

Facile Preparation of Tunable Polyborosiloxane Networks via Hydrosilylation

Colton A. D'Ambra,[▽] Patrick T. Getty,[▽] Taejun Eom, Michael Czuczola, Elizabeth A. Murphy, Souvagya Biswas, Allison Abdilla, Jodi M. Mecca, Thomas D. Bekemeier, Steven Swier, Alyssa Fielitz, Craig J. Hawker,* and Christopher M. Bates*



Cite This: *Chem. Mater.* 2024, 36, 5935–5942



Read Online

ACCESS |



Metrics & More

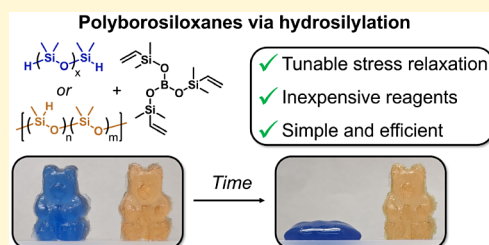


Article Recommendations



Supporting Information

ABSTRACT: Polyborosiloxanes are used in a variety of fields due to their unique dynamic properties. Traditionally, cross-linked polyborosiloxanes are prepared by incorporating boric acid into siloxane prepolymers, a process that is time-consuming, energy intensive, and challenging due to reagent immiscibility. Here, we report a versatile synthetic method to rapidly cure polyborosiloxane networks via hydrosilylation of chain end or backbone functionalized polydimethylsiloxane (PDMS) derivatives with an inexpensive trivinylboronate. Networks synthesized from these readily available building blocks cure in ~ 2 min at convenient temperatures (e.g., 90 °C) and exhibit enhanced viscoelastic behavior when compared to traditional polyborosiloxane networks fabricated via the conventional condensation route. By virtue of using efficient hydrosilylation chemistry, another key advantage of this synthetic platform is the ability to synthesize dynamic polyborosiloxanes with different network connectivity by simply using silicones with Si–H moieties placed at the chain ends (end-group) or distributed throughout the repeat-unit structure (pendant-group). The availability of other alkenes amenable to hydrosilylation provides an additional formulation handle to synthesize mixed dynamic–static networks with tunable control over stress relaxation and solvent resistance. In summary, the synthetic approach disclosed herein is a simple and accessible platform for preparing dynamic polyborosiloxanes with tunable material properties.



INTRODUCTION

Polyborosiloxane networks are a class of cross-linked polymers containing Si–O–B bonds. Since their discovery in the 1940s, the unique combination of dynamic material properties and thermal stability has generated significant industrial and academic interest, including the commercialization of a polyborosiloxane system known as Silly Putty.^{1,2} The useful viscoelasticity of polyborosiloxane networks arises from the dynamic character of borate ester (B–O) groups and the various mechanisms of exchange they undergo on different time scales, leading to frequency-dependent properties with control over a material flowing, bouncing, or breaking at different strain rates.³ Specifically, B–O covalent bonds can undergo rearrangement, which may occur through an associative or dissociative mechanism depending on the presence of water.^{4–10} In addition to covalent bond exchange, weaker intramolecular interactions also act as dynamic cross-links in polyborosiloxane networks. Dative bonds form between the empty p orbital of boron atoms and the lone pair electrons of oxygen atoms along the siloxane backbone. Residual water also results in partial hydrolysis of the B–O–Si bonds into B–OH groups that can then participate in additional hydrogen bonding.^{11,12} A combination of these numerous dynamic cross-links and the chemical/thermal stability of the parent polydimethylsiloxane building blocks explains the potential for polyborosiloxane-based materials to

find applications in shock-wave dissipators,^{13,14} impact-resistant composites,^{15,16} insulation,¹⁷ fireproofing,^{18,19} coatings,^{20,21} flexible conductors,^{22–24} and magnetic gels,²⁵ among other areas of contemporary importance.

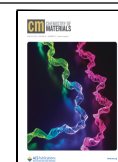
Despite such widespread use, the synthesis of polyborosiloxane networks has remained largely unchanged since the 1940s. The first reports of polyborosiloxane synthesis involved treating methyl-terminated PDMS with boric acid at elevated temperatures to produce a viscoelastic material.^{1,2} Since then, most reported methods rely on the condensation of boric acid and telechelic, silanol-terminated PDMS.^{3,26–30} There remain significant challenges with this approach. Notably, the condensation reaction of Si–OH and B–OH generates water as a byproduct that is deleterious to network integrity and, therefore, must be removed. Furthermore, boric acid is insoluble in PDMS, requiring high temperatures (>150 °C) to promote modest solubility. Alternatively, alcohol-based solvents may be used to dissolve boric acid into PDMS, but the solvent must then

Received: January 25, 2024

Revised: May 22, 2024

Accepted: May 23, 2024

Published: June 4, 2024



be removed through heat treatment. Both approaches require high temperature and long reaction times that cause chain-scission of the siloxane backbone, altering the final network structure and producing networks that are highly sensitive to preparation conditions.²⁷

A recently published, novel method for fabricating polyborosiloxane networks addresses these solubility problems and improves control over the resulting polymer network.³¹ Inspired by Rubinsztajn's 2014 report showcasing the dehydrocarbon condensation of trimethyl borate and diphenylsilane in the presence of tris(pentafluorophenylborane) to form a borosiloxane bond and the corresponding alkane hydrocarbon,³² the Muzafarov group synthesized polyborosiloxane networks by reacting alkyl borates with hydride-terminated PDMS and copolymers containing hydromethylsiloxane repeat units via hydrogen elimination.³¹ In doing so, they demonstrated unprecedented control over network architecture. However, this chemistry is intolerant to oxygen and produces flammable gaseous byproducts, limiting its viability in the development of new materials.

