Systematic Investigation of Silicon Substitution on Single Macromolecule Mechanics

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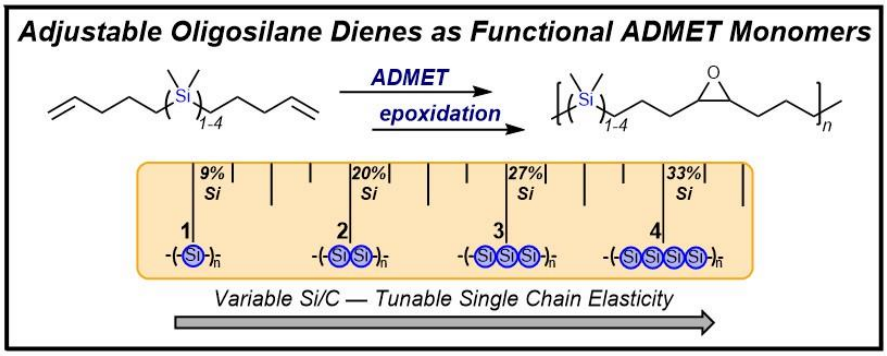


ABSTRACT

Four unsaturated polycarbooligosilanes (**P1**-**P4**) were prepared via acyclic diene metathesis (ADMET) polycondensation of new oligosilane diene monomers (**1**-**4**). These novel polymers with

varying main chain Si incorporation have high *trans* internal olefin stereochemistry (ca. 80%), and molecular weights (9,500 - 21,700 g mol^{-1}). Post-polymerization epoxidation converted all alkene moieties to epoxides and rendered the polymers (**P5**-**P8**) more electrophilic, which allowed for single molecule force spectroscopy studies via a modified atomic force microscope (AFM) set-up with a silicon tip and cantilever. The single-chain elasticity of the polycarbooligosilanes decreased with increasing numbers of Si–Si bonds, a finding reproduced by quantum chemical calculations.

INTRODUCTION

Organometallic polymers represent a compelling platform for advances in new materials due to the desirable electrical, magnetic, and optical properties that arise from the combination of both organic and metallic components.[1-6] While polymers with a backbone comprised of elements from group 14 (*e.g.,* Si, Ge, Sn)[7-9] absorb ultraviolet light, similar to π-conjugated organic polymers and unlike polyolefins, the number of organometallic polymers is far superseded by carbon-based polymers. This limited library of hybrid inorganic-organic polymers can be attributed to the challenges with synthesis and comparatively fewer number of monomers. For example, chain-growth polymerizations comparable to olefin polymerization are problematic for inorganic polymers as the appropriate multiply bonded monomers[10, 11] are difficult to prepare, air- and water-sensitive, and often require the use of bulky ligands.[6, 12]

An alternative approach is the polymerization of metallic segments, e.g., oligosilyl chains, capped with organic functional groups, which takes advantage of the functional group diversity of organic compounds while giving rise to macromolecules with alternating organic and metallic segments. Recent examples from Klausen *et al.* include Kumada polycondensation of dithienylcyclosilanes,[13] building on foundational examples from Ohshita,[14, 15] and ring-opening

metathesis polymerization (ROMP) of a strained cycloalkene with embedded oligosilanes (Figure 1a).[16]

These synthetic advances have resulted in the discovery of new properties, such as our finding of a reduced segment elasticity for enthalpic stretching in a polycarbooligosilane relative to all carbon backbones. In our earlier work using single-molecule force spectroscopy (SMFS), we found for polycyclooctene (PCO) an average segment elasticity of 3.5 ± 0.1 pN x 10^4 per unit L_0. For the macromolecule poly(*trans*-**SiCH**), in which 3 of the carbon atoms of polycycloheptene were replaced with silicon atoms, the segment elasticity decreased to 1.4 pN x 10^4 per unit L_0.

The reduced elasticity of poly(*trans*-**SiCH**) is attributed to the lower stiffness of the C–Si and Si–Si bonds relative to C–C bonds. The correlation between segment elasticity and bond stiffness can be intuitively understood by invoking the analogy of a chemical bond to a spring, typically used as a model for understanding bond vibrations and Infrared (IR) spectroscopy. Hooke's Law states that the force F needed to elongate a spring a distance x scales linearly with that distance x according to the equation $F = kx$ (eq 1) where k is the force constant, a constant that characterizes an individual spring's stiffness. A plot of force F vs. displacement x gives a straight line with a slope k. Therefore, a stiffer spring (steeper slope, larger k) requires a larger force than a softer spring (flatter slope, lower k) to displace the spring the same distance x. A stiffer spring is also more elastic and more readily returns to its original shape after deformation.

By analogy, when a polymer strand is stretched in the SMFS experiment, a stiffer strand will require more force than a more flexible strand to achieve the same elongation. The output of an SMFS experiment is a force-extension curve, and in the high-force, linear regime a steeper slope indicates a stiffer strand. To facilitate direct comparisons of different samples, the elasticity with units of pN per unit L_0 can be determined from the slope of the linear high-force regime, and the

details of this calculation are described in the SI of this manuscript and elsewhere. The characteristic force for chain stiffness k obtained here is related to the segment elasticity (k_{seg}) of extended freely jointed chain models of polymer elasticity by $k = k_{seg}b$, where b is the Kuhn length of the polymer strand.

