Influence of the Tetraalkoxysilane Crosslinker on the Properties of Polysiloxane-based Elastomers Prepared by the Lewis Acid-Catalysed Piers-Rubinsztajn Reaction

Andrew M. Hickman,a,b Nikola Chmel,c Neil R. Cameron,d,b Daniel J. Keddie,e Tara L. Schiller* a,b

We investigate the preparation of polysiloxane-based networks under solvent-free, ambient conditions using the Lewis acid catalysed Piers-Rubinsztajn (PR) reaction of hydride-terminated siloxanes with various tetrafunctional alkoxysilanes (tetraethoxysilane, tetrapropoxysilane, tetra-n-butoxysilane, tetra-s-butoxysilane, and tetrais(2-ethylbutoxy)silane) as crosslinkers. We explore the effects of polysiloxane chain length and crosslinker alkyl group on the rheological performance of the elastomers. By analysing the reaction progress by grazing angle Fourier-transform infrared spectroscopy (FTIR) and determining the rheological properties of the resulting materials, we show that the use of linear or branched alkoxysilanes strongly influences the morphology and properties of these network polymers. We have shown the PR process is can be tailored to reliably produce homogeneous, polysiloxane network materials. This work provides information on the relative rates of network formation under ambient conditions with an emphasis on the impact of crosslinker alkyl chain length. Our results show that electronics and sterics both play critical roles in influencing the rate of the curing reaction. Crucially, we newly demonstrate the benefit of having tertiary carbon α to the Si-O reaction centre, as is the case for the tetra-s-butoxysilane crosslinker, for delivering exceptionally rapid network cure and a concomitant enhancement in storage modulus of the resultant materials.

Introduction

Polysiloxanes (also commonly known as silicones) are polymers that consist of alternating covalently-linked silicon and oxygen atoms, with organic functionality on the silicon atoms. They are employed extensively in a range of applications such as sealants,1 contact lenses,2 adhesives,3 bakeware,4 cosmetics5 and implants.6 This is due to the desirable properties of siloxane-based materials including hydrophobicity, thermal stability, oxygen permeability, biocompatibility, and optical transparency.7

Current methods of polysiloxane-based network preparation is comprised of three main techniques: tin-catalysed moisture cure; high-temperature radical cure; and platinum-catalysed hydrosilylation.8 Achieving reproducibility in elastomeric properties is difficult through high-temperature radical cure.9 Tin-based catalysed reactions offer greater accuracy for material properties but as there is potential for environmental harm from tin residues, other routes are more desirable.4,9 Platinum-catalysed hydrosilylation is an efficient reaction, able to proceed at low catalyst loadings of ≤30 ppm and resulting in no by-products.10 Platinum-based catalysts are expensive, with Pt accounting for approximately 30% of the material cost.11 The catalyst is retrievable, however the recovery process is difficult and inefficient, with only 10–15% of Pt catalyst being reusable.12

A newer method for making siloxane bonds is the Piers-Rubinsztajn (PR) reaction. This reaction does not require transition metal catalysts and importantly proceeds efficiently at room temperature.13 Initial use of PR reaction for siloxane bond formation was displayed as polysiloxane production by coupling dihydridosilanes with dialkoxysilanes through a polycondensation reaction.13

The PR reaction proceeds through the complexation of the Lewis acid, B(C\text{F}3)\text{3}, with a Si-H intermediate A (see Scheme 1).14-15 Addition of an alkoxysilane to this intermediate leads to the reversible formation of the hydridosiloxane oxonium complex B (Scheme 1). From intermediate B there are three potential pathways: i) dissociation back to starting reagents (black pathway, Scheme 1); ii) reductive elimination of the alkyl group, resulting in the desired siloxane formation and alkane by-product (blue pathway, Scheme 1); and iii) undesired metathesis of the complex, transferring of the hydride to produce a new hydridosilane and alkoxysilane (red pathway, Scheme 1). Experimental evidence shows negligible metathesis, with siloxane formation the predominant outcome (pathway (ii) Scheme 1).16-17