Inspired by the aforementioned challenges, we developed a robust synthetic platform for synthesizing polyborosiloxane networks that is simple, scalable, and tunable (Figure 1). The

materials having different molecular weights and architectures (Figure 1), as well as the coinorporation of complementary cross-linkers to yield mixed dynamic–static networks. In summary, this versatile and simple synthetic strategy unlocks access to a diverse range of dynamic PDMS-based materials.

EXPERIMENTAL SECTION

General Sample Preparation. After degassing the Si–H functional PDMS precursor under vacuum to remove any dissolved oxygen, tris(dimethylvinylsilyl)borate was added in a 1:1 ratio of Si–H:alkene units. Then, a solution of Karstedt's catalyst inhibited with dimethyl fumarate was added such that the resulting reaction mixture contained 20 ppm Pt and 60 ppm dimethyl fumarate by mass (Scheme 1). The mixture was

Scheme 1. Synthesis of a Polyborosiloxane Network Using Si–H Containing PDMS Copolymer and Tris(dimethylvinylsilyl)borate through Hydrosilylation Catalyzed by 20 ppm of Platinum Introduced through Karstedt's Catalyst Inhibited with 60 ppm Dimethyl Fumarate with No Added Solvent

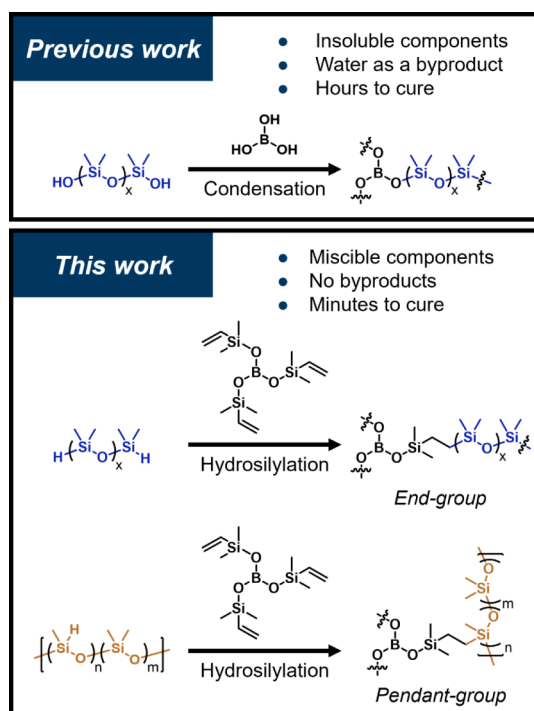
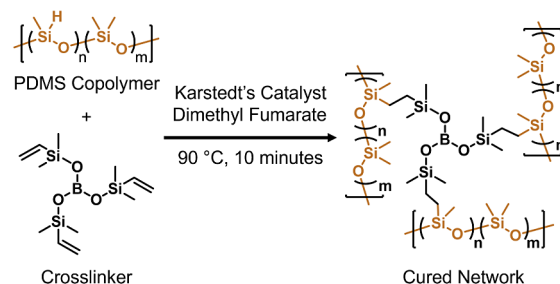


Figure 1. This work describes the efficient synthesis of polyborosiloxane networks by hydrosilylation chemistry, which is simple, efficient, and highly tunable in contrast to traditional condensation chemistry.

key ingredient in this method is the use of tris(dimethylvinylsilyl)borate as a cross-linker. This commercially available building block features both Si–O–B bonds and reactive alkenes that are amenable to hydrosilylation—a highly efficient addition reaction that proceeds rapidly in air.³³ An additional benefit of cross-linking via hydrosilylation chemistry rather than condensation reactions is that unwanted byproducts are avoided and the initial solubility of the cross-linker in PDMS is significantly improved (*vide infra*). As shown below, this approach is amenable to a wide variety of PDMS starting

poured into a container and heated at 90 °C for 10 min to form roughly 1.5 mm thick elastomers. Rheology discs with diameters of 25 mm were punched out at 140 °C and rapidly transferred to a rheometer. The temperature was chosen to minimize the impact of thermal expansion on the sample geometry during characterization.

RESULTS AND DISCUSSION

Rapid Mixing and Efficient Curing. The efficient mixing and curing of polyborosiloxane networks synthesized by hydrosilylation is evident visually (Figure 2a) and quantitatively as measured by rheometry (Figure 2b). As an initial demonstration, telechelic silyl-hydride-terminated PDMS (5 kDa), tris(dimethylvinylsilyl)borate, Karstedt's catalyst, and inhibitor (dimethyl fumarate) were mixed at room temperature, resulting in a transparent solution (Figure 2a, left).³⁴ As expected, after loading this solution onto a 25 mm rheometer plate, the mixture is a flowable liquid as evidenced by the storage modulus being less than the loss modulus ($G' < G''$). Subsequent heating of the solution to 90 °C at a rate of approximately 30 °C/min yielded an immediate increase in G' and solidification ($G' > G''$) followed by a plateau in G' and G'' within ~2 min (Figure 2b). Such rapid and complete curing at a moderate temperature with hydrosilylation is a significant advantage over traditional condensation, which typically takes hours to days at higher temperatures and may require the removal of solvent. As shown in Figure 2a (right), the resulting sample is transparent. Similar results were obtained for a variety of Si–H functional PDMS starting materials with varying

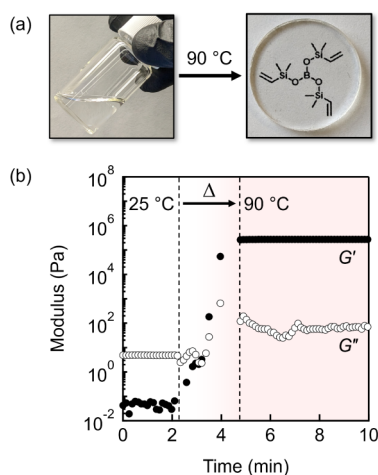


Figure 2. Rapid and efficient curing of polyborosiloxane networks via hydrosilylation. (a) Photograph of 5 kDa telechelic PDMS mixed with tris(dimethylvinylsilyl)borate, Karstedt's catalyst, and inhibitor (dimethyl fumarate) at room temperature followed by curing at 90 °C. (b) Oscillatory rheometry indicates fast and complete curing within minutes when heated from 25 to 90 °C at a rate of 30 °C/min.

molecular weights and Si–H groups either at the chain ends or distributed along the polymer backbone (Figure S1).

