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Linear and Star Architecture Methacrylate-functionalised PDMS

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Abstract

Methacrylate-terminated poly(dimethylsiloxane)s in both linear and star architectures have been produced through a time-efficient 1 pot, 2 stage reaction which involved hydrosilylation of small molecule silanes with allyl methacrylate and subsequent equilibration of the product with octamethylcyclotetrasiloxane (D_4) in the presence of an acid catalyst. This synthetic route required only one work-up procedure and the products were comparable to those produced by 2 step processes typically reported in literature. All methacrylate-terminated products were approximately double the molar masses anticipated based on reagent loadings. This is thought to be due to redistribution of siloxane bonds in the presence of the platinum hydrosilylation catalyst accompanied by a loss of silicon from the reaction by evaporation of dimethylsilane. It is believed that this is the first report of such siloxane equilibration occurring at room temperature.

Keywords: siloxane; polymer architecture; ring-opening polymerisation

1. Introduction

Siloxanes are used in a myriad of applications that often make use of their hydrophobicity, good thermal stability, excellent release properties, good resistance to UV radiation and high gas permeability [1–3]. They offer good lubricity, weak intermolecular forces and a useful balance of low volatility at high molar mass and high volatility at low molar mass [4]. A widely used siloxane is poly(dimethyl)siloxane (PDMS).

The properties of PDMS may be tailored by adding complimentary functional groups to the polymer [5–7]; adding functionality to the end of the PDMS chain produces α, ω-difunctional

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species. Such polymers may be macromonomers as with suitable functionality at the chain ends they may be coupled to form higher molar mass products. One route to α, ω-difunctional siloxanes is by equilibrium ring-opening polymerisation (ROP) of cyclic siloxanes such as hexamethylcyclotrisiloxane (D_3) or octamethylcyclosiloxane (D_4) in the presence of a difunctional small molecule siloxane such as tetramethyldisiloxane. Equilibrium polymerisations may be catalysed by strong acids or bases, including sulfuric acid [8, 9], trifluoromethanesulfonic acid (triflic acid) [3, 10–14], potassium hydroxide [15] or ammonium salts [8, 16, 17]. The choice of catalyst can be limited by the functionality present in the reagents, for example Si−H bonds are unstable in the presence of strong bases [12]. The dispersity (Đ) and yield are generally independent of the initiation method used, and the polymer molar mass is based on the ratio of cyclic siloxane to the small molecule disiloxane in the reaction mixture. The equilibrium state of a siloxane ROP is not trivial as it includes both cyclic and linear chains[18]; the cyclic species are mainly oligomers and they are often removed from the reaction product by distillation or precipitation to yield the linear siloxane. Cyclic formation is promoted by increased dilution and increasing size and polar character of the side groups [19]. As the equilibrium is established by a random process of bond breaking and formation, siloxane polymers produced by equilibrium ROP may be expected to have a relatively high dispersity of 2 [3, 20].

Hydrosilylation reactions are prolific in siloxane chemistry and involve the formation of a new Si−C bond by reaction of a silane (Si−H) with an olefin (C=C). Using 1,1,3,3-tetramethyldisiloxane in an equilibrium ROP siloxane synthesis produces α, ω-difunctional siloxanes containing Si−H end groups. These end groups may then be readily transformed into a range of functionalities by hydrosilylation reactions [8, 12, 13, 21–25]. Hydrosilylation reactions are often carried out under stringently controlled conditions, for example on a Schlenk line, as the presence of water causes undesirable side reactions [26]. One of the motivations of this work was to find a synthetic route that could be successfully carried out under less controlled conditions, specifically under a nitrogen atmosphere in a flame-dried vessel.

Methacrylate-terminated PDMS (**3**) was a target product which was obtained by combining the acid-catalysed ring-opening polymerisation of D_4 in the presence of a disiloxane and functionalisation by hydrosilylation with allyl methacrylate, as shown in Fig. 1. Changing the small-molecule disiloxane to a branched analogue allows end-functionalised branched siloxanes to be produced,
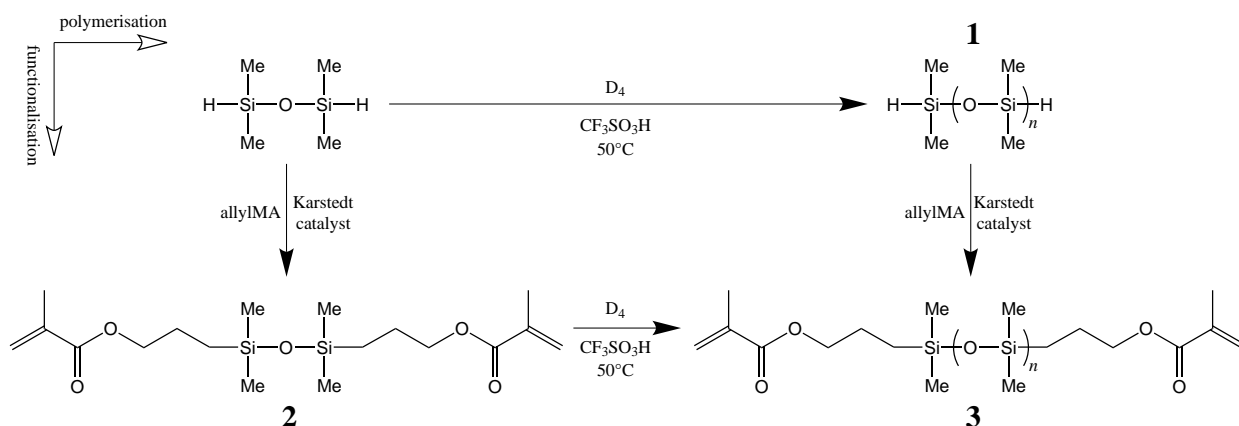
Figure 1: Routes of synthesis of α,ω-bis(methacryl)PDMS (**3**).

as shown in Fig. 2, which are not available commercially. The reported synthetic pathway is particularly flexible as it allows a range of polymers with distinctly different architectures (i.e. linear vs star) to be synthesised using the same reagents and reaction conditions, rather than requiring individual reactions to produce each species.

As illustrated in Fig. 1 methacrylate-terminated PDMS may be synthesised by 2 routes depending on the order in which the polymerisation and functionalisation reactions are carried out. One route, which is often quoted in literature, is to synthesise hydride-terminated PDMS (**1**) and subsequently functionalise the polymer to produce the desired product (**3**) [3, 13]. However, a more efficient route to comparable products which is under-represented in the literature is to first carry out the hydrosilylation reaction on the small-molecule disiloxane and to use this modified disiloxane in the polymerisation. In this latter technique the hydrosilylation reaction proceeds much quicker due to the greater mobility of the smaller disiloxane in contrast to the polymeric PDMS analogue. Furthermore the 2 reactions may be carried out consecutively in a 1 pot, 2 stage reaction requiring only one purification procedure.