In the context of siloxane-based polymeric materials, the metal-free Lewis acid PR reaction has demonstrated utility for siloxane network formation.18-20 This reaction leads to a

Scheme 1: The reaction pathways for Piers-Rubinsztajn reaction17

---

a. WMG, University of Warwick, Coventry CV4 7AL, United Kingdom
E-mail: T.L.Schiller@warwick.ac.uk
b. Department of Materials Science and Engineering, Monash University, 22 Alliance Lane, Clayton 3800, Victoria, Australia.
c. Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom,
d. School of Engineering, University of Warwick, Coventry CV4 7AL, United Kingdom
e. Faculty of Science and Engineering University of Wolverhampton, Wolverhampton WV1 1LY, United Kingdom

Electronic Supplementary Information (ESI) available: [further data mentioned in text]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/D1PY00872B

Please do not adjust margins
gaseous alkane by-product, which influences network formation and can lead to fragile foams. With this in mind, we sought to develop methods for reproducible gels, without foaming, under atmospheric conditions with a view to a wider scope of application for these materials.

In this paper we consider the impact of crosslinker alkyl chain length on rates of solvent-free gel network formation. The resultant materials, characterised by rheometry and FTIR, provide insights on the factors which influence the properties of the resultant networks.

**Experimental**

**Materials and methods**

α,ω-Hydride-terminated poly(dimethylsiloxane) (PDMS) 400-500 g mol\(^{-1}\) (M~n~ ≈ 800 g mol\(^{-1}\)), 1a, calculated by end-group analysis from \(^1\)H NMR spectroscopy, α,ω-hydride-terminated poly(dimethylsiloxane) (PDMS) 1000-1100 g mol\(^{-1}\) (M~n~ ≈ 1170 g mol\(^{-1}\)), 1b, calculated by end-group analysis from \(^1\)H NMR spectroscopy, tetra-n-butoxysilane 4, tetra-s-butoxysilane 6, tetrakis(2-ethylbutoxy)silane 5 were purchased from Gelest (Germany). Tris(pentafluorophenyl)borane (B(C\(\text{F}_5\))\(_3\)), tetrapropoxysilane 3, n-hexane, n-heptane, toluene and ethanol were purchased from Sigma-Aldrich (UK). Tetraethoxysilane 2 was purchased from Fischer Scientific (UK). All were used as received.

**Preparation of B(C\(\text{F}_5\))\(_3\) Catalyst Solutions.**

A 0.1 M stock solution was prepared by adding B(C\(\text{F}_5\))\(_3\) (0.512 g) into a volumetric flask (10 mL) and filling up to the mark with toluene. A subsequent 0.01 M stock solution was made by adding an aliquot (1 mL) from the 0.1 M stock solution to a volumetric flask (10 mL) and filling up to the mark with toluene.

**General Preparation of Silicone Elastomer.**

For silicone elastomer preparation, α,ω-hydride terminated PDMS (1a or 1b) was mixed with tetraalkoxysilane crosslinker (2, 3, 4, or 5) at a ratio of 2.125:1 (e.g. 1a = 1.7 mmol, 0.85 mL; 4 = 0.88mol, 0.285 mL) respectively, using a vortex mixer for 1 min. The catalyst (B(C\(\text{F}_5\))\(_3\)) is added (20 μL, 0.01 M, 2 × 10\(^{-4}\) mmol, 0.024 mol% to PDMS) to the silicone and crosslinker solution and immediately mixed on a vortex mixer for 10-20 seconds. The reaction solution was then left to cure at room temperature for 5-30 minutes. The curing was monitored and determined by visual state change from liquid to solid and gentle probing of sample.

**Characterisation**

**Fourier Transform Infrared Spectroscopy (FTIR).**

Infrared spectra of pre- and post-cured samples were obtained using a Jasco FTIR 4200 spectrometer, equipped with a VeeMax II with attenuated total reflectance (ATR), Pike Technologies accessory (grazing angle 30°, ZnSe crystal). Measurements were collected at a resolution of 2 cm\(^{-1}\) with 128 scans per sample. Background spectra were collected to remove atmospheric CO\(_2\) and H\(_2\)O peaks from sample measurements. Spectra were collected while continuous purging the instrument with N\(_2\) to minimise fluctuations in peaks for CO\(_2\) and atmospheric H\(_2\)O.

