of unreacted macromonomers in the network (confirmed by NMR, see **Figure S1** and **Figure S2** in ESI), the low molecular weight species must be free rings. Theoretically, the plateau of a diluted, well-entangled network is predicted to be $G_0 = G_N^0(1 - \varphi)^a$ (with $a=1.8-2.3$) where φ is the volume fraction of solvent²⁹⁻³¹; in this case, sol fractions of 50%, 60% and 85% would be needed to reach the plateaus of 44 kPa, 26 kPa and 2 kPa for 4 kDa, 15 kDa and 27 kPa networks, respectively. However, since the networks possess sol fractions of only approximately 13%, 19% and 51%, respectively (see **Figure S4** in ESI), the low G_0 of the concatenated networks cannot be exclusively due to contributions from an extractable sol fraction, but must also be due in part to dangling rings trapped in the network structure, thereby acting as internally trapped plasticizers. In other words, a simple possible network structure that explains these elastomers' behavior consists of a mixture of concatenated rings of various sizes, "dangling" concatenated chains (i.e. rings with only one concatenation in the network), and "sol" rings (rings that are not linked to the network), as illustrated in **Figure 1d**. The dangling and sol structures are mainly small rings due to the strong decrease in probability of longer chains not being concatenated.³² The fact that network dilution

by silicone oil in the curing phase causes classical scaling behavior is further evidence of this novel network structure; Elastomer-HV15 and Elastomer-HV22 were shown to possess a scaling exponent of 2.3 and 2.7 with the dilution, respectively (Figure S6 in ESI), and thus indicating a binary interaction rather than the scaling exponent of 1 for un-entangled networks (simple crosslink dilution). In other words, the network is dominated by entanglements despite the macromonomers (DMS-HV15) possessing a molecular weight below the classical entanglement threshold (12 kDa), however, it simultaneously displayed no rheological signature of classical entanglements. Rather, entanglement length appears to be governed by a combination of ring length and spatial restrictions imposed by the network.

To verify this proposed structure, we further investigated the ring formation. Direct detection of concatenated rings in the insoluble network fraction is challenging.³³ However, the hypothesized structure includes the presence of cyclic PDMS in the sol fraction, which can be distinguished from linear chains of the same molecular mass using size exclusion chromatography (SEC),³⁴ since the hydrodynamic volume of a cyclic polymer is smaller than its linear counterpart.³⁵ Specifically the mean span is smaller by a factor of $\pi/4$.³⁶ Figure 2a compares the SEC chromatogram of the extracted sol fraction from Elastomer-HV15 with the chromatogram of unreacted DMS-HV15. The sol fraction exhibits a peak with a higher maximum retention volume compared to DMS-HV15, proving that a PDMS with smaller hydrodynamic volume than the original macromonomer—i.e., cyclic PDMS—is present in the concatenated network. Furthermore, addition of unreacted DMS-HV15 to this diluted sol fraction leads the peak to shift towards that of DMS-HV15 (see inset in Figure 2a), accompanied by a corresponding increase in peak intensity, thereby eliminating experimental errors caused by pump flow variations.

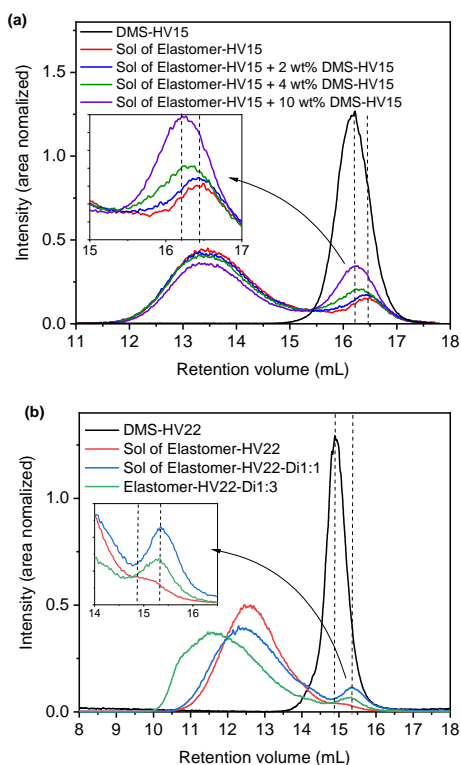
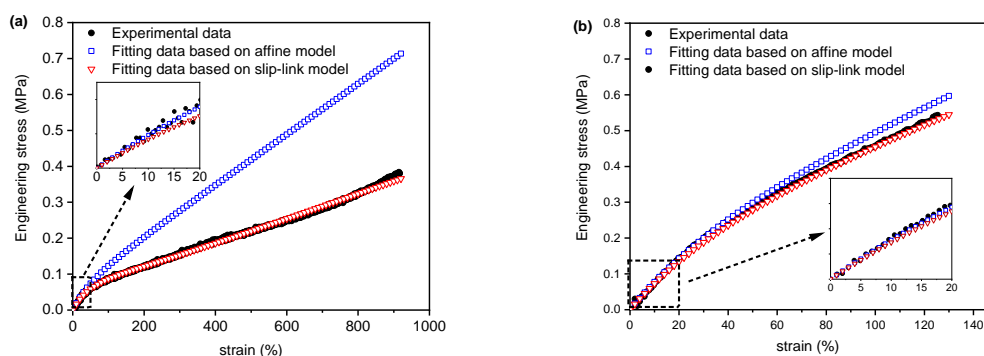