The production of end-functionalised branched siloxanes was also of interest. Branched structures are of considerable interest in polymer science as they can have distinctly different properties to analogous linear materials [3, 27, 28]. Types of branched polymers include stars, dendrimers and hyperbranched materials, with star structures being potentially the simplest type of branching; they have a single focal point from which the branches extend [29].

Star polymer analogues of the linear PDMS described above were synthesised. In a future
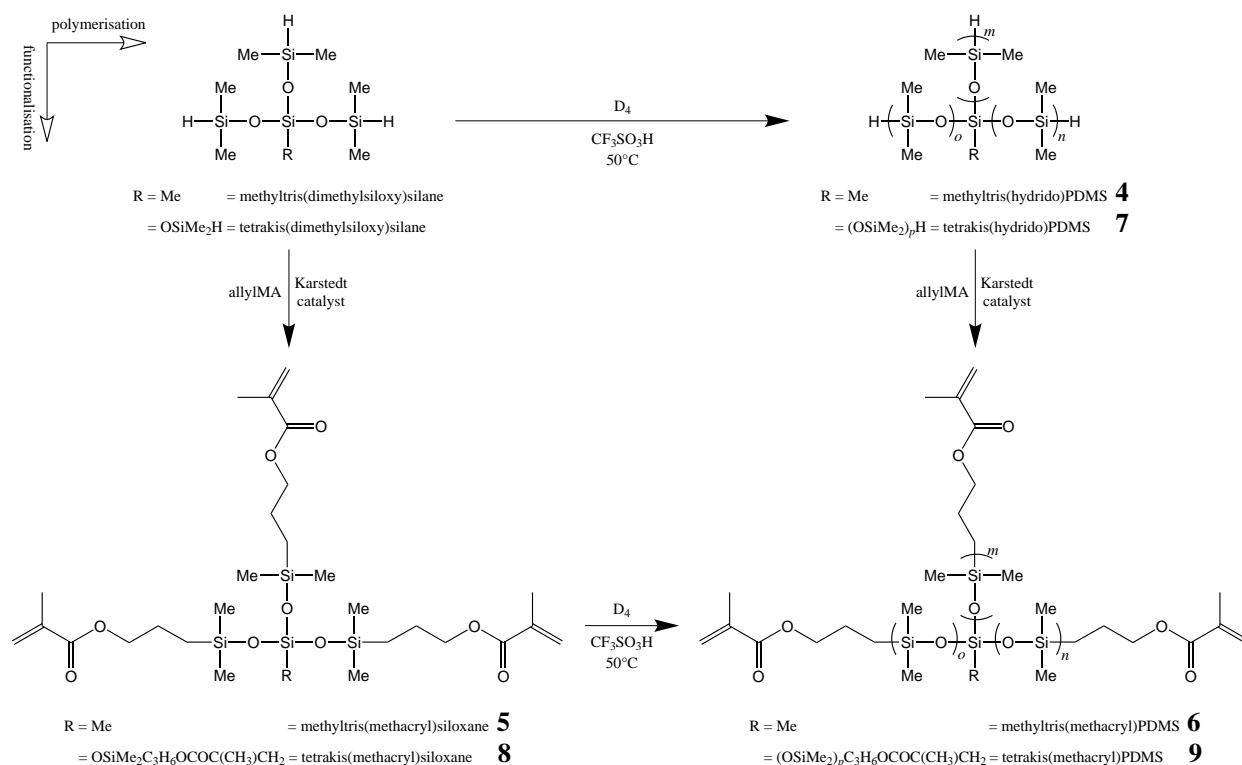
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Figure 2: Routes of synthesis of multi-armed methacrylate-terminated PDMS.

publication we will describe the cross-linking of these star polymers to form films and describe the effect of branching on the kinetics of film formation and the film properties.

Hydride-terminated 4-armed star PDMS has previously been synthesised by the equilibrium ring-opening polymerisation of D_4 in the presence of tetrakis(dimethylsiloxy)silane [3, 30]. Examples of 4-armed methacrylate-terminated star PDMS (**9**) have also been produced by subsequent hydrosilylation of the hydride-terminated PDMS with allyl methacrylate [31, 32]. An improvement to these 2 stage synthetic procedures was achieved by reversing the order of the reactions to implement the 1 pot, 2 stage reaction technique which had been refined for the synthesis of difunctional linear materials. In addition, methyltris(dimethylsiloxy)silane was used to synthesise 3-armed methacrylate-terminated star PDMS (**6**) as depicted by the reaction scheme in Fig. 2.

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2. Experimental

2.1. Materials

Octamethylcyclotetrasiloxane (D_4, 98%), 1,1,3,3-tetramethyldisiloxane (97%), methyltris(dimethylsiloxy)silane (97%) and tetrakis(dimethylsiloxy)silane were obtained from Fluorochem. Trifluoromethanesulfonic acid (triflic acid, 99%), Florisil® (60-100 mesh) and allyl methacrylate (allylMA, 98%) were purchased from Acros. Magnesium carbonate hexahydrate, Celite 521® and all SLR grade solvents were from Fisher Scientific. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex (Karstedt's catalyst, $\sim 2\,\mathrm{wt}\%$ Pt in xylenes) was bought from SigmaAldrich.

2.2. Analysis

^{1}H NMR spectra were recorded on a Varian $400\,\mathrm{MHz}$ spectrometer of dilute solutions in $CDCl_3$ using tetramethylsilane as a reference. Infra-red (IR) spectra of liquid samples were measured between sodium chloride plates on a Perkin Elmer Spectrum One Infra-red Spectrometer and were an average of 4 scans. Electrospray ionisation mass spectrometry (ESI-MS) was performed on a Bruker Daltonics 7 Tesla Apex 4 Fourier-transform ion cyclotron resonance mass spectrometer using an Apollo electrospray ionisation source at $4.5\,\mathrm{kV}$ ionisation potential using nitrogen as the drying gas at 200°C. An accurate-mass calibration (accurate to better than 5ppm) was obtained using a 20 point calibration from poly(ethylene glycol) covering the m/z rage of the analyses and acquired with the same source conditions. This enabled the confirmation of all molecular formulae with a vey high degree of certainty. ESI-MS was used in preference over EI and CI mass spectrometry as the latter techniques are not suitable for the ionisation of methacrylate-modified siloxanes due to the high levels of fragmentation produced making interpretation of spectra very problematic.

GPC analysis in THF eluent of the methacrylate-terminated PDMS products was not successful due to THF and PDMS being isorefractive. GPC analysis using chloroform eluent was carried out by Smithers Rapra Technology Ltd. Samples were run on a Viscotek TDA model 301 with associated pump and autosampler containing PLgel guard plus 2 mixed bed-D, $30\,\mathrm{cm}$, $5\,\mu\mathrm{m}$ columns with a flow rate of $1.0\,\mathrm{mL/min}$. Signals were detected on a refractive index detector with differential pressure and light scattering although only the conventional GPC data were found to be reliable. The data were collected and analysed using Polymer Labs 'Cirrus' software and were reported against linear polystyrene standards.