Spectra were analysed using Origin 2019b. Rheological measurements were taken on an Anton Paar MCR510 rheometer (Graz, Austria) using a parallel plate with a diameter of 8 mm and a measuring gap of 0.18 mm. The change of phase from solution to gel was monitored by measuring the storage moduli and loss moduli. The force was kept constant at 0 N, with the temperature of the Peltier plates was kept at 25 °C during all measurements. Stock solutions for each composition, including initiator, were prepared and stored on ice to eliminate early onset of reaction. 25 μL aliquot of a stock solution was used for each measurement. The reaction was measured with constant frequency of 6.28 rad s\(^{-1}\) and constant strain of 10 %. The amplitude sweep was performed at a constant frequency of 6.28 rad s\(^{-1}\) was used and the strain was increased logarithmically from 1-500 %. The frequency sweep was conducted at a constant strain of 10 % and the frequency was increased logarithmically from 1-550 rad s\(^{-1}\). All data was analysed using the rheocompass (Anton Paar, Austria) software.

**Results and discussion**

**Optimisation of network formation**

Siloxane preparation catalysed by metal-free based compounds is a particularly attractive process, due to the cost and environmental issues metal-based catalysts can pose. Our initial examination of network formation involved experiments using a low molar mass hydride-terminated PDMS 1a, tetraethoxysilane 2 as crosslinker and n-hexane as solvent; foamed networks were formed (see experimental section for stoichiometry, Table S1, Entry 1). Following the success of the PR reaction 1a with 2, we investigated the effect of the alkyl group of the tetraalkoxysilane crosslinker using the ethyl 2, propyl 3, n-butyl 4, 2-ethylbutyl 5, and s-butyl 6 analogues for Piers-Rubinsztajn network formation (see Scheme 2). We observed that an increase in alkyl length of the crosslinker generally led to networks which were denser in appearance (see Figure S1). Preparation of materials with the bulkier 2-ethylbutyl 5 proved unsuccessful; samples only partially cured with the materials remaining liquid. It is known that larger alkoxysilane ‘R’ groups result in a decrease in reaction rate due to the increase in sterics.

Following our initial successes, we then sought to prepare siloxane elastomers, without foaming, via the PR reaction. Here we investigated the impact of the tetraalkoxysilane crosslinker alkyl chain length on rate of gelation as well as the resultant materials properties. To avoid the foaming seen in the previous samples, we ascertained that the rate of reaction needed to be
low enough to allow the bulk of gas evolved from the reaction to escape during network formation, but remain sufficiently high to allow for complete cure. In this context, we first sought to reduce the rate of reaction by lowering the B(C₆F₃)₃ catalyst concentration, in relation to conditions reported in previous studies.²¹,²³ These experiments (see Table S1) showed that, as expected, the B(C₆F₃)₃ catalyst concentration greatly influences the rate of reaction (including gaseous alkane production). The initial reactions discussed above were undertaken using a relatively high catalyst amount (2 × 10⁻³ mmol; 20 μL of 0.1 M stock solution). These resulted samples that were brittle and highly disordered, open celled foams (see Figure S1 (a)). Further studies. Note, these systems display induction periods of approximately 10 kJ mol⁻¹; n-heptane reduces the volume of additional gas produced during the PR curing under otherwise the same reaction conditions.

The cured samples prepared using either n-hexane or n-heptane were found to contract following solvent evaporation which led to sample fracture (possibly due to increased strain present within the network in a contracted state). Omission of solvent from the reaction mixtures was investigated in an attempt to overcome this problem. Without solvent, a reduction in swelling and a decreased incidence of sample fracture was observed. While the occurrence of voids was not completely eliminated, solventless reactions were deemed the best approach for preparing our samples; all samples discussed in subsequent sections were prepared without solvent.