A key advantage of polyborosiloxane networks synthesized via hydrosilylation with tris(dimethylvinylsilyl)borate is synthetic choice. Other commercially available PDMS prepolymers can be used to form dynamic networks. For example, fast and efficient curing analogous to Figure 2 was also observed with various copolymers consisting of monomers of dimethylsiloxane and hydromethylsiloxane, where multiple Si–H groups are statistically distributed along the polymer chain (as summarized in Table S1), resulting in pendant-group networks. Significantly, tris(dimethylvinylsilyl)borate was miscible at all tested concentrations for every PDMS prepolymer studied. In all cases, transparent networks were formed with a 1:1 stoichiometry of Si–H groups to vinyl groups (Figure S1).

Network formation was further confirmed through infrared and nuclear magnetic resonance spectroscopy as shown in Figure 3; note that these data are shown for formulations containing PDMS copolymer as a representative example. Infrared spectra (Figure 3a) highlight the disappearance of Si–H bond vibrations at 2250 cm^{-1} , suggesting the hydrosilylation reaction reaches high conversion. Furthermore, both the cross-linker and the cured networks show vibrations at 1350 cm^{-1} as expected for Si–O–B bonds.³⁵ These data are further reinforced by ^{29}Si NMR (Figure 3b): a distinct peak at $\delta = 0.8$ ppm in the cross-linker shifts to $\delta = 13$ ppm after the addition of PDMS Si–H units to the vinyl groups. Peaks corresponding to Si–H bonds in the PDMS prepolymer that are present between $\delta = -35$ to -39 ppm also disappear upon coupling. Small peaks in the vicinity of $\delta = 6.6$ ppm corresponding to the trimethylsilyl end groups are also visible in both the starting material and the product.

Tunable Stress Relaxation. To compare the viscoelastic properties of polyborosiloxane networks prepared via our novel synthetic method (hydrosilylation) and previous approaches (condensation), stress-relaxation experiments were performed in triplicate for two sets of networks prepared via hydrosilylation: (i) end-group networks prepared from a 5 kDa telechelic Si–H functional PDMS and (ii) pendant-group networks prepared from a 6 kDa PDMS copolymer with an

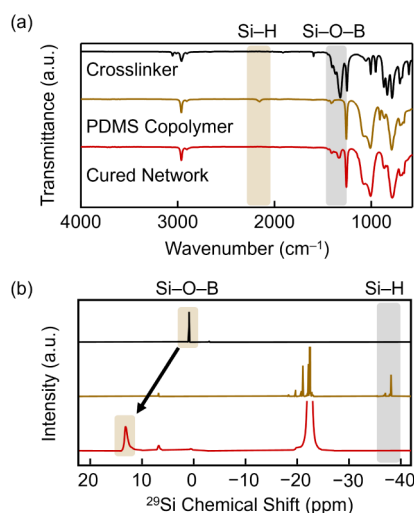


Figure 3. Efficient formation of polyborosiloxane networks containing a 20 kDa PDMS copolymer with 20 Si–H units as a representative example. (a) Fourier-transform infrared spectroscopy shows consumption of Si–H units from hydrosilylation and retention of Si–O–B bonds in the cured network. (b) ^{29}Si nuclear magnetic resonance spectroscopy shows a shift in the Si–O–B moiety from hydrosilylation and consumption of Si–H units. Note that the cross-linker and copolymer NMR were collected in CDCl_3 , while the spectrum of the cured network was necessarily acquired in the solid state.

average of 6 Si–H units per polymer chain.^{5,37} Step-strain measurements were collected over a range of temperatures to capture temperature-dependent stress-relaxation behavior (Figure 4a,b). Note that the temperature range shown for the pendant-group network is higher than that of the end-group material due to slower dynamics of the former. Experimental characteristic relaxation times ($\tau_{1/e}$) were determined as the time required for the relaxation modulus (G) to reach 0.37 of its original value.³⁸ Our polyborosiloxane networks show an Arrhenius relationship between the rate of stress relaxation and temperature (T) as expected for dynamic covalent networks (Figure 4c).³⁹ The average activation energy (E_a) of end-group (48 ± 2 kJ/mol) and pendant-group (41 ± 1 kJ/mol) networks falls within the range previously reported for similar dynamic motifs (34–77 kJ/mol),^{5,28,37,40} indicating that our polyborosiloxanes have similar material properties to traditional systems with greatly enhanced synthetic availability. Networks fabricated from precursors of different molecular weights also follow expected trends in activation energy for both end-group³⁷ and pendant-group networks.⁴¹ Specifically, the activation energy of end-group networks is independent of the molecular weight of the PDMS precursor (Figure S6), while the activation energy of pendant-group networks increases with increasing molecular weight of the PDMS precursor (Figure S7).