2.3. α, ω-bis(methacryl)PDMS (3) Synthesis by a 1 Pot, 2 Stage Reaction (Functionalisation followed by Polymerisation)

The following is an example synthesis of α, ω-bis(methacryl)PDMS where the intended number average molar mass, $\bar{M}_n$, is $10,000\,\mathrm{g\,mol^{-1}}$. Materials of alternative molar mass were synthesised by changing the disiloxane : D_4 mole ratio.

All apparatus were cleaned and dried and the reaction vessel was flame-dried in air before use. To a nitrogen-purged 250 mL 3-necked round-bottomed flask equipped with a septum, magnetic stirrer bar, condenser and nitrogen flow, allyl methacrylate (0.948 g, 7.5 mmol, 1.5 equivs cf. Si$-$H), Karstedt catalyst (0.005 g, $\sim$ 2 wt% Pt, 0.01 mol% Pt wrt Si$-$H) and D_4 (4.90 g, to act as solvent) were added. 1,1,3,3-tetramethyldisiloxane (0.341 g, 2.6 mmol) was added to the clear colourless reaction mixture and the reaction mixture was stirred at room temperature (24°C). The hydrosilylation reaction progress was monitored by the presence of a peak due to Si$-$H at $2120\,\mathrm{cm^{-1}}$ in the IR spectrum of the crude reaction mixture. After 16 hour's reaction, no Si$-$H peak was visible at $2120\,\mathrm{cm^{-1}}$ indicating the hydrosilylation reaction was complete, so D_4 (19.80 g) and dichloromethane (10 mL) were added to the reaction mixture. Triflic acid (0.5 mL) was added and the reaction vessel was immersed in a pre-heated oil bath set at 50°C and stirred for 1 hour before magnesium carbonate hexahydrate (3 g) and dichloromethane (20 mL) were added to the reaction mixture, which was removed from heat and stirred for 2 hours. The opaque white reaction mixture was passed through a pad of Florisil under mild vacuum using 3:1 hexane : dichloromethane as eluent. The majority of solvents were removed from the clear colourless filtrate under reduced pressure at 40°C on a rotary evaporator. To remove low molar mass species, cyclics and unreacted allyl methacrylate, the resulting clear colourless liquid was precipitated in methanol and stirred for 2 hours before being transferred to a separating funnel and left to separate. The lower cloudy PDMS phase was removed and dried under reduced pressure at 40°C on a rotary evaporator. A clear colourless viscous liquid product (16.47 g, 66% yield) was obtained. The molar mass of the product was calculated by ^{1}H NMR end group integration and was determined to be $\bar{M}_n \approx 22,900\,\mathrm{g\,mol^{-1}}$. The ^{1}H NMR spectrum of the α, ω-bis(methacryl)PDMS (3) product of this 1 pot, 2 stage reaction is included as Supporting Information.

2.4. α,ω-bis(methacryl)PDMS (**3**) Synthesis by a 2 Stage Process (Polymerisation followed by Functionalisation)

Similar methacrylate-terminated PDMS products were produced by 2 stage syntheses wherein the hydride-terminated PDMS (**1**) was first synthesised & isolated before subsequent hydrosilylation with allyl methacrylate to yield the intended product (**3**). The experimental conditions for each stage were similar to those described above for the 1 pot, 2 stage reaction, maintaining the mole ratio of catalyst to reagents.

2.5. 1,3-bis(methacryl)tetramethyldisiloxane (**2**) Synthesis

The small-molecule modified siloxane intermediate (**2**) was obtained through an analogous reaction to the 1 pot, 2 stage reaction procedure described above, stopping when the hydrosilylation reaction was deemed to have gone to completion.

2.6. Multi-armed Methacrylate-terminated PDMS (**6** & **9**) Synthesis

Methyltris(methacryl)PDMS (**6**) and tetrakis(methacryl)PDMS (**9**) were synthesised by substituting 1,1,3,3-tetramethyldisiloxane with methyltris(dimethylsiloxy)silane or tetrakis(dimethylsiloxy)silane in the 1 pot, 2 stage procedure described above, modifying the reagent loadings in the hydrosilylation stage to maintain the same molar equivalents of reagents to Si$-$H bonds.

2.7. Methyltris- (**5**) & Tetrakis(methacryl)siloxane (**8**) Synthesis

The branched small-molecule siloxane intermediates (**5** & **8**) were obtained by following the 1 pot, 2 stage reaction procedure described above for branched multi-armed PDMS, stopping when the hydrosilylation reaction was complete.

3. Results and discussion

3.1. α,ω-bis(hydrido)PDMS (**1**) Synthesis & Hydrosilylation

α,ω-bis(hydrido)PDMS (**1**) was successfully synthesised by acid-catalysed equilibration polymerisation of D_4 in the presence of 1,1,3,3-tetramethyldisiloxane as reported previously [3, 13]. The molar mass was controlled by the disiloxane : D_4 ratio and ^{1}H NMR demonstrated that the $\bar{M}_n$ was as expected, as shown in Table 1.

Functionalisation of α,ω-bis(hydrido)PDMS (**1**) by hydrosilylation with allyl methacrylate was successful given sufficient catalyst and reaction time. NMR of the products confirmed the presence of methacrylate functionality indicating that the hydrosilylation had been directed through the

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Table 1: Number-average molar mass ($\mathrm{g\,mol^{-1}}$) of α,ω-bis(hydrido)PDMS (**1**) & α,ω-bis(methacryl)PDMS (**3**).

Intended $\bar{M}_\mathrm{n}$	α,ω-bis(hydrido)PDMS (**1**)			α,ω-bis(methacryl)PDMS (**3**)		
	NMR[†]	GPC[‡]	Đ[§]	NMR[†]	GPC[‡]	Đ[§]
α,ω-bis(hydrido)PDMS (**1**) synthesis & subsequent hydrosilylation						
2,000	2,590	1,710	2.3	5,050		
10,000	9,220	8,480	1.9	26,200		
20,000	20,500	13,900	2.1	55,890		
1 pot, 2 stage, α,ω-bis(methacryl)PDMS (**3**) synthesis						
2,000	-	-	-	5,060	5,010	1.4
10,000	-	-	-	17,500	12,400	1.9
20,000	-	-	-	56,800	21,100	2.8

[†] ^{1}H NMR end group integration
[‡] against polystyrene standards
[§] from GPC

allyl group. This functionalisation, however, was observed to proceed with an increase in molar mass. The molar mass was expected to increase by $\sim 250\,\mathrm{g\,mol^{-1}}$ as the methacrylate end groups are added, but a much greater increase was consistently recorded. Table 1 shows the approximate doubling of molar mass typically observed in both ^{1}H NMR and GPC analyses (GPC data included in the Supporting Information). NMR data showed that oligomerisation/polymerisation of the methacrylate had not occurred. While absolute molar mass values measured by GPC may not be accurate as they are reported against polystyrene standards, the monomodal elution peaks may be used as a comparative measure as shown in Table 1. The functionalised materials were also more viscous than the corresponding hydride-terminated PDMS which were intended to be of similar molar mass indicating that the increased molar mass was a real effect, not an artefact of the measurement technique.