While our first manuscript comparing the elastic force constants of PCO and poly(*trans*-**SiCH**) provided evidence that silicon incorporation reduces the force constant of the strand, it had two limitations that the current manuscript will address. First, a low frequency of poly(*trans*-**SiCH**) strand pick-up during SMFS resulted in an insufficient number of pulls to assess experimental error. Second, the requirement for high ring strain in ROMP limited us to a single example of a polycarbooligosilane, whereas our hypothesis suggested that each additional flexible bond should lower the elastic force constant, k.

Acyclic diene metathesis (ADMET), a step-growth polymerization of linear monomers, appeared to be a promising alternative to ring-opening metathesis that would afford access to a homologous series of macromolecules with different length of oligosilane segments. Prior work by Wagener demonstrated that polycarbosilanes[17, 18] and polycarbogermanes[19] are readily obtainable by acyclic diene metathesis (Figure 1b), which led us to hypothesize that the family of monomers (**1**-**4**) with 1 to 4 consecutive silicon atoms could afford the desired macromolecules (Figure 1c). To our knowledge, no reports of ADMET currently exist for polymers containing Si–Si bonds. We further anticipated the postpolymerization functionalization of ADMET polymers, perhaps via epoxidation, could increase the frequency of strand pick-up in the SMFS experiment by introducing polar functional groups.

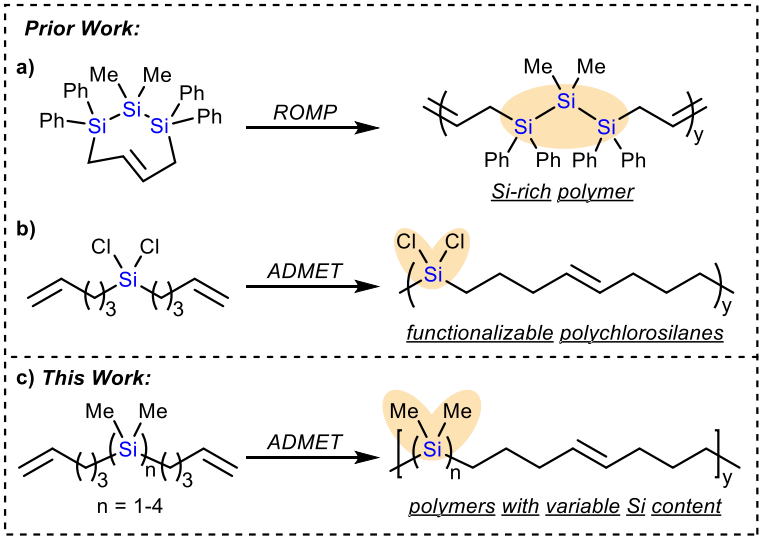


Figure 1. a) Ring opening metathesis polymerization of *trans*-silacycloheptene. b) Acyclic diene metathesis of dichlorodipentenylsilane with Si–Cl bonds that can be readily functionalized. c) New oligosilane-dienes that undergo acyclic diene metathesis to form polymers with variable silicon content (*this work*).

Herein we report the synthesis of oligosilane dienes and their corresponding ADMET polymers (Figure 1c). In addition, we functionalized the poly-dienes via epoxidation to increase the rate of strand pick-up during SMFS and studied the micromechanical properties of the polySi_n-epoxides as a function of Si content via SMFS. With an increasing number of Si–Si bonds in polycarboligosilanes, we observed an overall decrease in elasticity that is in agreement with our calculations.

RESULTS AND DISCUSSION

To begin our studies, we synthesized a class of oligosilyl dienes from 5-pentenylmagnesium bromide and dichlorooligosilanes (Scheme 1). The dienes were isolated as colorless oils in 48-80% yields after rigorous purification by column chromatography followed by vacuum distillation. Dienes **1**-**4** were characterized by ^{29}Si {^{1}H} NMR where one [**1** (2.3 ppm) and **2** (-17.9 ppm)] or

two [**3** (-14.1, -49.1 ppm) and **4** (-13.4, -45.0 ppm)] diagnostic silicon environments were observed to support their purity (Table 1). Additionally, the dienes themselves were characterized by size exclusion chromatography (SEC), and an increase in retention time with the number of silicon atoms was observed (Figure S61).

Scheme 1. Synthesis of oligosilane dienes via pentenyl Grignard reagent.

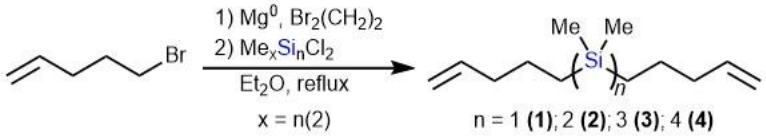


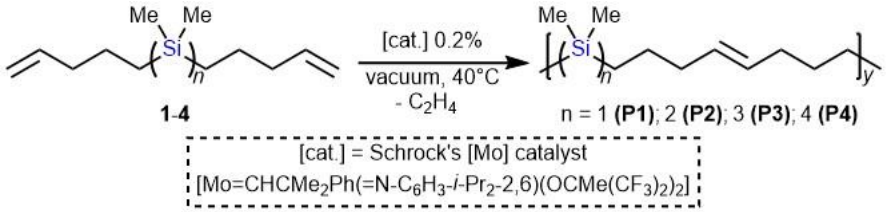
Table 1. Observed NMR chemical shifts for the ^{29}Si and ^{1}H nuclei in dienes **1-4** in $CDCl_3$.