**Investigating rate of network formation**

To examine the effect of changing the alkyl R-groups of the tetraalkoxysilane crosslinker (i.e., ethyl 2, propyl 3, n-butyl 4, 2-ethylbutyl 5, and s-butyl 6) on the rate and extent of PR network formation and the final mechanical properties these possess, the curing reactions were studied by both grazing-angle FTIR and rheology. Note, these systems display induction periods of
Table 1: Results from FTIR and rheology measurements of elastomer systems

| Entry | Hydride-terminated PDMS | Tetraalkoxysilane | Conversion % | $G'$ (kPa) |
|-------|--------------------------|-------------------|--------------|-----------|
| 1a    | 1a                       | 2 (ethyl)         | 100          | 82.0      |
| 2a    | 1a                       | 3 (propyl)        | 100          | 38.4      |
| 3a    | 1a                       | 4 (n-butyl)       | 100          | 32.6      |
| 4a    | 1a                       | 5 (2-ethylbutyl)  | 38           | —         |
| 5a    | 1a                       | 6 (s-butyl)       | 99           | 137       |
| 6b    | 1b                       | 2 (ethyl)         | 98           | 444       |
| 7b    | 1b                       | 3 (propyl)        | 94           | 241       |
| 8b    | 1b                       | 4 (n-butyl)       | 100          | 337       |
| 9b    | 1b                       | 5 (2-ethylbutyl)  | 38           | —         |
| 10b   | 1b                       | 6 (s-butyl)       | 98           | 428       |

$^a$PDMS 1a $M_1$ = 800 g mol$^{-1}$, [1a] = 1.7 mmol, [alkoxysilane] = 0.8 mmol, [B(C$_6$F$_5$)$_3$] = 2 × 10$^{-4}$ mmol; $^b$PDMS 1b $M_1$ = 1170 g mol$^{-1}$, [1b] = 0.85 mmol, [alkoxysilane] = 0.4 mmol, [B(C$_6$F$_5$)$_3$] = 1 × 10$^{-4}$ mmol; $^c$Conversion % based on consumption of Si-H (2126 cm$^{-1}$) calculated by $\% = 100 - \frac{((post - cure absorbance)/(pre - cure absorbance)) \times 100}$; $^d$Peak storage modulus obtained from rheology analysis; $^e$Not measured due to insufficient cure.

Figure 2: Absorbance normalised 30° grazing angle FTIR spectra for (top) PDMS system 1a propyl 3 pre- and post-cure measurements, Si-H peak at 2126 cm$^{-1}$ disappears from pre- to post-cure measurements, and (bottom) PDMS system 1a 2-ethylbutyl 5 pre- and post-cure measurements, Si-H peak found at 2126 cm$^{-1}$ decreases from pre- to post-cure measurements. Varying lengths of time prior to cure, consistent with that previously reported for the PR reaction. The commercial samples we used were not pre-dried and therefore contain unknown, varying amounts of moisture. This results in these differing induction periods.

Pre- and post-cure grazing-angle FTIR for the samples prepared from PDMS 1a was first undertaken. Absorbance peaks at 2126 cm$^{-1}$ and 907 cm$^{-1}$, were not found in the post-cure measurements (see Figure 2, top), indicating consumption of Si-H$^2$-$^8$ groups. Complete cure was estimated for systems using 1a with ethyl 2, propyl 3, n-butyl 4 or s-butyl 6 (see entries 1-3 & 5, Table 1), achieving almost full consumption of Si-H functional groups PDMS 1a with ethyl 2 (see Entry 1, Table 1; Figure 3 (a)) reacted rapidly, indicated by sharp increase in modulus at ~30 seconds, this was followed by a gradual increase to a plateau modulus of 82 kPa.

In contrast to the ethyl 2 sample (see Entry 1, Table 1; Figure 3 (a)), the propyl 3 and n-butyl 4 gelation curves displayed similar characteristics with a peak in G’ followed by a slight decrease to a plateau of 37.2 kPa and 32.1 kPa respectively (see Entries 2 & 3, Table 1; Figure 3 (b & c)). This suggests these are more homogeneous than the ethyl sample, lacking voids. This is also consistent with the qualitative evidence discussed above (For images see Figure S1).