3.2. α,ω-bis(methacryl)PDMS (3) Synthesis by a 1 Pot, 2 Stage Reaction

Combining the functionalisation and polymerisation reactions into a 1 pot, 2 stage reaction presented a more time-efficient method of synthesising α,ω-bis(methacryl)PDMS (**3**). The hydrosilylation reaction was carried out first as the small-molecule hydrosilylation was faster than the equivalent reaction on a polymer with Si$-$H end groups. This difference in reaction kinetics is quite

reasonable considering the large difference in diffusion coefficients that would be expected for the reactants in the two hydrosilylation reactions. However, a slightly increased volume of triflic acid catalyst was required to achieve the polymerisation over a similar 1 hour timescale as achieved in earlier α,ω-bis(hydrido)PDMS syntheses.

^{1}H NMR of the modified PDMS products demonstrated that both functionalisation and polymerisation had been achieved. The relative integrals of the protons in the end groups confirmed the presence of methacrylate functionality and the spectrum was dominated by the peak at $\delta\,0.07$ ppm from the $Si-CH_3$ on the PDMS backbone. However, as had been observed previously, the molar mass of the methacrylate-terminated PDMS products were consistently double that expected based on reagent loadings. A Karstedt catalyst-catalyzed hydrosilylation at the acrylate is also conceivable and if it were to occur it would influence the molecular weight; however, such products are not seen in the ^{1}H-NMR spectra.

The approximate doubling of molar mass appeared to be an effect of the hydrosilylation reaction so efforts were directed to characterising the hydrosilylation of 1,1,3,3-tetramethyldisiloxane with allyl methacrylate.

3.3. 1,3-bis(methacryl)tetramethyldisiloxane (2) Synthesis

Methacrylate functionality was successfully introduced to small molecule silanes by hydrosilylation with allyl methacrylate in the presence of Karstedt's catalyst. It was expected that the hydrosilylation of 1,1,3,3-tetramethyldisiloxane with allyl methacrylate would produce 1,3-bis(methacryl)disiloxane (2) which could subsequently be equilibrated with D_4 to produce α,ω-bis(methacryl)PDMS (3) in a 1 pot, 2 stage reaction without the need to isolate the intermediate.

The products formed in the hydrosilylation reaction between 1,1,3,3-tetramethyldisiloxane and allyl methacrylate were analysed by electrospray ionisation mass spectrometry (ESI-MS). An example of the resulting spectra is presented in Fig. 3. The highest intensity peak at m/z 409.1837 corresponds to the mass expected for the intended product, 1,3-bis(methacryl)tetramethyldisiloxane (2), plus a sodium ion (Na^+, 22.99 Da) and peaks at higher m/z ratios (795.3777 & 669.3105) are consistent with 2 modified disiloxane molecules coordinating with a single sodium ion. In addition, there are two important observations on the ESI-MS spectrum which are discussed in detail below; some material has undergone siloxane chain extension, and the peaks representative of methacrylated species are often accompanied by satellite peaks with masses of 42.05 Da less than

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the modified siloxane.

Hydrosilylation reactions must be carried out under anhydrous conditions as the Karstedt catalyst is known to catalyse the addition of water to silicon hydrides, forming higher order siloxanes [13]. Such condensation may be one explanation of siloxane chain extension therefore steps were taken to exclude water from the hydrosilylation reaction. These steps were notably not directed to exclude oxygen as hydrosilylation reactions require small amounts of oxygen to proceed [33]. A control synthesis carried out under stringently dry conditions in a glove box using vacuum distilled reagents (still containing traces of oxygen) formed comparable products to reactions carried out under a nitrogen atmosphere.

Solvent choice was observed to have a large effect on the hydrosilylation reaction speed, with reactions taking up to 4 times longer in dichloromethane (DCM) than if tetrahydrofuran (THF) or D_4 were used as solvent [34]. Syntheses were carried out with various reagent loadings & catalyst concentrations; in all cases the products were comparable.

Siloxane Chain Extension

In addition to the expected methacrylated disiloxane (**2**), the ESI spectrum exhibits peaks at m/z ratios consistent with methacrylated tri- and tetrasiloxanes (m/z 483.2015 & 557.2213 respectively). Equilibration of siloxane chain lengths as shown in Fig. 4 has been reported previously for hydrosilylation reactions [35, 36]. However, these previous observations were made in studies carried out at elevated temperatures ($> 80°C$), whereas the hydrosilylation reactions carried out in this study were performed at room temperature.

The presence of multiple siloxane species in the crude reaction product is supported by its ^{1}H NMR spectrum (included in Supporting Information) where the $Si-CH_3$ region shows several peaks whose integral was greater than the 12 protons that would be expected for a methacrylated *di*siloxane. Such chain extension is significant in this work as molar mass control in equilibrium polymerisations is achieved by controlling the molar ratio of disiloxane to chain extender (in this study D_4) and the formation of higher order siloxanes in the hydrosilylation step effectively reduces the number of moles of modified siloxane.