Diene	$^{29}Si\{^{1}H\}$ (ppm)	^{1}H (ppm) [H_2C=CH-]
1	2.3	5.03-4.92 (m, 4H), 5.80 (ddt, 2H)
2	-17.9	5.05-4.93 (m, 4H), 5.81 (ddt, 2H)
3	-14.1, -49.1	5.04-4.93 (m, 4H), 5.81 (ddt, 2H)
4	-13.4, -45.0	5.05-4.94 (m, 4H), 5.81 (ddt, 2H)

We were then interested in polymerizing the dienes to obtain polymers with varying numbers of silicon atoms in effort to understand the effect silicon plays on the micromechanical properties of the polymer chain. Due to the successful polymerization of di(4-pentenyl)dichlorosilane reported by Wagener, we chose to use Schrock's molybdenum catalyst for the ADMET polymerization.[17, 20-22] Using a monomer-to-catalyst ratio of 500:1 (0.2 mol% catalyst), Schrock's [Mo] catalyst was added to the dienes, and immediate bubbling (ethylene evolution) was observed. The polymerizations were stirred at room temperature under intermittent vacuum for 1 hr, followed by

dynamic vacuum at 40 °C for 3 days, during which the reaction solutions turned into viscous oils and stirring ceased (Scheme 2). The viscous oils were purified by precipitation into ice cold methanol to remove the [Mo] catalyst, leaving behind off-white tacky polymers (**P1**-**P4**). In some instances, the polymers remained a slight yellow-green color due to remaining trace amounts of the Schrock catalyst that could not be separated.

Scheme 2. ADMET polymerizations of Si-dienes **1**-**4**.



P1-**P4** were fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy which confirmed their structures. In the ^{1}H NMR spectra, a disappearance of the two vinyl proton resonances and the appearance of a new broad alkene feature at 5.38 ppm was observed, confirming the release of ethylene. PolySi$_n$-dienes (**P1**-**P4**) had ^{13}C NMR resonances consistent with the presence of both internal *cis*- and *trans*-olefins (Table 2). The content of *trans*-alkenes was determined to be ca. 80% by quantitative ^{13}C NMR studies which was consistent with what Wagener has reported in other polyolefins obtained via ADMET.[23] No change in ^{29}Si chemical shifts was observed between the monomers and polymers.

The molecular weights (M_n) of **P1**-**P4** determined by size exclusion chromatography (SEC) ranged from 9,500 - 21,700 g mol^{-1} with dispersities close to 2, which is typical for polymers generated from ADMET (Table 2).[24] An exception is **P3** (M_w/M_n = 4.3), which we hypothesize might be due to the formation of cyclic and/or oligomeric byproducts that could not be separated during polymer precipitation. Given Si's tendency to lessen ring strain relative to a carbocycle of

the same number of atoms,[16, 25, 26] the ring/chain equilibria in ADMET of Si-based polymers likely follow trends distinctive from all-carbon backbones; indeed, Wagener has characterized the significant formation of a 9-membered macrocycle (Z/E = 4:1) via post-polymerization back-biting.[27, 28] However, attempts to conclusively identify cyclic and/or oligomeric species by MALDI-TOF mass spectrometry were not conclusive due to challenges in ionization.

We attribute the decrease in molecular weight from **P2**-**P4** to uncontrollable differences in experimental conditions when the viscosity of the polymers caused a significant decrease in stirring rate. UV-vis studies of **P3** and **P4** in THF solutions revealed absorption maxima at 216 and 236 nm (Figures S74 and S75), respectively, which are consistent with the photophysical properties of **3**, **4**, and previously reported oligosilanes.[29-33] The mono- and disilane moieties of **P1** and **P2** were expected to absorb high-energy UV light (<200 nm) outside the window of our spectrophotometer ($Me_3SiSiMe_3$ λ_{max} = 197.5 nm)[32] and therefore UV-vis spectra for these samples were not obtained.

Table 2. Molecular weight, stereochemical, and thermal properties of polySi_n-dienes and polySi_n-epoxides.

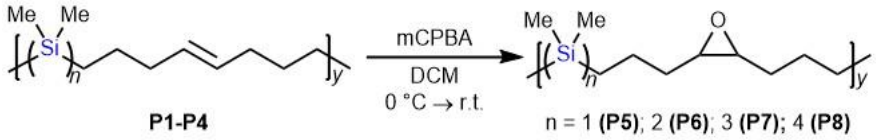
Polymer	M_n (kg mol^{-1})[a]	M_w/M_n	% trans	T_g (°C)
P1	20.3	2.0	83	n.d.[b]
P2	21.7	2.4	81	-80.4
P3	14.4	4.3	81	-82.8
P4	9.50	2.8	82	-77.5
P5	9.12	2.1	80	-54.7
P6	12.9	2.3	82	-61.9
P7	6.02	2.4	82	-62.7
P8	5.06	2.4	81	-51.8

[a]Molecular weight (M_n) was determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [polymer] = 1 mg/mL, 40 °C, 0.35 mL min^{-1}, 10 μL injection). [b]Lower T_g than the limit of the instrument.