Comparing the error bars in Figure 4c, pendant-group networks showed significantly better reproducibility than their end-group counterparts. While the error in activation energy is small for both networks, variation in the Arrhenius prefactor for the end-group system is evident. This sample-to-sample variation may be due to chain-end fidelity and differences in the number of Si–H bonds per molecule for the different PDMS precursors. The network connectivity would be significantly impacted by lower-than-ideal chain-end fidelity (e.g., for $n = 2$), resulting in network defects and potentially dramatic variability in mechanical properties with small changes in formulation or

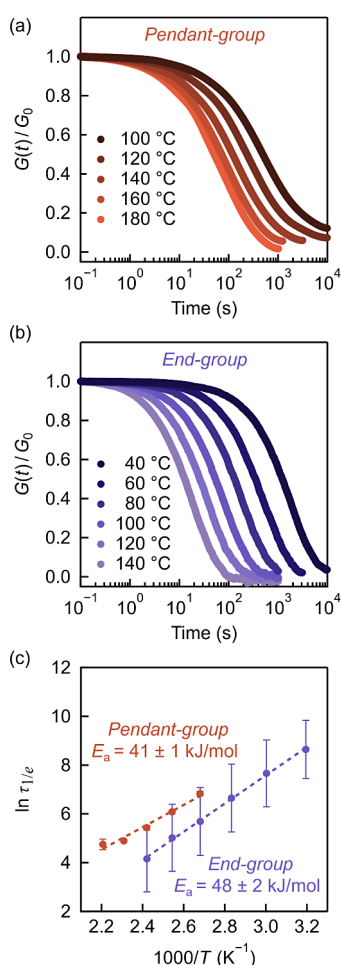


Figure 4. Polyborosiloxanes synthesized via hydrosilylation are dynamic and undergo tunable stress relaxation based on network architecture resulting from the use of different precursors (end-group vs pendant-group). Decay of normalized modulus over time after applying a 1% step strain at varying temperatures for (a) a pendant-group network prepared from a 6 kDa PDMS copolymer with an average of 6 Si–H units per polymer chain and (b) an end-group network prepared from a 5 kDa telechelic PDMS. (c) Arrhenius temperature dependence of the relaxation time measured via stress relaxation for both networks. Error bars represent standard deviations calculated from triplicate measurements.

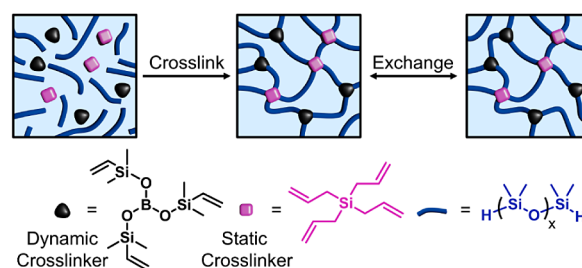
curing conditions. Conversely, the copolymer precursor has an average of 6 Si–H bonds per chain. Variation in the number of Si–H bonds, therefore, has less of an effect on overall connectivity in pendant-group networks, leading to improved reproducibility. We emphasize that the ability to use Si–H-containing PDMS copolymers as a starting material in the synthesis of polyborosiloxane networks is another distinguishing advantage of the hydrosilylation synthetic route, as analogous precursors with silanols distributed along the backbone (for traditional condensation networks) are not commercially available.

Single and stretched exponential fits applied to the stress-relaxation data further suggest more homogeneous networks are generated from hydrosilylation compared to traditional condensation polymerization. Representative fits are shown in Figure S8. The data (Tables S2 and S3) display good agreement for three different time constants— $\tau_{1/e}$, τ_{exp} , and τ_{KWW} —calculated via three different methods—experimental, single

exponential fit, and stretched exponential fit, respectively. For end-group networks, the stretched exponential model provides the best fit and β values near 1 (0.84–0.89), suggesting modest heterogeneity in the relaxation environment. In contrast, recent work from Porath and Evans³⁷ on similar polyborosiloxane networks synthesized via condensation inferred $\beta = 0.64$ –0.83. The higher values of β and tighter range suggest networks prepared via hydrosilylation are more homogeneous, likely due to the high conversion of hydrosilylation and lack of deleterious water produced by condensation. Polyborosiloxane networks prepared from PDMS precursors of different molecular weights all yielded similar qualitative results, with differences in relaxation times related to architecture, the concentration of cross-links, and network defectivity (Figure S9).

Mixed Cross-Linkers. An additional advantage of hydrosilylation is the ability to introduce multiple, different cross-linking groups into the starting formation. This provides a simple mechanism to tune dynamics and mechanical properties through formulation in analogy to other types of dynamic chemistry.^{4,42–45} As an illustrative example, tetraallylsilane was selected as a co-cross-linker to improve the dimensional stability of polyborosiloxane networks by introducing static cross-links in addition to dynamic cross-links derived from tris(dimethylvinylsilyl)borate (Scheme 2).

Scheme 2. Hydrosilylation Chemistry Unlocks the Ability to Mix Dynamic and Static Cross-Linkers to Produce Mixed Polyborosiloxane Systems; Tetraallylsilane Is Shown as a Representative Example of a Static Cross-Linker



The rate of stress relaxation in polyborosiloxanes containing mixed cross-linkers was found to be readily tunable based on the stoichiometric ratio between dynamic and static cross-links (Figure 5). As the incorporation of static cross-links increases, the rate of stress relaxation decreases due to a reduction in the number of exchangeable bonds. To visually showcase the different stress-relaxation dynamics, bear-shaped samples were created from different formulations and monitored over time under ambient conditions (Figure 5a). The incorporation of static cross-links significantly slowed stress relaxation at room temperature. A fully dynamic material (0% static cross-links) showed significant deformation after 6 days, while the three samples with static cross-links exhibited no such change. After 16 days, the sample with 30% static cross-links started to show slight deformation that became more pronounced after 30 days. Even after this extended amount of time, samples with a higher loading of static cross-linker (70% and 100%) retained their original dimensions. The rheometry data in Figure 5b quantify this behavior and highlight the pronounced effect static cross-linker has on the rate of stress relaxation, as depicted, at 140 °C; samples can be readily designed to fully relax (0% static) or undergo minimal relaxation (100% static) with intermediate behavior readily achieved by simply tuning the starting