Figure 2. a) SEC curves of starting material DMS-HV15, sol fraction of Elastomer-HV15, and mixtures of the two (2-10 wt% DMS-HV15). b) SEC curves of DMS-HV22, sol fraction of Elastomer-HV22, sol fraction of Elastomer-HV22 prepared with dilution ratio of 1:1 (sol of Elastomer-HV22-Di1:1), and Elastomer-HV22 prepared with dilution ratio of 1:3 (Elastomer-HV22-Di1:3)

The DMS-HV22 network and corresponding sol fraction were also analyzed (see Figure 2b). The sol fraction exhibits only a small shoulder at around 15 mL, which occurs at larger elution volumes than for DMS-HV22. While this may indicate the presence of a small quantity of cyclics, further analysis is complicated by the overlap with the starting macromonomers and the low concentration of the elution volume at around 15 mL. If cyclic PDMS is indeed formed, more cyclics will be formed under dilute conditions, as the probability of intramolecular reaction increases with dilution.³⁷ Therefore networks prepared under dilute conditions were tested. As expected, peaks appear under dilute reaction conditions (macromonomer diluted 1:1 and 1:3 with solvent, respectively, before reaction) at a larger elution volume compared to the undiluted sample, verifying the presence of cyclic low-molecular weight species in the concatenated network prepared from larger macromonomers, albeit in lower concentrations than in the corresponding network prepared from a lower molecular weight macromonomer. The analyses performed in this study only definitively establish the presence of mono-cyclic rings with retention volumes larger than those of the macromers, which can therefore be distinguished from the initial macromer. However, theoretical studies have verified that, for a linear step growth polymerization system, macrocyclic PDMS of various sizes are formed containing concatenated rings.³⁸

Modeling of stress-strain behavior. Using scaling arguments, Vilgis and Otto suggest that monodisperse concatenated rings would exhibit very low elasticity.³⁹ Given that the present system is far from monodisperse we here use affine and slip-link models to model the stress-strain behavior and investigate the origin and nature of elasticity for the two network types. The least-square fitting parameters from both models can be seen in Figure 3.^{40,41} The affine model accurately predicts the stress-strain behavior of the conventional network, but overestimates the stresses at strains of more than 50% for all concatenated networks due to the sliding nature of the concatenated rings compared to more sterically hindered covalent crosslinks. This sliding ability becomes more prominent with larger ring size, as shown by the fact that the prediction model's performance worsens when the molecular weight of the macromonomer is increased (also see Figure S8). The slip-link model, on the other hand, accounts for this partial sliding nature via a transient modulus (G_s) in addition to the classical, permanent elastic modulus (G_c), making it a natural model for entangled networks or networks resulting from concatenated rings. As Figure 3c makes evident, the contributions from both types of elasticity are of similar magnitude for both concatenated networks. Due to the absence of crosslinks, these will be referred to as pseudo-crosslinks moving forward. The concatenated rings initially behave as normal crosslinked or entangled polymer chains; for larger stretches, however, their mobility becomes limited due to the concatenation. In the conventional network, the crosslinks constitute the principal source of elasticity ($G_c/G_s=10$), since the molecular weight of the precursor chain (15 kDa) is so close to M_e for PDMS (12 kDa) that the contribution from entanglements is limited.¹⁵



(c)

Samples	Molecular weight of precursor PDMS	G_c (MPa)	G_s (MPa)	$G=(G_c + G_s)$ (MPa)
Elastomer-HV15	4 kDa	0.063	0.021	0.084
Elastomer-HV22	15 kDa	0.036	0.041	0.077
Elastomer-HV31	27 kDa	0.003	0.008	0.011
Elastomer-V25	15 kDa	0.251	0.025	0.276

Figure 3. Experimental stress-strain and fitting curves based on affine and slip-link models, respectively, for a) Elastomer-HV22 and b) traditionally crosslinked Elastomer-V25. c) Fitting parameters based on the slip-link model.

In summary, in this work we demonstrated for the first time that the elasticity of the soft elastomers prepared from α -monovinyl- ω -monohydride terminated PDMS through hydrosilylation derives from a network structure of elastically active concatenated rings, with dangling structures of concatenated rings and a sol fraction consisting of single rings and slightly concatenated rings. The formation of monocyclic PDMS during crosslinking was confirmed via SEC chromatography, and the permanent nature of the network was demonstrated using swelling and tensile tests. Rheology and scaling studies revealed a new type of elastic behavior arising from the novel concatenated network structure. From a scaling point of view, the elastomers behave as highly entangled melts, but display no rheological signature of classical entanglements due to the fact that their entanglement length is dependent upon the ring size and tightness of the network structure. By circumventing the entanglement threshold, this novel network structure provides a foundation for the future preparation of numerous inherently soft, stable elastomers capable of meeting the complicated requirements of soft robotics applications.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

Supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

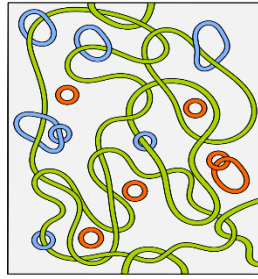
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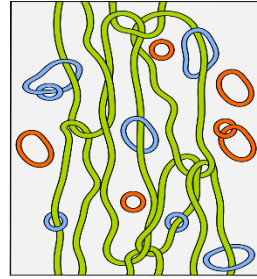
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Relaxed state



Stretched state