We hypothesized that the olefin moieties of isolated **P1-P4** could be epoxidized to facilitate our ability to study their mechanical properties via SMFS, as has been done previously with other main-chain olefins.[34-36] To ensure that the Si–Si bonds within the polymer backbone were stable to the strong oxidizing conditions of epoxidation, we first explored the reaction of **3** and *meta*-chloroperoxybenzoic acid (*m*CPBA). A DCM solution of *m*CPBA was added to a cooled solution of **3** in DCM, and slowly warmed to room temperature over 20 hours. Analysis by ^{1}H NMR spectroscopy of the unpurified reaction mixture showed only 3-chlorbenzoic acid and signals

consistent with the di-epoxy. After basic aqueous work-up to remove the benzoic acid, the ^{1}H NMR spectrum showed the disappearance of the alkene proton resonances and the appearance of three new resonances between 2.46 and 2.90 ppm. These new peaks are consistent with previous reports of a similar alkoxide substituted silacyclobutane[37] and main-chain epoxides,[38, 39] and are therefore assigned as such. Further, no evidence of oxygen insertion into the Si–Si bonds or silicon bond cleavage was observed via ^{1}H NMR and IR (Figures S25-27, S52). Using the same conditions for the epoxidation of **3**, the new functionalized polymers (**P5**-**P8**) were isolated as colorless viscous liquids in 62-96% yields (Scheme 3). A nearly 50% decrease in molecular weight is observed via SEC when comparing the polySi_n-dienes to the polySi_n-epoxides, which could be associated with a difference in the hydrodynamic volume once the alkenes are functionalized with epoxide units. The polySi_n-epoxides were characterized structurally in solution by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Both ^{1}H and ^{13}C NMR spectra displayed resonances attributed to the presence of *cis*- and *trans*-epoxides on the polymer chains. For example, in the ^{1}H NMR spectrum of **P6**, chemical shifts at 2.91 and 2.66 ppm are assigned to the *cis*- and *trans*-epoxide protons, respectively (Figure 3a). Additional ^{1}H-^{1}H homonuclear correlation spectroscopy (COSY) shows cross peaks between the *cis*- and *trans*-epoxide protons and the neighboring CH_2 (1.56 ppm) (Figure 3b). ^{1}H-^{13}C heteronuclear single-quantum correlation spectroscopy (HSQC) allows the *cis*- and *trans*-carbon environments to be assigned due to an observed cross peak between the *cis*-proton resonance at 2.91 ppm and the carbon resonance at 57.0 ppm (Figure 3c). The *cis/trans* ratio after epoxidation (18:82) is in agreement with the *cis/trans* ratio of the starting polySi_2-diene (19:81) (Table 2). Absorption maxima for **P7** (215 nm) and **P8** (237 nm) are in agreement with **P3** and **P4** and support the absence of Si–O–Si units within polymer strands (Figure S76).

Scheme 3. Post-polymerization epoxidation of polymers **P1-P4**.



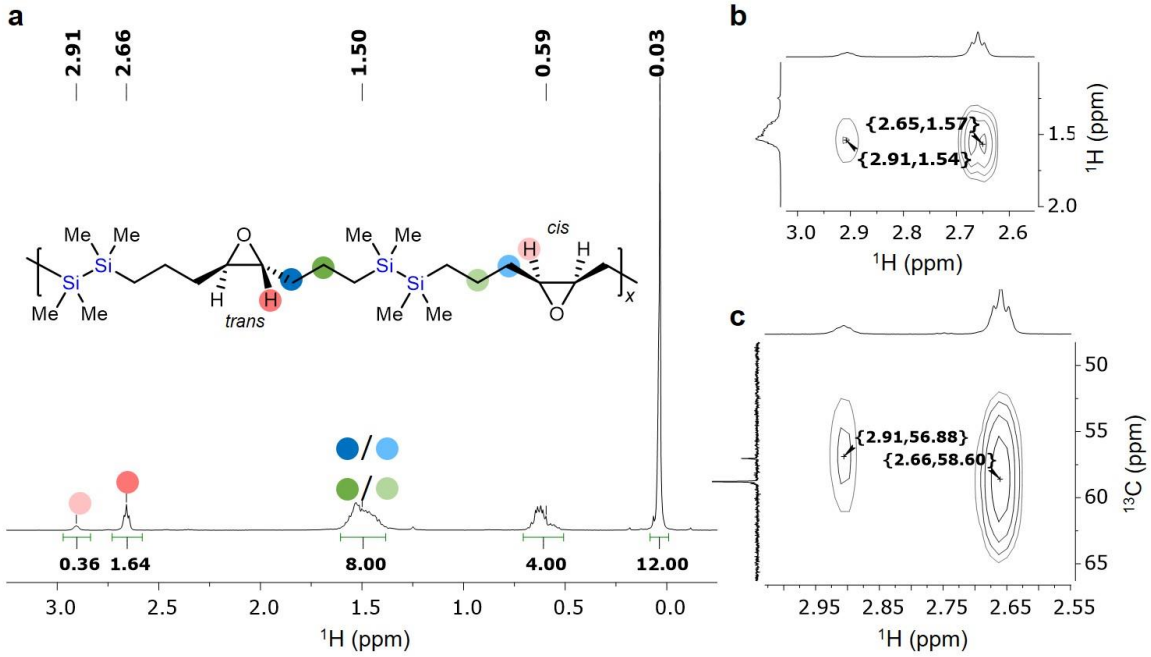


Figure 3. a) Cropped ^{1}H NMR spectrum of poly(epoxy-disilane) in $CDCl_3$ highlighting presence of *cis*- and *trans*-epoxide protons. b) ^{1}H-^{1}H COSY depicting cross peaks between *cis/trans*-epoxide protons and neighboring CH_2 resonance. c) ^{1}H-^{13}C HSQC confirms chemical shifts of carbon environments of *cis*- and *trans*-epoxides.