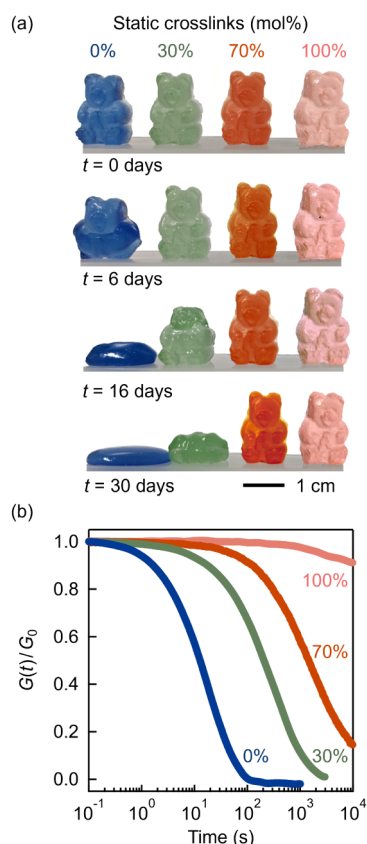


Figure 5. Mixtures of static and dynamic cross-linkers provide fine control over relaxation dynamics in polyborosiloxane networks. (a) Visual representation of changes in shape over time for an end-group network prepared from a 5 kDa telechelic PDMS with varied amounts of tris(dimethylvinylsilyl)borate as the dynamic cross-linker and tetraallylsilane as the static cross-linker. The listed composition corresponds to the percentage of cross-links from tetraallylsilane relative to the total number of cross-links. (b) Corresponding stress-relaxation measurements performed at 140 °C.

formulation, i.e., the relative ratio of static to dynamic cross-linker. As expected, however, the increase in dimensional stability afforded by the static co-cross-linker is offset by a decrease in the ability to reprocess these networks (Figure S11).

Typical polyborosiloxane networks are susceptible to hydrolysis and alcoholysis of Si–O–B bonds, which can limit the applicability of these materials. For example, a common method to remove Silly Putty from clothing is the use of rubbing alcohol (isopropanol) to degrade the network. We postulated that introducing static cross-links would also impart alcohol-based solvent resistance by stabilizing the network. To test this hypothesis, fish-shaped samples were prepared with different ratios of static and dynamic cross-links (Figure S13), followed by soaking in methanol for 4 days (Figure 6). Significantly, the introduction of static cross-links to both the end-group and pendant-group networks provides structural integrity that prevents complete dissolution after methanolysis of the borate ester bonds.⁴⁶

CONCLUSIONS

A novel method for preparing polyborosiloxane networks was developed to take advantage of commercially available starting materials and robust hydrosilylation chemistry. Key to this approach is the use of tris(dimethylvinylsilyl)borate as an

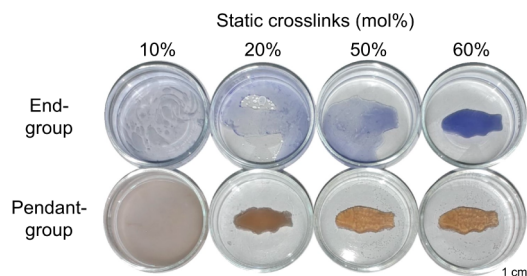


Figure 6. Introduction of static cross-linker in the hydrosilylation formulation imparts structural stability in the presence of reactive solvent (as depicted: methanol) that disrupts borate ester cross-links. Images show end-group networks prepared from a 5 kDa telechelic PDMS (top, blue) and pendant-group networks prepared from a 6 kDa PDMS copolymer with an average of 6 Si–H units per polymer chain (bottom, orange). Cross-linkers used were tris(dimethylvinylsilyl)borate (dynamic) and tetraallylsilane (static). The listed composition corresponds to the percentage of cross-links from tetraallylsilane relative to the total number of cross-links. The dishes were covered during evaluation to limit evaporation of methanol.

efficient cross-linker for PDMS precursors that contain Si–H bonds. The placement of Si–H groups at either the chain ends or throughout a copolymer backbone leads to significantly different network structures and performance. The efficient nature of cross-linking via hydrosilylation was confirmed with rheometry, infrared spectroscopy, and ²⁹Si nuclear magnetic resonance spectroscopy.³⁶ Complete curing can be achieved in minutes at 90 °C, yielding dynamic networks that undergo tunable stress relaxation as a function of formulation and temperature. Importantly, the relaxation time and Arrhenius temperature dependence are consistent with previously reported polyborosiloxane-based materials that were synthesized by traditional condensation chemistry. In addition to efficient, low-temperature curing, hydrosilylation readily enables the incorporation mixture of static and dynamic cross-links through formulation to control relaxation dynamics and solvent resistance. In summary, hydrosilylation is a simple, powerful, and accessible synthetic platform for creating dynamic siloxane-based materials that we anticipate will be broadly useful throughout the materials community and beyond.

ASSOCIATED CONTENT

Data Availability Statement

Data is available free of charge from the Dryad repository at: DOI: 10.5061/dryad.tx95x6b54.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.4c00224>.

Detailed experimental procedures and information on NMR and FTIR instrumentation and data collection procedures; summary of pendant-group Si–H functional PDMS copolymers utilized during the study (Table S1); representative image of rheology discs made from the listed starting polymer and tris(dimethylvinylsilyl) borate (Figure S1); triplicate stress relaxation measurements for a pendant-group network prepared from a 6 kDa PDMS copolymer with an average of 6 Si–H moieties per polymer chain (Figure S2); triplicate stress relaxation measurements for an end-group network prepared from a 5 kDa telechelic PDMS (Figure S3); 140 °C for an end-group network prepared from a 5 kDa telechelic PDMS