Trace water in the hydrosilylation reaction mixture would lead to coupling of the disiloxane molecules and would cause chain extension. However, water-catalysed chain extension cannot produce *tri*siloxanes which were observed in the ESI-MS spectra. In addition, chain extension
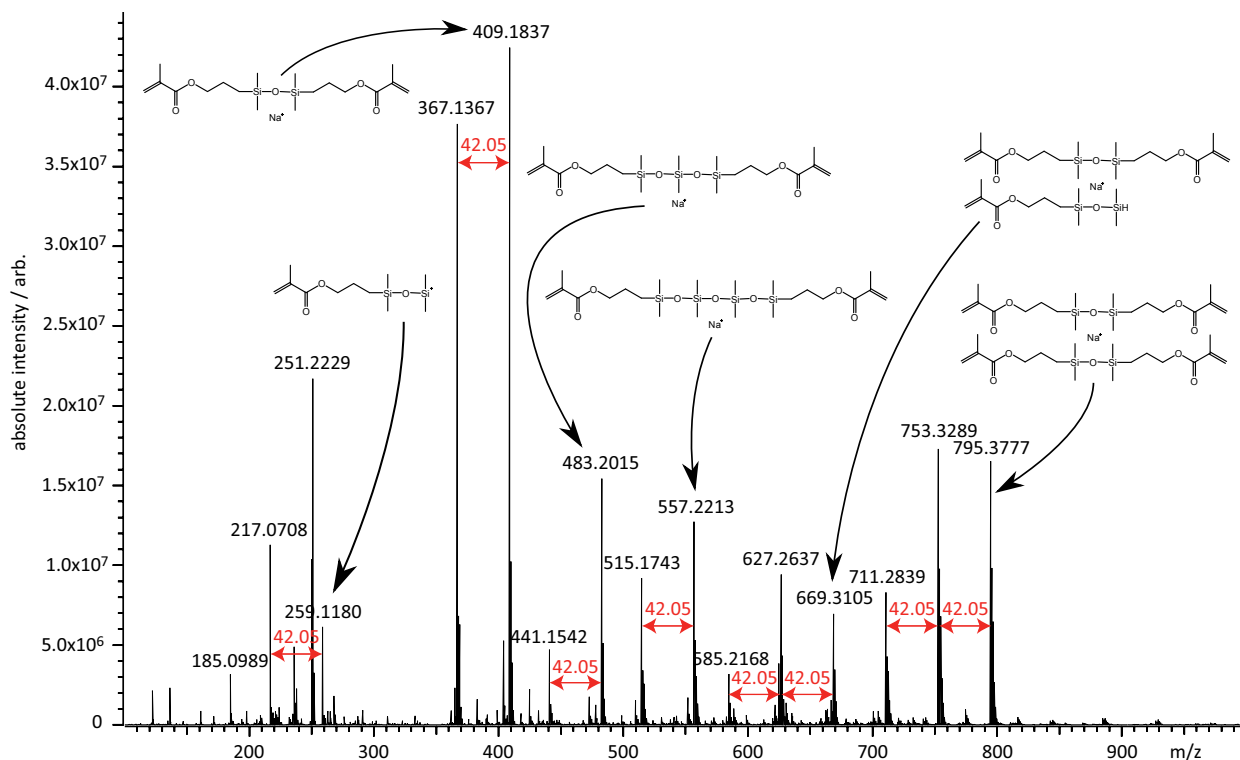
Figure 3: ESI-MS spectrum of the crude reaction product of hydrosilylation reaction between 1,1,3,3-tetramethyldisiloxane and allyl methacrylate (intended product: 1,3-bis(methacryl)tetramethyldisiloxane (**2**), m/z 409.1837). The spectrum indicates that modified tri- and tetrasiloxanes are also present in the product, and the presence of 42.05 Da satellites is thought to be due to the direct attachment of the methacryl ester to silicon - a reaction which proceeds with the elimination of propene.
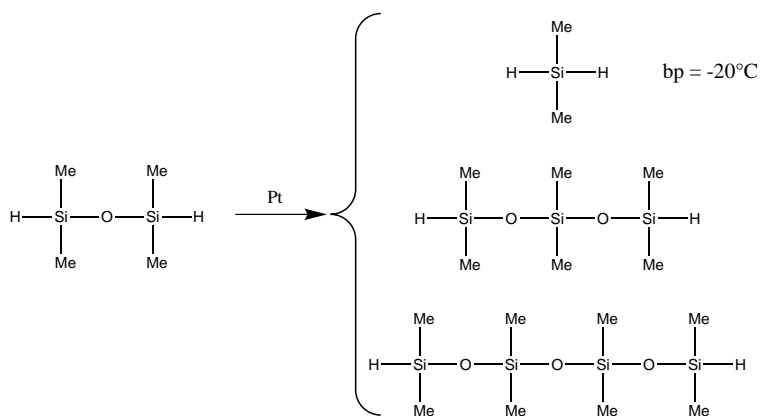

Figure 4: Proposed hydrosilylation side reaction resulting in an equilibration of siloxane chain lengths [35].

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persisted when the synthesis was carried out under stringently anhydrous conditions in a glove box using vacuum distilled reagents, discounting water incorporation as the cause of the observed siloxane chain extension.

The presence of a mixture of di-, tri- and tetrasiloxanes in the crude hydrosilylation reaction product does not explain the approximate doubling of molar mass (i.e. a molar mass increase factor of approximately 2) that was observed in PDMS products formed from 1 pot, 2 stage reactions. If the amount of silicon is preserved throughout the reaction, a molar mass increase factor of 2 would be caused by halving the number of moles of siloxane molecules, for example by complete conversion of the disiloxane to tetrasiloxane. The presence of di-, tri- and tetrasiloxanes would result in a molar mass increase factor of less than 2, with the exact factor depending on the relative proportions of each species.

The molar mass increase factor of 2 would, however, be explained by a loss of silicon through the reaction. As shown in Fig. 4, the equilibration of siloxane chain lengths also produces a species with only one silicon atom, dimethylsilane, but the ESI-MS spectrum does not show the corresponding methacrylate-functionalised derivative which would be expected at m/z 312.18. It is thought that the dimethylsilane is formed but evaporates from the hydrosilylation reaction mixture (boiling point[37] $-20°C$), hence why the modified monosiloxane is not observed in the ESI-MS spectrum. The evaporation of dimethylsilane from the reaction mixture would decrease the amount of silicon in the system and could explain the observed molar mass increase factor of 2.

42.05 Da Satellites

Fig. 3, in common with many other ESI-MS spectra on these products showed satellite peaks of significant intensity at m/z ratios 42.047 Da less than the methacrylated siloxanes, for example at m/z 367.1367, 441.1542 and 515.1743. Other peaks were assigned to fragments of the expected product, for example monofunctionalised tetramethyldisiloxane at m/z 259.1180, however the 42.047 Da spacing was observed throughout the spectrum and could not be described by any expected fragmentation. It is thought that these 42.047 Da satellites are due to the elimination of propene in the hydrosilylation reaction [38–41] as shown in Fig. 5. These 42.047 Da satellite peaks correspond to the attachment of the methacryl ester directly to the terminal silicon atoms by Si−O bond, **2a** in Fig. 5. It must be emphasised that a well-calibrated ESI-MS has this level of mass-accuracy and that 42.047 Da corresponds precisely to the exact mass of propene.
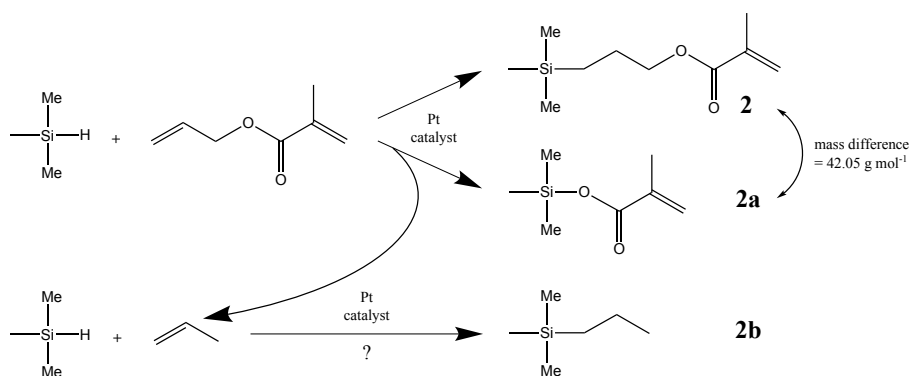
Figure 5: Reaction scheme showing the hydrosilylation of Si−H with allyl methacrylate proceeding as intended, and with the elimination of propene $(42.05\,\mathrm{g\,mol^{-1}})$ which has potential to react with Si−H.