The thermal properties of polymers **P1-P8** were studied via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Given the well-known pyrolysis of polycarbosilanes and polysilanes to silicon carbide, under inert atmosphere,[40, 41] and the thermal decomposition of polysilanes typically beginning around 200-250 °C, we obtained air-free TGA data on **P1-P4** to determine the onset temperature for decomposition. Notably, **P2-P8** all exhibit low glass transition temperatures (T_g) which we attribute to the high degree of flexibility within

the polymer chains, and the small pendent groups on silicon. This is in contrast to our previous study wherein the poly(*trans*-SiCH) has a significantly higher T_g of 39.7 °C due to the presence of bulkier Ph substituents. The T_g of **P1** is below the limit of the DSC instrument employed (-90 °C), which is in agreement with the polycarbosilane previously reported by Wagener.[17] Additionally, an overall trend of higher T_g values for the polySi$_n$-epoxides was observed in comparison to the polySi$_n$-dienes. We attribute this trend to increased interchain interactions arising from the more polar epoxy groups that could reduce overall free volume and increase T_g.

We hypothesized that the high force elasticity of the polymer could be modulated by the number of silicon atoms along the polymer strand. To test this hypothesis, we carried out a DFT study of epoxidized monomer units capped by methyl groups, where the amount of dimethylsilene or methylene groups were varied (Figure 4). The structures of these compounds were optimized under external pulling force using the external force is explicitly included (EFEI) formalism,[42] where the force was applied to terminal methyl groups in increments of 50 pN ranging from force-free conditions to 3000 pN. We observed that silicon-silicon and silicon-carbon bonds tended to distort more under external force. Similarly, we found that bond angles around silicon atoms tend to distort along the strand more easily when compared to bond angles around carbon atoms. For example, at 3 nN, a ∠C-C-C bond angle distorted by 4.1° relative to the optimized structure at 0 nN, while a similarly situated ∠Si-Si-Si bond angle distorted by 15.4°. The monomer elasticity was calculated by determining the slope of the force-extension curves of the terminal methyl groups of monomers in linear regions from 1.5−3.0 nN. The monomer lengths were normalized by the distance between the two terminal methyl groups optimized under force-free conditions (Figure S100).

Consistent with our hypothesis, we found that by increasing the amount of dimethylsilene, the elasticity of the monomer decreases gradually with each additional Si atom along the strand, from 2.36 to 1.82 × 10^4 pN per unit L_0, whereas similar effects are not observed by incorporating additional methylene groups in the monomer strand (Figure 4).

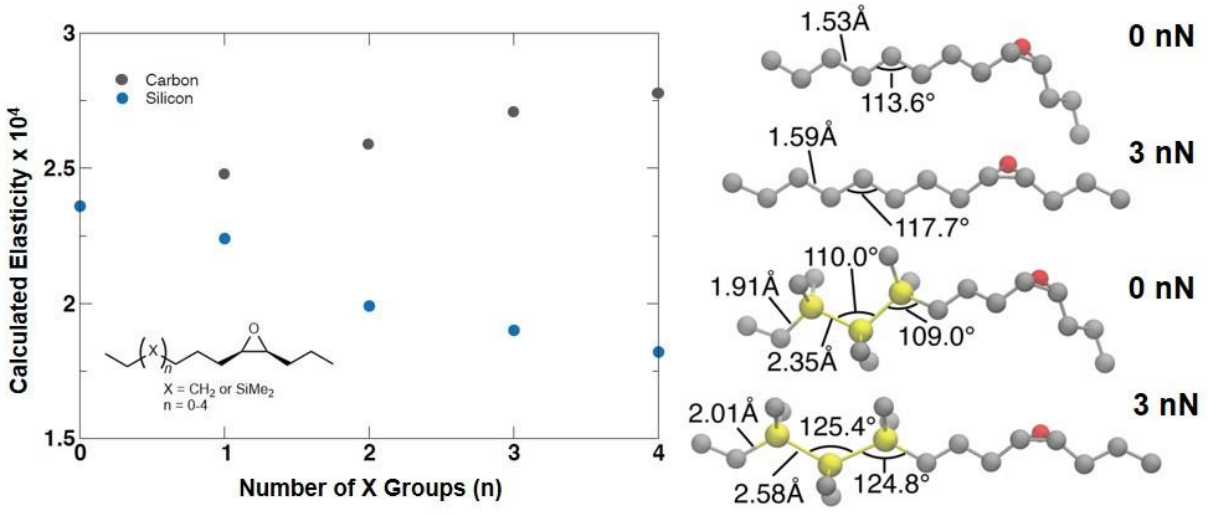


Figure 4. Calculated elasticity of epoxidized monomers containing different numbers of dimethylsilylene or methylene groups (left). Optimized structures of monomers with 3 dimethylsilene (bottom) or methylene (top) groups, at force-free (top) and 3 nN external applied force (right). Carbon is shown in grey, silicon in yellow, and oxygen in red, while hydrogens are omitted for clarity.