with (a) 30% static cross-links and (b) 70% static cross-links (Figure S4); representative example of determining appropriate strain for stress-relaxation experiments (Figure S5); stress relaxation at varying temperature for an end-group network prepared from a 20 kDa PDMS precursor (Figure S6); stress relaxation at varying temperature for a pendant-group network prepared from a 20 kDa PDMS copolymer with an average of 20 Si–H units per polymer chain (Figure S7); representative single and stretched exponential fits for stress relaxation measurements for an end-group network prepared from a 5 kDa telechelic PDMS (Figure S8); average stress relaxation times determined via experiment ($\tau_{1/e}$) and single (τ_{exp}) and stretched (τ_{KWW}) exponential fits for an end-group network prepared from a 5 kDa telechelic PDMS (Table S2); average stress-relaxation times determined via experiment ($\tau_{1/e}$) and single (τ_{exp}) and stretched (τ_{KWW}) exponential fits for a pendant-group network prepared from a 6 kDa PDMS copolymer with an average of 6 Si–H moieties per polymer chain (Table S3); stress-relaxation experiments for both pendant- and end-group networks prepared from PDMS precursors of varying molecular weights (Figure S9); frequency sweeps conducted at 100 °C and 1% strain of (a) an end-group network fabricated from a 5 kDa PDMS precursor and (b) a pendant-group network fabricated from a 6 kDa PDMS copolymer with an average of 6 Si–H moieties per polymer chain (Figure S10); reprocessing of end-group networks fabricated with varying amounts of static co-cross-linker (Figure S11); swelling ratio and gel fraction of pendant-group networks prepared from a 6 kDa PDMS copolymer with an average of 6 Si–H moieties per polymer chain and end-group networks prepared from a 5 kDa telechelic PDMS with the corresponding ratio of static cross-links produced by tuning the ratio of tris(dimethylvinylsilyl)borate to tetraallylsilane (Figure S12); initial image of fish-shaped cross-linked networks prepared from 5 kDa end-group Si–H functional PDMS (*top*, blue) or 6 kDa pendant-group Si–H functional PDMS (*bottom*, orange) containing an average of 6 Si–H moieties per polymer chain (Figure S13) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Craig J. Hawker – Materials Department, Materials Research Laboratory, and Department of Chemistry and Biochemistry, University of California, California, Santa Barbara 93106, United States; orcid.org/0000-0001-9951-851X; Email: hawker@mrl.ucsb.edu

Christopher M. Bates – Materials Department, Materials Research Laboratory, Department of Chemistry and Biochemistry, and Department of Chemical Engineering, University of California, California, Santa Barbara 93106, United States; orcid.org/0000-0002-1598-794X; Email: cbates@ucsb.edu

Authors

Colton A. D'Ambra – Materials Department, University of California, California, Santa Barbara 93106, United States

Patrick T. Getty – Materials Department, University of California, California, Santa Barbara 93106, United States

Taejun Eom – Materials Research Laboratory, University of California, California, Santa Barbara 93106, United States

Michael Czuczola – Department of Chemistry and Biochemistry, University of California, California, Santa Barbara 93106, United States

Elizabeth A. Murphy – Department of Chemistry and Biochemistry, University of California, California, Santa Barbara 93106, United States; orcid.org/0000-0003-0846-7943

Souvagya Biswas – Core R&D, Midland, Michigan 48674, United States; orcid.org/0000-0001-5201-2562

Allison Abdilla – Dow Performance Silicones, Auburn, Michigan 48611, United States

Jodi M. Mecca – Dow Performance Silicones, Auburn, Michigan 48611, United States

Thomas D. Bekemeier – Core R&D, Midland, Michigan 48674, United States

Steven Swier – Dow Performance Silicones, Auburn, Michigan 48611, United States

Alyssa Fielitz – Core R&D, Midland, Michigan 48674, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.chemmater.4c00224>

Author Contributions

[†]C.A.D. and P.T.G. contributed equally. The manuscript was written by C.A.D., P.T.G., T.E., M.C., E.A.M., J.M.M., T.D.B., S.S., C.J.H., and C.M.B. Experiments were designed by C.A.D., P.T.G., T.E., M.C., E.A.M., J.M.M., T.D.B., S.S., C.J.H., and C.M.B. and performed by C.A.D., P.T.G., and T.E. All authors have given approval to the final version of the manuscript.

Funding

The research reported here was primarily supported by the National Science Foundation Materials Research Science and Engineering Center (MRSEC) at UC Santa Barbara (DMR-2308708, IRG-1, C.M.B. and C.J.H., synthesis) and the BioPACIFIC Materials Innovation Platform of the National Science Foundation under Award No. DMR-1933487 (C.M.B., C.J.H., equipment and characterization). The research reported here made use of shared facilities of the UC Santa Barbara MRSEC (NSF DMR-2308708), a member of the Materials Research Facilities Network (www.mrfn.org). This research was also supported by Dow through the Dow Materials Institute at UC Santa Barbara.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Prof. Rachel A. Segalman and Prof. Glenn H. Fredrickson for intellectual discussions, Dr. Hongjun Zhou and Dr. Jerry Hu for help with NMR experiments, Dr. Rachel Behrens for assistance with rheology characterization, and Dr. Amanda Strom for assistance with FTIR characterization.

REFERENCES

- (1) Wright, J. G. E. Process for Making Puttylike Elastic Plastic, Siloxane Derivative Composition Containing Zinc Hydroxide US 2,541,851 A, 1951.
- (2) McGregor, R. R.; Warrick, E. Treating Dimethyl Silicone Polymer with Boric Oxide US 2,431,878 A, 1947.
- (3) Tang, M.; Wang, W.; Xu, D.; Wang, Z. Synthesis of Structure-Controlled Polyborosiloxanes and Investigation on Their Viscoelastic Response to Molecular Mass of Polydimethylsiloxane Triggered by Both Chemical and Physical Interactions. *Ind. Eng. Chem. Res.* **2016**, *55* (49), 12582–12589.