The curing of the PDMS 1a/s-butyl 6 sample also displayed sharp increase in modulus (to 137.2 kPa); resulting, after a small decrease, in the highest modulus observed (129.6 kPa) (see Figure 3(d) and Entry 5, Table 1). It was observed that the reaction rate was higher, with the reaction able to proceed at 0 °C; in contrast this temperature retarded the reactions using the crosslinkers 2-5.

The clear difference between s-butyl 6 crosslinker and the other crosslinkers 2-5 is the presence of a tertiary carbon α to the SiO group; the other crosslinkers 2-5 all have secondary carbons in this position (see Scheme 2). Since the predominant reaction pathway (see Scheme 1, (iii)) proceeds via a hydride shift to the
Figure 3: Time-resolved rheology gelation curves over 200 seconds shown by $G'$ and $G''$ for elastomers derived from PDMS 1a and the (a) ethyl, (b) propyl, (c) n-butyl, and (d) s-butyl alkoxysilane (also see Entries 1-5, Table 1). Note the omitted data as per Table 1.

alkoxy carbon atom, we postulate that this difference in electronics between 6 and the other crosslinkers (i.e. 2-5) at this reaction centre is key. An enhanced ability for the tertiary carbon(s) on 6 to stabilise a (partial) positive charge, which is expected to contribute to the transition state, would account for the observed increase in reaction rate. Indeed, this crude hypothesis is consistent with a detailed mechanistic summary of the PR reaction published by Chojnowski et al.\textsuperscript{25}

Increasing the bulk of the crosslinker alkyl chain (with minimal change to electronics of the carbon α to the SiO-group) using the 2-ethylbutyl 5 (see Entry 4, Table 1) resulted in significantly lower % cure in the final ‘cured’ sample; it remained liquid, indicating only partial cure. The FTIR analysis supports this, displaying only partial consumption of Si-H (see Figure 2, bottom), with the calculated percentage of conversion being 38%.\textsuperscript{7} A gelation curve was not obtained as 2-ethylbutyl 5 did not cure on the rheometer, this is consistent with the FTIR data. s-butyl 6 exhibited an efficient reaction; resulting in an increased final $G'$ and a high conversion percentage. This was determined to be the optimal crosslinker (See Entry 5, Table 1; Figure 3(d)).

Networks prepared with longer chain length PDMS

Tailoring thermo-mechanical properties is vital to the application of polymeric materials. In this context, chain length between crosslinks is known to influence these properties.\textsuperscript{29-30} The rate of cure is also influenced by the chain length of end-group functional polymers.

In this context, the reaction conditions optimised for lower molar mass PDMS 1a were adjusted for a higher molar mass hydride-terminate PDMS 1b ($M_n, 1170$ g mol$^{-1}$), to ensure reaction volume and stoichiometries were comparable. For these reactions we maintained a similar volume (~1 mL) and as such the amount of polymer, crosslinker and catalyst were halved (i.e., 0.85 mmol polymer, 0.4 mmol crosslinker and 1 × 10$^{-4}$ mmol catalyst). Keeping the reaction volume similar allowed for more direct comparison between the samples derived from 1a and 1b polymer groups; samples of larger volume (by using the same number of moles of 1b as 1a) led to more defects in the resultant elastomers, due to the greater distance the gaseous alkane by-product needed to travel to escape the network.
The PDMS 1b derived samples prepared using the ethyl 2,
propyl 3, or n-butyl 4 crosslinkers readily cured, yielding
conversions of 98%, 93% and 99%, respectively (see Table 1,
entries 6, 7, and 8 respectively). These three samples post-cure
were solid materials, with no tackiness from unreacted starting
reagents. The PDMS 1b/2-ethylbutyl 5 sample did not
completely cure, with the sample again remaining in a liquid
state (see Entry 9, Table 1). From FTIR analysis, the conversion
was calculated to be 38%, comparable to the PDMS 1a/2-
ethylbutyl 5 sample (see Entry 4, Table 1), which also exhibited
partial curing.