To further analyze the force-coupled behaviors of the polymers, we performed SMFS experiments on **P5-P8**. Achieving attachments that persist to high (~nN) forces is difficult for nonpolar and unreactive polymers such as **P1-P4**, but the combination of silicon AFM probes and epoxide functionality in **P5-P8** resulted in a sufficient number of pulling events to obtain statistically meaningful data about the relative single chain mechanics. Each force-separation curve was first fit with a modified freely jointed chain model to determine the contour length (L_0)

of the polymer subchain that was trapped between the cantilever tip of the AFM and the surface on which the substrate was adsorbed. The separation for each curve was then normalized to the length of its unit contour length as L/L_0 (Figure 5). To quantitatively evaluate the impact of increasing Si atoms on chain elasticity, the slopes of force-extension curves (f_{elastic}) in the enthalpic distortion region from 1000 pN to F_{max} at which the polymer detaches from the cantilever (analysis is limited to curves in which $F_{max} > 1{,}500$ pN), were compared across the series **P5-P8** (Table 3). The values of f_{elastic} have an experimental uncertainty of 15-25% across the series, which we attribute to the low molecular weights of the polymers. The characterization of short polymer strands is complicated by greater contributions from off-angle pulling[43, 44] and greater relative error from uncertainty in the spatial measurement. Nonetheless, the data are broadly consistent with the computational predictions. First, f_{elastic} of all of the polymers ($1.6 – 3.4 \times 10^4$ pN per unit L_0) is lower than that of the carbon-based polymer polycyclooctene (3.5×10^4 pN per unit L_0).[16] Second, the measured f_{elastic} is greater for the low Si-content polymers **P5** and **P6** (2.9×10^4 and 3.1×10^4 pN/L_0, respectively) than for the higher Si-content polymers **P7** and **P8** (2.1×10^4 and 1.6×10^4 pN/L_0, respectively). This variation in force constant corresponds to an increase of 9% to 33% in Si atom content per repeat unit. While **P5** does not have an f_{elastic} value higher than **P6-P8** as expected, it is the only polymer without Si–Si bonds, and due to its lower molecular weight, achieving a higher number of pulling events from SMFS to produce a statistical difference proved to be difficult.

The overall reduction in f_{elastic} with increasing Si content suggests an opportunity to tune the chain extension behavior through subtle variation in monomer design in a way that can eventually be used to probe the connection between the micromechanical properties of single strands and the properties of polymer networks made from those polymers. Furthermore, **P5-P8** all had higher

elasticity than our previously reported poly(*trans*-SiCH) (1.4 x 10^4 pN/L_0) with a silicon incorporation of 43% which is in agreement with the calculated trends.[16]

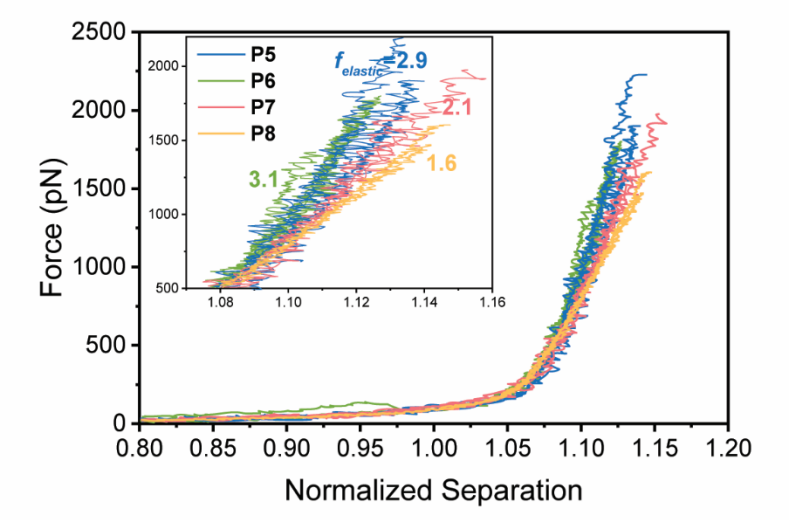


Figure 5. Representative single-molecule force-extension curves of **P5-P8** normalized at 500 pN.

Table 3. Slopes of the high-force region (F > 1000 pN) of the force-extension curves of **P5-P8**.

Polymer	$f_{elastic}$ (pN × 10^4 per unit L_0)
polycyclooctene	3.5 ± 0.1
P5	2.9 ± 0.3
P6	3.1 ± 0.3
P7	2.1 ± 0.3
P8	1.6 ± 0.4

CONCLUSIONS

In summary, we report the preparation of a new class of oligosilane dienes and their ADMET polymers. The polycarbooligosilanes were characterized in solution via NMR, which revealed polymer chains with a high percent of internal *trans*-olefins. DFT studies supported our hypothesis of polymer elasticity decreasing with an increasing number of Si–Si bonds. Functionalization of

the ADMET polymers with epoxide groups allowed us to experimentally investigate the elastic properties via SMFS, which was in agreement with the same trend. These data suggest that substitution of carbon with silicon in linear polymers will have a substantial effect on the mechanical properties of materials, and motivates the design of polymer networks with heavier carbon analogues that will be future synthetic targets in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge. Experimental procedures for monomer and polymer syntheses; spectral data (^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, IR, UV-vis); gel permeation chromatograms; thermal data (TGA and DSC); force-extension curves obtained from SMFS experiments; and computational details (PDF)

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REFERENCES

1. Abd-El-Aziz, A. S., Organometallic Polymers of the Transition Metals. *Macromol. Rapid Commun.* **2002,** *23* (17), 995-1031.

2. Carraher, C. E., Jr., Organometallic polymers. *J. Chem. Ed.* **1981,** *58* (11), 921.

3. Vidal, F.; Jäkle, F., Functional Polymeric Materials Based on Main-Group Elements. *Angew. Chem. Int. Ed.* **2019,** *58* (18), 5846-5870.