- (4) Cash, J. J.; Kubo, T.; Dobbins, D. J.; Sumerlin, B. S. Maximizing the Symbiosis of Static and Dynamic Bonds in Self-Healing Boronic Ester Networks. *Polym. Chem.* **2018**, *9* (15), 2011–2020.
- (5) Röttger, M.; Domenech, T.; Van Der Weegen, R.; Breuillac, A.; Nicolăi, R.; Leibler, L. High-Performance Vitrimers from Commodity Thermoplastics through Dioxaborolane Metathesis. *Science* **2017**, *356*, 62–65.
- (6) Cash, J. J.; Kubo, T.; Bapat, A. P.; Sumerlin, B. S. Room-Temperature Self-Healing Polymers Based on Dynamic-Covalent Boronic Esters. *Macromolecules* **2015**, *48* (7), 2098–2106.
- (7) Yang, Y.; Du, F. S.; Li, Z. C. Thermally Healable and Reprocessable Polymethacrylate Networks Based on Diol-Mediated Metathesis of 6-Membered Boronic Esters. *Polym. Chem.* **2020**, *11* (11), 1860–1870.
- (8) Cho, S.; Hwang, S. Y.; Oh, D. X.; Park, J. Recent Progress in Self-Healing Polymers and Hydrogels Based on Reversible Dynamic B-O Bonds: Boronic/Boronate Esters, Borax, and Benzoxaborole. *J. Mater. Chem. A Mater.* **2021**, *9* (26), 14630–14655.
- (9) Zhang, X.; Zhao, Y.; Wang, S.; Jing, X. Cross-Linked Polymers Based on B-O Bonds: Synthesis, Structure and Properties. *Mater. Chem. Front* **2021**, *5* (15), 5534–5548.
- (10) Bapat, A. P.; Sumerlin, B. S.; Sutti, A. Bulk Network Polymers with Dynamic B-O Bonds: Healable and Reprocessable Materials. *Mater. Horiz.* **2020**, *7* (3), 694–714.
- (11) Tang, M.; Zheng, P.; Wang, K.; Qin, Y.; Jiang, Y.; Cheng, Y.; Li, Z.; Wu, L. Autonomous self-healing, Self-Adhesive, Highly Conductive Composites Based on a Silver-Filled Polyborosiloxane/Polydimethylsiloxane Double-Network Elastomer. *J. Mater. Chem. A* **2019**, *7* (48), 27278–27288.
- (12) Liu, F.; Lin, Y.; Yang, X.; Zhang, D.; Xu, D.; Luan, S. Study of Hydrolysis Behaviour of Polyborosiloxane. *Polymer* **2023**, *278*, 126005.
- (13) Lee, J.; Jing, B. B.; Porath, L. E.; Sottos, N. R.; Evans, C. M. Shock Wave Energy Dissipation in Catalyst-Free Poly(Dimethylsiloxane) Vitrimers. *Macromolecules* **2020**, *53* (12), 4741–4747.
- (14) Zhao, J.; Jiang, N.; Zhang, D.; He, B.; Chen, X. Study on Optimization of Damping Performance and Damping Temperature Range of Silicone Rubber by Polyborosiloxane Gel. *Polymers* **2020**, *12* (5), 1196.
- (15) Xu, C.; Wang, Y.; Wu, J.; Song, S.; Cao, S.; Xuan, S.; Jiang, W.; Gong, X. Anti-Impact Response of Kevlar Sandwich Structure with Silly Putty Core. *Compos. Sci. Technol.* **2017**, *153*, 168–177.
- (16) Myronidis, K.; Thielke, M.; Kopeć, M.; Meo, M.; Pinto, F. Polyborosiloxane-based, dynamic shear stiffening multilayer coating for the protection of composite laminates under Low Velocity Impact. *Compos. Sci. Technol.* **2022**, *222*, 109395.
- (17) Yue, C.; Zhao, L.; Guan, L.; Zhang, X.; Qu, C.; Wang, D.; Weng, L. Vitrimeric Silicone Composite with High Thermal Conductivity and High Repairing Efficiency as Thermal Interface Materials. *J. Colloid Interface Sci.* **2022**, *620*, 273–283.
- (18) Qiu, J.; Lai, X.; Li, H.; Gao, J.; Zeng, X.; Liao, X. Facile Fabrication of a Novel Polyborosiloxane-Decorated Layered Double Hydroxide for Remarkably Reducing Fire Hazard of Silicone Rubber. *Composites, Part B* **2019**, *175*, 107068.
- (19) Dong, Y.; Chen, W.; Zhou, X. Synthesis and Characterization of Amino-Terminated Phosphorous Polyborosiloxane and Its Effect on Flame Retardancy of Polymethacrylimide. *Mater. Today Chem.* **2021**, *20*, 100437.
- (20) Ma, J.; Porath, L. E.; Haque, M. F.; Sett, S.; Rabbi, K. F.; Nam, S. W.; Miljkovic, N.; Evans, C. M. Ultra-Thin Self-Healing Vitriimer Coatings for Durable Hydrophobicity. *Nat. Commun.* **2021**, *12* (1), 5210.
- (21) Liu, K.; Pei, A.; Lee, H. R.; Kong, B.; Liu, N.; Lin, D.; Liu, Y.; Liu, C.; Hsu, P. C.; Bao, Z.; Cui, Y. Lithium Metal Anodes with an Adaptive “Solid-Liquid” Interfacial Protective Layer. *J. Am. Chem. Soc.* **2017**, *139* (13), 4815–4820.
- (22) Wu, Q.; Xiong, H.; Peng, Y.; Yang, Y.; Kang, J.; Huang, G.; Ren, X.; Wu, J. Highly Stretchable and Self-Healing “Solid-Liquid” Elastomer with Strain-Rate Sensing Capability. *ACS Appl. Mater. Interfaces* **2019**, *11* (21), 19534–19540.
- (23) Wu, T.; Chen, B. Synthesis of Multiwalled Carbon Nanotube-Reinforced Polyborosiloxane Nanocomposites with Mechanically Adaptive and Self-Healing Capabilities for Flexible Conductors. *ACS Appl. Mater. Interfaces* **2016**, *8* (36), 24071–24078.
- (24) Zhao, C.; Wang, Y.; Gao, L.; Xu, Y.; Fan, Z.; Liu, X.; Ni, Y.; Xuan, S.; Deng, H.; Gong, X. High-Performance Liquid Metal/Polyborosiloxane Elastomer toward Thermally Conductive Applications. *ACS Appl. Mater. Interfaces* **2022**, *14* (18), 21564.