The ethyl 2 sample displayed the highest initial G’, with a
steep increase to 444 kPa, followed by a gradual decrease to
388 kPa (see Figure 4 (a) and Entry 6, Table 1). Changing the
crosslinkers alkyl chain to propyl 3 resulted in a decrease in the
initial gelation storage modulus, peaking at 241 kPa. The initial
peak in G’ of the propyl 3 system (see Figure 4 (b) and Entry 7-
Table 1) was followed by a decrease to 151 kPa, similar to
observations for the ethyl 2 system. The storage modulus (G’)
of the n-butyl 4 sample (peaked at 337 kPa see Figure 4 (c) and
Entry 8, Table 1), however the transition from the initial steep
period to peak G’ was more gradual, indicating a reduction in
reaction rate in comparison to ethyl 2 and propyl 3 systems.

After the modulus peaked, a gradual decrease was seen again,
reaching 224 kPa. The s-butyl 6 sample initial curing led to a
peak G’ of 428 kPa (see Figure 4 (d) and Entry 10, Table 1), the
best from all crosslinkers tested. Interestingly, the gelation
curve did not exhibit the same gradual decrease in storage
modulus as seen in samples using PDMS 1b and the ethyl 2,
propyl 3 and n-butyl 4 (see Entries 6-7, Table 1). This system
(1b/6) does display a higher storage modulus relative to
crosslinkers 3 & 4, similar to the analogous system using the
smaller PDMS (1a/6). Further investigation is required into s-
butyl 6 systems to understand why this phenomenon occurs,
which is outside the scope of our current work.

Conclusions

Parameters for reproducible, solvent-free PR systems for
the synthesis of polysiloxane (silicone) elastomers were
established. A range of alkoxysilane crosslinkers ethyl 2, propyl
3, n-butyl 4, 2-ethylbutyl 5 and s-butyl 6 were investigated with
two siloxane polymers 1a (Mn ~800 g mol⁻¹) & 1b (Mn~1170 g
mol⁻¹). Increasing the crosslinker alkyl chain length from ethyl 2
to n-butyl 4 resulted in an observable change in reaction rate
and the appearance of the final product. The propyl 3 and n-
butyl 4 crosslinkers resulted in decreased foaming compared to ethyl 2, resulting in elastomers. The percentage cure, determined by FTIR, for crosslinkers ethyl 2, propyl 3, n-butyl 4 and s-butyl 6 were estimated to be between 94-100% for both polymers 1a and 1b, whilst the branched 2-ethylbutyl 5 resulted in a much lower cure of 38%.

Time-resolved rheological studies showed gelation curves with a rapid increase in modulus, after a short induction period, followed by a plateau for each of the crosslinkers ethyl 2, propyl 3, n-butyl 4 and s-butyl 6. The ethyl 2 derived samples displayed a noticeable difference in their gelation curves, exhibiting a more gradual transition to the plateau. Samples containing s-butyl 6 displayed a larger increase in modulus comparatively to any of the linear counterparts. Use of a larger branched alkyl chain crosslinker (2-ethylbutyl 5) reduced the rate of reaction considerably, leading to incomplete curing in both systems.

This work has provided an insight into the influence of crosslinker alkyl chain on PR silicone elastomer formation. We have shown that increasing the size of the alkyl group away from the SiO reaction centre, reduces the rate of reaction. In contrast we have demonstrated that altering the electronics of crosslinker, by changing the group directly bonded to the SiO reaction centre from secondary to tertiary, greatly enhances the reaction rate. In this context, the s-Butyl 6 displays both a more rapid cure and a higher storage modulus than the other crosslinkers tested and is the ideal choice for further investigations in PR elastomer preparation.