4. Wolf, M. O., Recent Advances in Conjugated Transition Metal-containing Polymers and Materials. *J. Inorg. Organomet. Polym. Mater.* **2006,** *16* (3), 189-199.

5. Duan, C.; Cai, W.; Huang, F.; Zhang, J.; Wang, M.; Yang, T.; Zhong, C.; Gong, X.; Cao, Y., Novel Silafluorene-Based Conjugated Polymers with Pendant Acceptor Groups for High Performance Solar Cells. *Macromolecules* **2010,** *43* (12), 5262-5268.

6. Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P., Polymers and the p-block elements. *Chem. Soc. Rev.* **2016,** *45* (4), 922-953.

7. Caseri, W., Polystannanes: processible molecular metals with defined chemical structures. *Chem. Soc. Rev.* **2016,** *45* (19), 5187-5199.

8. Katz, S. M.; Reichl, J. A.; Berry, D. H., Catalytic Synthesis of Poly(arylmethylgermanes) by Demethanative Coupling: A Mild Route to σ-Conjugated Polymers. *J. Am. Chem. Soc.* **1998,** *120* (38), 9844-9849.

9. Kumar, V. B.; Leitao, E. M., Properties and applications of polysilanes. *Appl. Organomet. Chem.* **2020,** *34* (3), e5402.

10. Power, P. P., An Update on Multiple Bonding between Heavier Main Group Elements: The Importance of Pauli Repulsion, Charge-Shift Character, and London Dispersion Force Effects. *Organometallics* **2020,** *39* (23), 4127-4138.

11. P. Power, P., Homonuclear multiple bonding in heavier main group elements. *J. Am. Chem. Soc., Dalton Trans.* **1998,** (18), 2939-2951.

12. Manners, I., Polymers and the Periodic Table: Recent Developments in Inorganic Polymer Science. *Angew. Chem. Int. Ed. Engl.* **1996,** *35* (15), 1602-1621.

13. Jiang, Q.; Gittens, A. F.; Wong, S.; Siegler, M. A.; Klausen, R. S., Highly selective addition of cyclosilanes to alkynes enabling new conjugated materials. *Chem. Sci.* **2022,** *13* (25), 7587-7593.

14. Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Nagamoto, I.; Ohshita, J.; Ishikawa, M.; Tanaka, K., Polymeric Organosilicon Systems. 26. Synthesis and Photochemical and Conducting Properties of Poly[(tetraethyldisilanylene)oligo(2,5-thienylenes)]. *Organometallics* **1996,** *15* (8), 2000-2008.

15. Ohshita, J.; Takata, A.; Kai, H.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K.; Harima, Y.; Kunugi, Y.; Yamashita, K.; Ishikawa, M., Synthesis of Polymers with Alternating Organosilanylene and Oligothienylene Units and Their Optical, Conducting, and Hole-Transporting Properties. *Organometallics* **2000,** *19* (22), 4492-4498.

16. Wakefield, H. t.; Kevlishvili, I.; Wentz, K. E.; Yao, Y.; Kouznetsova, T. B.; Melvin, S. J.; Ambrosius, E. G.; Herzog-Arbeitman, A.; Siegler, M. A.; Johnson, J. A.; Craig, S. L.; Kulik, H. J.; Klausen, R. S., Synthesis and Ring-Opening Metathesis Polymerization of a Strained trans-Silacycloheptene and Single-Molecule Mechanics of Its Polymer. *J. Am. Chem. Soc.* **2023,** *145* (18), 10187-10196.

17. Church, A. C.; Pawlow, J. H.; Wagener, K. B., Synthesis of Functionalized Polycarbosilanes via One-Pot ADMET Polymerization−Macromolecular Substitution. *Macromolecules* **2002,** *35* (15), 5746-5751.

18. Matloka, P. P.; Wagener, K. B., The acyclic diene metathesis (ADMET) polymerization approach to silicon containing materials. *J. Mol. Catal. A. Chem.* **2006,** *257* (1), 89-98.

19. Gómez, F. J.; Wagener, K. B., Germanium-containing polymers via acyclic diene metathesis. *J. Organomet. Chem.* **1999,** *592* (2), 271-277.

20. Bazan, G. C.; Oskam, J. H.; Cho, H. N.; Park, L. Y.; Schrock, R. R., Living ring-opening metathesis polymerization of 2,3-difunctionalized 7-oxanorbornenes and 7-oxanorbornadienes by Mo(CHCMe2R)(NC6H3-iso-Pr2-2,6)(O-tert-Bu)2 and Mo(CHCMe2R)(NC6H3-iso-Pr2-2,6)(OCMe2CF3)2. *J. Am. Chem. Soc.* **1991,** *113* (18), 6899-6907.

21. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M., Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins. *J. Am. Chem. Soc.* **1990,** *112* (10), 3875-3886.

22. Schrock, R. R., Recent Advances in High Oxidation State Mo and W Imido Alkylidene Chemistry. *Chem. Rev.* **2009,** *109* (8), 3211-3226.

23. Wagener, K. B.; Boncella, J. M.; Nel, J. G., Acyclic diene metathesis (ADMET) polymerization. *Macromolecules* **1991,** *24* (10), 2649-2657.