- (25) Wang, Y.; Wang, S.; Xu, C.; Xuan, S.; Jiang, W.; Gong, X. Dynamic Behavior of Magnetically Responsive Shear-Stiffening Gel under High Strain Rate. *Compos. Sci. Technol.* **2016**, *127*, 169–176.
- (26) Liu, Z.; Picken, S. J.; Besseling, N. A. M. Polyborosiloxanes (PBSs), Synthetic Kinetics, and Characterization. *Macromolecules* **2014**, *47* (14), 4531–4537.
- (27) Kurkin, A.; Lipik, V.; Tan, K. B. L.; Seah, G. L.; Zhang, X.; Tok, A. I. Y. Correlations Between Precursor Molecular Weight and Dynamic Mechanical Properties of Polyborosiloxane (PBS). *Macromol. Mater. Eng.* **2021**, *306* (11), 2100360.
- (28) Porath, L.; Huang, J.; Ramlawi, N.; Derkaloustian, M.; Ewoldt, R. H.; Evans, C. M. Relaxation of Vitrimers with Kinetically Distinct Mixed Dynamic Bonds. *Macromolecules* **2022**, *55* (11), 4450–4458.
- (29) Zhao, Y.; Qin, T.; Jiang, C.; Li, J.; Xiong, Y.; Liu, S.; Qin, J.; Shi, X.; Zhang, G. Boronic Ester-Based Vitrimeric Methylvinyl Silicone Elastomer with “Solid-Liquid” Feature and Rate-Dependent Mechanical Performance. *Polymer* **2023**, *265*, 125545.
- (30) Seetapan, N.; Fuongfuchai, A.; Sirikitikul, D.; Limpanyoon, N. Unimodal and Bimodal Networks of Physically Crosslinked Polyborodimethylsiloxane: Viscoelastic and Equibiaxial Extension Behaviors. *J. Polym. Res.* **2013**, *20*, 183.
- (31) Drozdov, F. V.; Milenin, S. A.; Gorodov, V. V.; Demchenko, N. V.; Buzin, M. I.; Muzafarov, A. M. Crosslinked Polymers Based on Polyborosiloxanes: Synthesis and Properties. *J. Organomet. Chem.* **2019**, *891*, 72–77.
- (32) Rubinsztajn, S. New Facile Process for Synthesis of Borosiloxane Resins. *J. Inorg. Organomet. Polym. Mater.* **2014**, *24* (6), 1092–1095.
- (33) Hofmann, R. J.; Vlatkovic, M.; Wiesbrock, F. Fifty Years of Hydrosilylation in Polymer Science: A Review of Current Trends of Low-Cost Transition-Metal and Metal-Free Catalysts, Non-Thermally Triggered Hydrosilylation Reactions, and Industrial Applications. *Polymers* **2017**, *9* (10), 534.
- (34) Lukin, R. Y.; Kuchkaev, A. M.; Sukhov, A. V.; Bekmukhamedov, G. E.; Yakhvarov, D. G. Platinum-Catalyzed Hydrosilylation in Polymer Chemistry. *Polymers* **2020**, *12* (10), 2174.
- (35) Zinchenko, G. A.; Milieshekevich, V. P.; Kozlova, N. Investigation of the Synthesis and Hydrolytic Degradation of Polyborodimethylsiloxanes. *Polym. Sci. U.S.S.R.* **1981**, *23* (6), 1421–1429.
- (36) Drozdov, F. V.; Manokhina, E. A.; Vu, T. D.; Muzafarov, A. M. Polyborosiloxanes (PBS): Evolution of Approaches to the Synthesis and the Prospects of Their Application. *Polymers* **2022**, *14* (22), 4824.
- (37) Porath, L. E.; Evans, C. M. Importance of Broad Temperature Windows and Multiple Rheological Approaches for Probing Viscoelasticity and Entropic Elasticity in Vitrimers. *Macromolecules* **2021**, *54* (10), 4782–4791.
- (38) Christopher, W. M. Rheology: Principles. In *Measurements, and Applications*; VCH, 1994.
- (39) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965–968.
- (40) Cromwell, O. R.; Chung, J.; Guan, Z. Malleable and Self-Healing Covalent Polymer Networks through Tunable Dynamic Boronic Ester Bonds. *J. Am. Chem. Soc.* **2015**, *137* (20), 6492–6495.
- (41) Lessard, J. J.; Stewart, K. A.; Sumerlin, B. S. Controlling Dynamics of Associative Networks through Primary Chain Length. *Macromolecules* **2022**, *55* (22), 10052–10061.
- (42) Robinson, L. L.; Self, J. L.; Fusi, A. D.; Bates, M. W.; Hawker, C. J.; Bates, C. M.; Sample, C. S. Chemical and Mechanical Tunability of 3D-Printed Dynamic Covalent Networks Based on Boronate Esters. *ACS Macro Lett.* **2021**, *10*, 857–863.

(43) Li, L.; Chen, X.; Jin, K.; Torkelson, J. M. Vitrimers Designed Both to Strongly Suppress Creep and to Recover Original Cross-Link Density after Reprocessing: Quantitative Theory and Experiments. *Macromolecules* **2018**, *51* (15), 5537–5546.

(44) Breuillac, A.; Kassalias, A.; Nicolăy, R. Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and Dynamic Cross-Links. *Macromolecules* **2019**, *52* (18), 7102–7113.

(45) Saed, M. O.; Gablier, A.; Terentejv, E. M. Liquid Crystalline Vitrimers with Full or Partial Boronic-Ester Bond Exchange. *Adv. Funct. Mater.* **2020**, *30* (3), 1906458.

(46) Konuray, O.; Fernández-Francos, X.; Ramis, X. Structural Design of CANs with Fine-Tunable Relaxation Properties: A Theoretical Framework Based on Network Structure and Kinetics Modeling. *Macromolecules* **2023**, *56* (13), 4855–4873.