Whilst the presence of these alternatively modified siloxanes is undesirable, it was not considered problematic for this work as they still contain methacrylate functionality at the chain ends and so are polymerisable. The unsaturated propene evolved in the formation of **2a** may potentially react with Si−H which would form a product with saturated chain ends (**2b**). This would be highly undesirable for this study as the unsaturation of the end groups will be essential in producing materials which have potential to cross-link in a free-radical reaction. However, peaks representative of siloxanes modified with unsaturated chain ends were not observed in the ESI-MS spectrum of the crude reaction product (Fig. 3), which for a disiloxane would be expected at m/z ratios of 302.17, 260.13 or 218.15 (M+Na 325.16, 283.13 or 241.14) depending on the modification to the other end of the molecule.

The formation of **2a** (or **2b**) in the hydrosilylation reaction would be expected to affect the relative integrals in the ^{1}H NMR spectrum of the reaction product. However, this was not observed (as shown in Supporting Information) and the peaks at $\delta\,6.10$, 5.55 & 4.10 ppm show a $2:2:4$ relationship as would be expected for the intended product 1,3-bis(methacryl)disiloxane (**2**) and its chain extended analogues. It is worthy of note that ESI-MS is not a quantitative technique which may explain why **2a** is not observed in the NMR spectra of the product.

3.4. Star Architecture Siloxanes: Methyltris- (5) & Tetrakis(methacryl)siloxane (8) Synthesis

Following the findings of the work presented above, synthesis of multi-armed methacrylate-terminated PDMS materials (**6** & **9**) was not carried out by formation of multi-armed hydride-terminated PDMS materials (**4** & **7**) and subsequent hydrosilylation with allyl methacrylate.

Products were instead formed by the more efficient 1 pot, 2 stage reaction process.

The first stage of the 1 pot, 2 stage reactions involved the formation of methyltris- (**5**) or tetrakis(methacryl)siloxane (**8**) intermediates which were subsequently equilibrated with D_4 to form multi-armed methacrylate-terminated PDMS. The small-molecule intermediates were investigated by NMR and their ESI-MS spectra are included in the Supporting Information.

The ESI-MS spectra of the reaction products contain peaks at the m/z ratios expected for methyltris- (**5**, m/z 669.27) or tetrakis(methacryl)siloxane (**8**, m/z 855.35). These peaks also have 42.05 Da satellites consistent with the direct attachment of silicon to the methacryl ester which proceeds with the elimination of propene [38–40] as depicted in Fig. 5. Multiple 42.05 Da satellites may be expected due to the multifunctional nature of the silanes, up to a maximum of 3 for the 3-armed species and 4 in the case of 4-armed materials. As was discussed in relation to the linear products, the propene that is eliminated in this reaction has the potential to react with Si−H through its C=C bond, however, peaks are not observed in the ESI-MS spectra at m/z ratios that would indicate the presence of such silanes modified with a saturated C_3 chain.

Interestingly, unlike the linear difunctional intermediates, the ESI-MS spectra of 3- and 4-armed methacrylate-terminated siloxanes do not show siloxane chain extension. If chain extension were to occur, peaks would be expected at m/z ratios of $n \times 74.02$ Da higher than the intended product (which may also have 42.05 Da satellites) for example at m/z 743.29 or 929.36.

3.5. Star Architecture Methacrylate-terminated PDMS (*6* & *9*) Synthesis

The 1 pot, 2 stage reactions proceeded as expected and an example ^{1}H NMR spectrum of the polymeric liquid products is included as Supporting Information. The peak integrals were calibrated to the ester protons at δ 4.10 ppm (t) which were set to either 6.0 in 3-armed products or 8.0 in 4-armed materials to calculate the ^{1}H NMR $\bar{M}_n$.

Three molar masses for each architecture polymer were produced which were intended to be comparable to the linear materials produced earlier. The length of PDMS chain between methacrylate groups was kept constant so that future studies may probe the effect of introducing branching into the polymers whilst maintaining the ratio of methacrylate groups to PDMS segments. For example, the lowest molar mass linear materials were intended to be $\bar{M}_n$ 2,000 g mol^{-1}, which corresponds to a lowest molar mass for 3-armed materials of $\bar{M}_n$ 3,000 g mol^{-1} and $\bar{M}_n$ 4,000 g mol^{-1} for 4-armed polymers. All of these architectures should have an average PDMS segment of $\sim$

Table 2: Number-average molar mass (g mol^{-1}) of multi-armed methacrylate-terminated PDMS.

Intended	NMR	GPC [†]	
$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{n}$	$\bar{M}_\mathrm{n}$	Đ
methyltris(methacryl)PDMS (**6**)			
3,000	7,150	3,765	1.5
15,000	30,450	11,900	3.1
30,000	56,780	18,800	4.0
tetrakis(methacryl)PDMS (**9**)			
4,000	12,940	6,200	1.9
20,000	69,080	15,950	3.7
40,000	85,870	18,100	4.5

[†] against polystyrene standards

$2,000 \, \mathrm{g\,mol}^{-1}$ between methacrylate end groups.

The molar mass of multi-armed PDMS products are included in Table 2 and the corresponding GPC data are in the Supporting Information. As was observed with linear materials, the $\bar{M}_\mathrm{n}$ of the multi-armed PDMS products determined by ^{1}H NMR end group integration are approximately double that intended. An extensive set of experiments indicate that the difference between intended and observed $\bar{M}_\mathrm{n}$ is not due to factors such as trace water presence, reaction conditions, reagent purity or loadings; the reason for this discrepancy remains unclear. For linear materials, the discrepancy between intended and observed molar mass was attributed to siloxane chain extension and loss of silicon from the reaction mixture (Fig. 4). However, siloxane chain extension was not observed in the ESI-MS analysis of branched small-molecule intermediates whilst the molar mass discrepancy remained. This may be explained by the chain extended products not showing up in the ESI-MS of the intermediates, for example by failing to become ionised under the conditions used and so not being registered, although this is unlikely, as the intended products were registered in the spectra. Alternatively, the molar mass discrepancy may be caused by a further factor which has yet to be identified.

4. Conclusions

A time-efficient 1 pot, 2 stage reaction has been used to produce methacrylate-terminated PDMS of linear (**3**) and star (**6** & **9**) architectures by hydrosilylating a small molecule siloxane with allyl methacrylate and equilibrating the product with D_4 in the presence of an acid catalyst. This 1 pot, 2 stage reaction is a more time- and reagent-efficient route to comparable products to the standard hydride-terminated PDMS synthesis and subsequent hydrosilylation procedures which are often quoted in the literature. The 1 pot, 2 stage reaction approach is expected to afford similar efficiency gains to many other siloxane syntheses and is not limited to the reported reactions.

All methacrylate-terminated products were approximately double the molar mass intended based on reagent loadings. Unfunctionalised α, ω-bis(hydrido)PDMS (**1**) products did not exhibit such discrepancy and the cause of the molar mass increase is thought to be in the hydrosilylation reaction.