Author Contributions
AH: validation, investigation, drafted original manuscript, review and editing of manuscript; NC: FTIR investigation, review of manuscript; NRC: student co-supervision, review and editing of manuscript; DJK: student co-supervision, conceptualization, review and editing of manuscript; TJS: student main supervision, conceptualization, helped draft original manuscript, review and editing of manuscript

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
The authors would like to thank Dr Daniel Lester from the Warwick Polymer Research Technology Platform for his assistance with the Rheometer and Dr Ahmed Eissa for his assistance with the $^1$H NMR.

Notes and references
5 This differing modulus plateau may be due to forced gas evolution of ethyl 2 reducing contact with the plates. The shear from the rheology plates promotes mixing and once the gas escapes the system, better contact can be established with the solid material, leading to a gradual increase in storage modulus.
6 Conventional gelation theory states that an A3β8 system (where A is an α,ω-hydride terminated PDMs and B is a tetraalkoxysilane) three-dimensional structure forms beyond 33% conversion.11-12 Entry 4, Table 1 has an estimated conversion of 38%; although beyond the theoretical 33% required for network formation, there is a margin of error in the calculation. In addition, FTIR only analyses a small region of the sample, both of which will contribute to variations in conversion data. The decrease in estimated percentage conversion, compared to other formulations, is likely due to the increase in steric hindrance by the larger, branched alkyl chain, leading to a reduction in rate of the PR reaction.