24. Li, H.; Caire da Silva, L.; Schulz, M. D.; Rojas, G.; Wagener, K. B., A review of how to do an acyclic diene metathesis reaction. *Polym. Int.* **2017,** *66* (1), 7-12.

25. Fang, Y.; Zhang, H.; Huang, Z.; Scinto, S. L.; Yang, J. C.; am Ende, Christopher W.; Dmitrenko, O.; Johnson, D. S.; Fox, J. M., Photochemical syntheses, transformations, and bioorthogonal chemistry of trans-cycloheptene and sila trans-cycloheptene Ag(i) complexes. *Chem. Sci.* **2018,** *9* (7), 1953-1963.

26. Shimizu, T.; Shimizu, K.; Ando, W., Synthesis, structure, and stabilities of trans-1,2-diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene. *J. Am. Chem. Soc.* **1991,** *113* (1), 354-355.

27. Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B., Solvent-free cyclization of linear dienes using olefin metathesis and the Thorpe-Ingold effect. *J. Am. Chem. Soc.* **1992,** *114* (27), 10978-10980.

28. Smith, D. W., Jr.; Wagener, K. B., Acyclic diene metathesis (ADMET) polymerization. Design and synthesis of unsaturated poly(carbosiloxanes). *Macromolecules* **1993,** *26* (7), 1633-1642.

29. Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A., Conformation Control of Oligosilanes Based on Configurationally Constrained Bicyclic Disilane Units. *Angew. Chem. Int. Ed.* **2000,** *39* (18), 3287-3290.

30. Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K., σσ* Transition in anti,cisoid Alternating Oligosilanes: Clear-Cut Evidence for Suppression of Conjugation Effect by a cisoid Turn. *J. Am. Chem. Soc.* **2003,** *125* (25), 7486-7487.

31. Gilman, H.; Atwell, W. H., The ultraviolet properties of some perphenylated linear and cyclic polysilanes. *J. Organomet. Chem.* **1965,** *4* (2), 176-178.

32. Gilman, H.; Atwell, W. H.; Schwebke, G. L., Ultraviolet properties of compounds containing the silicon-silicon bond. *J. Organomet. Chem.* **1964,** *2* (4), 369-371.

33. Fukazawa, A.; Tsuji, H.; Tamao, K., all-anti-Octasilane: Conformation Control of Silicon Chains Using the Bicyclic Trisilane as a Building Block. *J. Am. Chem. Soc.* **2006,** *128* (21), 6800-6801.

34. Bowser, B. H.; Wang, S.; Kouznetsova, T. B.; Beech, H. K.; Olsen, B. D.; Rubinstein, M.; Craig, S. L., Single-Event Spectroscopy and Unravelling Kinetics of Covalent Domains Based on Cyclobutane Mechanophores. *J. Am. Chem. Soc.* **2021,** *143* (13), 5269-5276.

35. Horst, M.; Yang, J.; Meisner, J.; Kouznetsova, T. B.; Martínez, T. J.; Craig, S. L.; Xia, Y., Understanding the Mechanochemistry of Ladder-Type Cyclobutane Mechanophores by Single Molecule Force Spectroscopy. *J. Am. Chem. Soc.* **2021,** *143* (31), 12328-12334.

36. Wang, L.; Zheng, X.; Kouznetsova, T. B.; Yen, T.; Ouchi, T.; Brown, C. L.; Craig, S. L., Mechanochemistry of Cubane. *J. Am. Chem. Soc.* **2022,** *144* (50), 22865-22869.

37. Matsumoto, K.; Kakehashi, M.; Ouchi, H.; Yuasa, M.; Endo, T., Synthesis and Properties of Polycarbosilanes Having 5-Membered Cyclic Carbonate Groups as Solid Polymer Electrolytes. *Macromolecules* **2016,** *49* (24), 9441-9448.

38. Bradbury, J. H.; Perera, M. C. S., Epoxidation of natural rubber studied by nmr spectroscopy. *J. Appl. Polym. Sci.* **1985,** *30* (8), 3347-3364.

39. Matic, A.; Hess, A.; Schanzenbach, D.; Schlaad, H., Epoxidized 1,4-polymyrcene. *Polym. Chem.* **2020,** *11* (7), 1364-1368.

40. Birot, M.; Pillot, J.-P.; Dunogues, J., Comprehensive Chemistry of Polycarbosilanes, Polysilazanes, and Polycarbosilazanes as Precursors of Ceramics. *Chem. Rev.* **1995,** *95* (5), 1443-1477.

41. Yajima, S.; Hasegawa, Y.; Okamura, K.; Matsuzawa, T., Development of high tensile strength silicon carbide fibre using an organosilicon polymer precursor. *Nature* **1978,** *273* (5663), 525-527.

42. Ribas-Arino, J.; Shiga, M.; Marx, D., Understanding Covalent Mechanochemistry. *Angew. Chem. Int. Ed.* **2009,** *48* (23), 4190-4193.

43. Ke, C.; Jiang, Y.; Rivera, M.; Clark, R. L.; Marszalek, P. E., Pulling Geometry-Induced Errors in Single Molecule Force Spectroscopy Measurements. *Biophys. J.* **2007,** *92* (9), L76-L78.

44. Rivera, M.; Lee, W.; Ke, C.; Marszalek, P. E.; Cole, D. G.; Clark, R. L., Minimizing Pulling Geometry Errors in Atomic Force Microscope Single Molecule Force Spectroscopy. *Biophys. J.* **2008,** *95* (8), 3991-3998.