When the small-molecule products of the hydrosilylation reaction between of 1,1,3,3-tetramethyldisiloxane and allyl methacrylate were studied, the hydrosilylation reaction was observed to proceed with an equilibration of siloxane chain lengths, accompanied by loss of silicon from the system by evaporation of dimethylsilane. Experiments have indicated that this siloxane chain length redistribution is independent of catalyst concentration, reagent loadings, solvent, work-up procedure, rate of addition and exposure to daylight, and a method of performing the hydrosilylation reaction without incurring this siloxane chain extension has not been found.

The same molar mass discrepancy was observed for branched methacrylate-terminated PDMS, however ESI-MS analysis of the small-molecule intermediates (**5** & **8**) did not show the same siloxane chain extension as was seen for the linear species. The underlying reason for either the redistributed chains not showing in the analysis, or siloxane chain extension not occurring in the branched siloxanes has not been ascertained.

The methacrylate-terminated PDMS macromonomers synthesised in this study have been successfully used to form films by UV-induced cross-linking and the investigations into the properties of the cross-linked films are the topic of future publications.

# References

[1] R. Yoda, *Journal of Biomaterials Science Polymer Edition* **1998**, *9*, 561–626.

[2] P. Hron, *Polymer International* **2003**, *52*, 1531–1539.

[3] G. Cai, W. P. Weber, *Polymer* **2004**, *45*, 2941–2948.

[4] *Polymer Data Handbook*, (Ed.: J. E. Mark), Oxford University Press, **1999**.

[5] C. Racles, M. Alexandru, A. Bele, V. E. Musteata, M. Cazacu, D. M. Opris, *RSC Adv.* **2014**, *4*, 37620–37628.

[6] M. Cole, K. M. Schreck, C. N. Bowman, *Polymer Preprints* **2011**, *52*, 270.

[7] X. Zeng, Z. Lu, Y. Liu, *Journal of Surfactants and Detergents* **2013**, *16*, 131–137.

[8] S. Feng, M. Cui, *Reactive and Functional Polymers* **2000**, *45*, 79–83.

[9] P. Yan, L. Qiu, *Polymer Bulletin* **2007**, *59*, 351–362.

[10] J. Chojnowski, L. Wilczek, *Die Makromolekulare Chemie* **1979**, *180*, 117–130.

[11] J.-J. Lebrun, G. Sauvet, P. Sigwalt, *Die Makromolekulare Chemie Rapid Communications* **1982**, *3*, 757–763.

[12] Y. Chujo, J. E. McGrath, *Journal of Macromolecular Science Part A* **1995**, *32*, 29–40.

[13] T. M. Gädda, W. P. Weber, *Journal of Polymer Science Part A: Polymer Chemistry* **2005**, *43*, 3007–3017.

[14] J. Künzler, R. Ozark, *Journal of Applied Polymer Science* **1997**, *65*, 1081–1089.

[15] M. H. Yang, C. Chou, C. H. Lin, *Journal Of The Chinese Chemical Society* **1998**, *45*, 199–207.

[16] K. Matsukawa, H. Inoue, *Polymer* **1992**, *33*, 667–670.

[17] A. Ekin, D. C. Webster, *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 6146.

[18] J. Chojnowski, J. Kurjata, W. Fortuniak, S. Rubinsztajn, B. Trzebicka, *Macromolecules* **2012**, *45*, 2654–2661.

[19] *Siloxane Polymers*, (Eds.: S. J. Clarson, J. A. Semlyen), Prentice Hall, **1993**.

[20] D. W. Scott, *Journal of the American Chemical Society* **1946**, *68*, 2294–2298.

[21] J. Künzler, R. Ozark, *Journal of Applied Polymer Science* **1995**, *55*, 611–619.

[22] L. G. Britcher, D. C. Kehoe, J. G. Matisons, A. G. Swincer, *Macromolecules* **1995**, *28*, 3110–3118.

[23] V. Hamciuc, L. Pricop, D.-S. Pricop, M. Marcu, *Journal of Macromolecular Science Part A* **2001**, *38*, 79–89.

[24] G. Colomines, S. Andre, X. Andrieu, A. Rousseau, B. Boutevin, *Journal of Applied Polymer Science* **2003**, *90*, 2021–2026.

[25] D. A. Brown, G. J. Price, *Polymer* **2001**, *42*, 4767–4771.

[26] B. Dudziec, M. Rzonsowska, B. Marciniec, D. Brzakalski, B. Wozniak, *Dalton Trans.* **2014**, *43*, 13201–13207.

[27] J. F. Miravet, J. M. J. Fréchet, *Macromolecules* **1998**, *31*, 3461–3468.

[28] C. Gong, J. M. J. Fréchet, *J. Polym. Sci. A Polym. Chem.* **2000**, *38*, 2970–2978.

[29] O. Novozhilov, I. Pavlichenko, N. Demchenko, A. Buzin, N. Vasilenko, A. Muzafarov, *Russian Chemical Bulletin* **2010**, *59*, 1909–1917.

[30] M. A. Grunlan, N. S. Lee, F. Mansfeld, E. Kus, J. A. Finlay, J. A. Callow, M. E. Callow, W. P. Weber, *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 2551–2566.

[31] D. J. Munoz-Pinto, R. E. McMahon, M. A. Kanzelberger, A. C. Jimenez-Vergara, M. A. Grunlan, M. S. Hahn, *Journal of Biomedical Materials Research Part A* **2010**, *94A*, 112–121.

[32] Y. Hou, C. A. Schoener, K. R. Regan, D. Munoz-Pinto, M. S. Hahn, M. A. Grunlan, *Biomacromolecules* **2010**, *11*, 648–656.

[33] L. N. Lewis, *Journal of the American Chemical Society* **1990**, *112*, 5998–6004.

[34] D. Chung, T. Kim, *Journal of Industrial and Engineering Chemistry* **2007**, *13*, 979–984.

[35] C. W. Macosko, J. C. Saam, *Polymer Bulletin* **1987**, *18*, 463–471.

[36] M. R. Stober, M. C. Musolf, J. L. Speier, *The Journal of Organic Chemistry* **1965**, *30*, 1651–1652.

[37] *CRC Handbook of Chemistry and Physics*, (Ed.: D. R. Lide), CRC Press, 89th ed., **2008**.

[38] E. Beyou, P. Babin, B. Bennetau, J. Dunogues, D. Teyssie, S. Boileau, *Journal of Polymer Science Part A: Polymer Chemistry* **1994**, *32*, 1673–1681.

[39] S. Q. S. Lin, S. T. Nakos, *US Patent*, 4,503,208, **1985**.

[40] J. M. Yu, D. Teyssie, S. Boileau, *Polymer Bulletin* **1992**, *28*, 435–440.