1. Owen, M. J.; Klosowski, I. M., Durability of Silicone Sealants. In Adhesives, Sealants, and Coatings for Space and Harsh Environments, Lee, L.-H., Ed. Springer US: Boston, MA, 1988; pp 281-291.
2. Musgrave, C. S. A.; Fang, F., Contact Lens Materials: A Materials Science Perspective. Materials (Basel) 2019, 12 (2), 261.
3. Lin, S. B., New silicone pressure-sensitive adhesive technology. International Journal of Adhesion and Adhesives 1994, 14 (3), 185-191.
4. Fromme, H.; Witte, M.; Fembacher, L.; Gruber, L.; Hagi, T.; Smolic, S.; Fiedler, D.; Sysolitseva, M.; Schober, W., Siloxane in baking moulds, emission to indoor air and migration to food during baking with an electric oven. Environment International 2019, 126, 145-152.
5. O’Lenick, A. J.; O’Lenick, K. A., Silicone Polymers in Skin Care. MRS Bulletin 2007, 32 (10), 801-806.
6. Arkyes, B., Silicones in Biomedical Applications. 1983; pp 749-768.
7. Noll, W., Chemistry and technology of silicones. Elsevier: 2012.
8. Brook, M. A., Silicon in Organic Organometallic, and Polymer Chemistry. John Wiley & Sons, Inc.: New York, 2000.
9. de Carvalho Oliveira, R.; Santelli, R. E., Occurrence and chemical speciation analysis of organotin compounds in the environment: A review. Talanta 2010, 82 (1), 9-24.
10. Nakajima, Y.; Shimada, S., Hydrosilylation reaction of olefins: recent advances and perspectives. RSC Adv. 2015, 5 (26), 20603-20616.
11. Schuster, C. H.; Diao, T.; Pappas, I.; Chirik, P. J., Bench-Stable, Substrate-Activated Cobalt Carboxylate Pre-Catalysts for Alkene Hydrosilylation with Tertiary Silanes. ACS Catalysis 2016, 6 (4), 2632-2636.
12. Lykissa, E. D.; Kala, S. V.; Hurley, J. B.; Lebovitz, R. M., Release of Low Molecular Weight Silicones and Platinum from Silicone Breast Implants. Analytical Chemistry 1997, 69 (23), 4912-4916.
13. Rubinsztajn, S.; Cella, J. A., A New Polycondensation Process for the Preparation of Polysiloxane Copolymers. Macromolecules 2005, 38 (4), 1061-1063.
14. Parks, D. J.; Blackwell, J. M.; Piers, W. E., Studies on the Mechanism of B(C6F5)3-Catalyzed Hydrosilation of Carboxyl Functions. The Journal of Organic Chemistry 2000, 65 (10), 3090-3098.
15. Piers, W. E.; Marwitz, A. J. V.; Mercier, L. G., Mechanistic Aspects of Bond Activation with Perfluoroarylboranes. Inorganic Chemistry 2011, 50 (24), 12252-12262.
16. Thompson, D. B.; Brook, M. A., Rapid assembly of complex 3D silicone architectures. J. Am. Chem. Soc. 2008, 130 (1), 32-+.
17. Grande, J. B.; Thompson, D. B.; Gonzaga, F.; Brook, M. A., Testing the functional tolerance of the Piers–Rubinsztajn reaction: a new strategy for functional silicones. Chemical Communications 2010, 46 (27), 4988-4990.
18. Keddie, D. J.; Grande, J. B.; Gonzaga, F.; Brook, M. A.; Dargaville, T. R., Amphiphilic Silicone Architectures via Anaerobic Thiol–Ene Chemistry. Org. Lett. 2011, 13 (22), 6006-6009.
19. Zhang, J.; Chen, Y.; Sewell, P.; Brook, M. A., Utilization of softwood lignin as both crosslinker and reinforcing agent in silicone elastomers. Green Chem. 2015, 17 (3), 1811-1819.
20. Brook, M. A., New Control Over Silicone Synthesis using SiH Chemistry: The Piers–Rubinsztajn Reaction. *Chemistry – A European Journal* **2018**, 24 (34), 8458-8469.
21. Grande, J. B.; Fawcett, A. S.; McLaughlin, A. J.; Gonzaga, F.; Bender, T. P.; Brook, M. A., Anhydrous formation of foamed silicone elastomers using the Piers–Rubinsztajn reaction. *Polymer* **2012**, 53 (15), 3135-3142.
22. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A., NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities. *The Journal of Organic Chemistry* **1997**, 62 (21), 7512-7515.
23. Fawcett, A. S.; Grande, J. B.; Brook, M. A., Rapid, metal-free room temperature vulcanization produces silicone elastomers. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, 51 (3), 644-652.
24. Kehiaian, H., *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation* ; Chemical Data Series No. 32. Oxford, Blackwell Scientific Publications: 1985.
25. Chojnowski, J.; Rubinsztajn, S.; Cella, J. A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kaźmierski, K., Mechanism of the B(C6F5)3-Catalyzed Reaction of Silyl Hydrides with Alkoxysilanes. Kinetic and Spectroscopic Studies. *Organometallics* **2005**, 24 (25), 6077-6084.
26. Schneider, A. F.; Chen, Y.; Brook, M. A., Trace water affects tris(pentafluorophenyl)borane catalytic activity in the Piers–Rubinsztajn reaction. *Dalton Trans.* **2019**, 48 (36), 13599-13606.
27. Launer, P.; Arkles, B., Infrared Analysis of Organosilicon Compounds. 2013; pp 175-178.
28. Risangud, N.; Li, Z.; Anastasaki, A.; Wilson, P.; Kempe, K.; Haddleton, D. M., Hydrosilylation as an efficient tool for polymer synthesis and modification with methacrylates. *RSC Advances* **2015**, 5 (8), 5879-5885.
29. Clark, A. H.; Gidley, M. J.; Richardson, R. K.; Ross-Murphy, S. B., Rheological studies of aqueous amylose gels: the effect of chain length and concentration on gel modulus. *Macromolecules* **1989**, 22 (1), 346-351.
30. Mark, J. E., Improved elastomers through control of network chain-length distributions. *Rubber Chemistry and Technology* **1999**, 72 (3), 465.
31. Miller, D. R.; Macosko, C. W., A New Derivation of Post Gel Properties of Network Polymers. *Macromolecules* **1976**, 9 (2), 206-211.
32. Cook, W. D.; Schiller, T. L.; Chen, F.; Moorhoff, C.; Thang, S. H.; Bowman, C. N.; Scott, T. F., Effect of Cross-Link Density on Photoplasticity of Epoxide Networks Containing Allylic Dithioether Moieties. *Macromolecules* **2012**, 45 (24), 9734-9741.