[41] B. Boutevin, F. Guida-Pietrasanta, A. Ratsimihety, *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, *38*, 3722–3728.
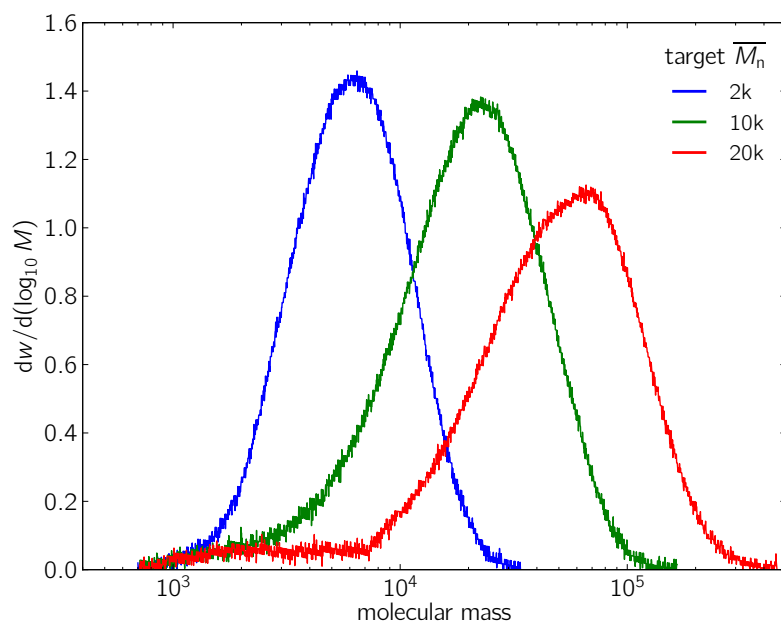
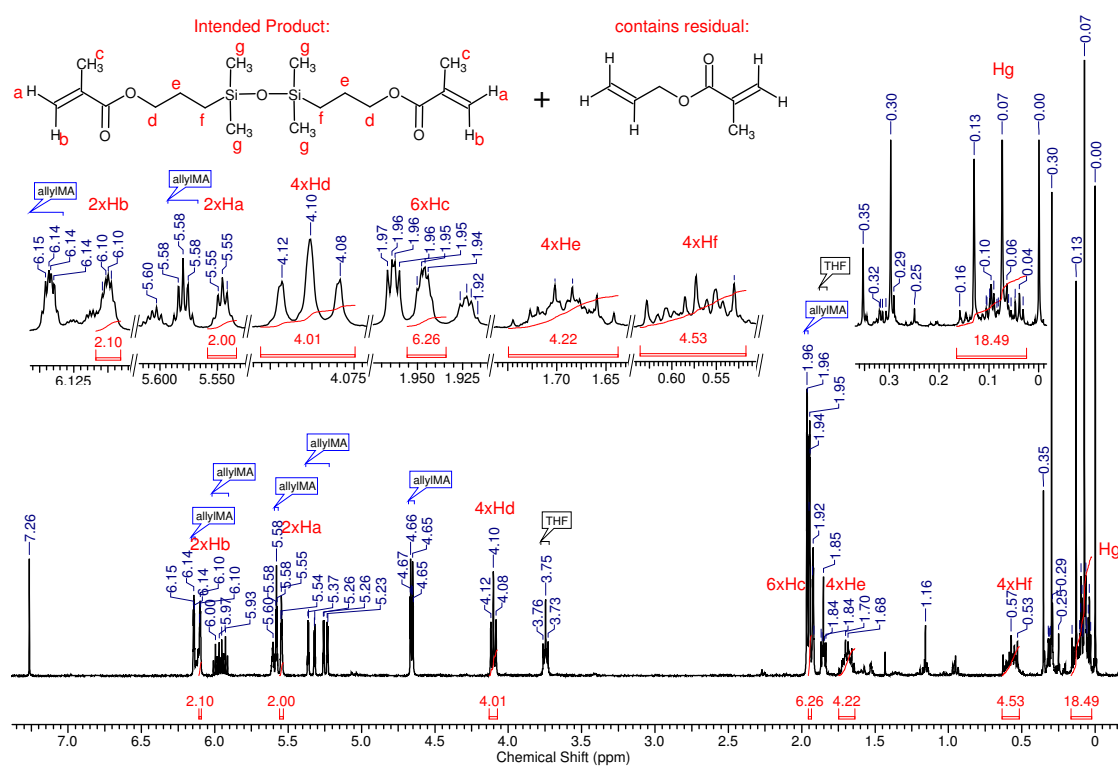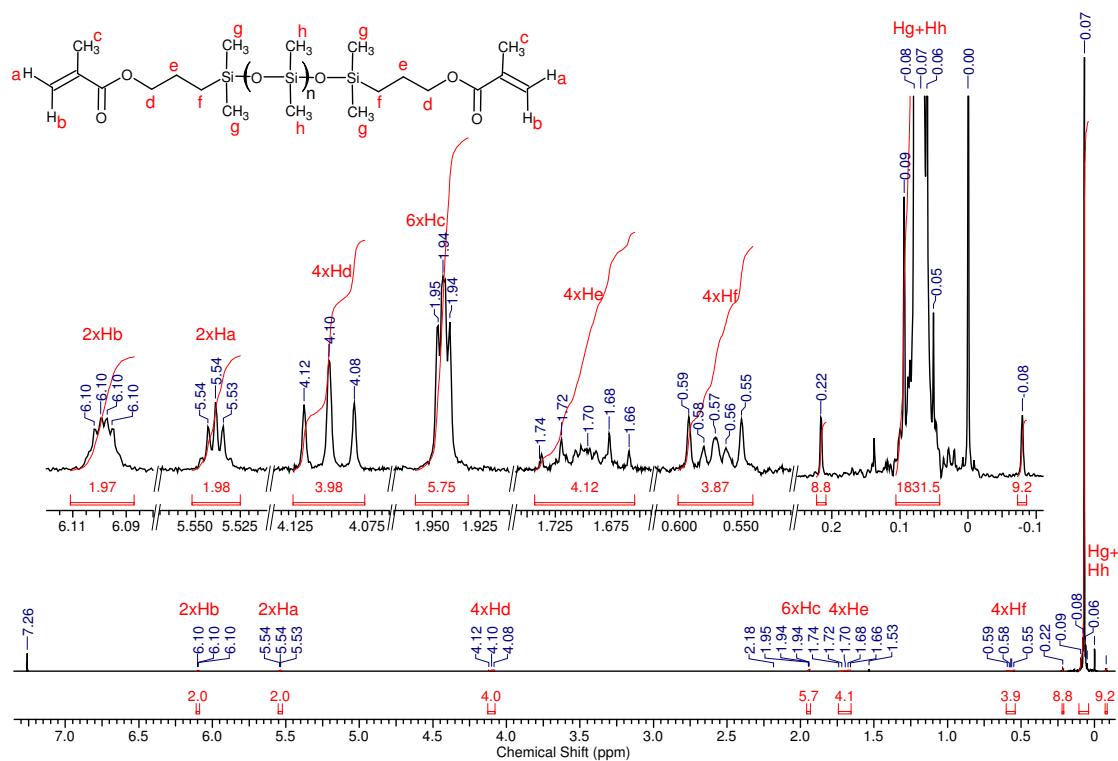# Linear and Star Architecture Methacrylate-functionalised PDMS
Supporting information

Cheesman, Gates, Castle, Cosgrove, Prescott
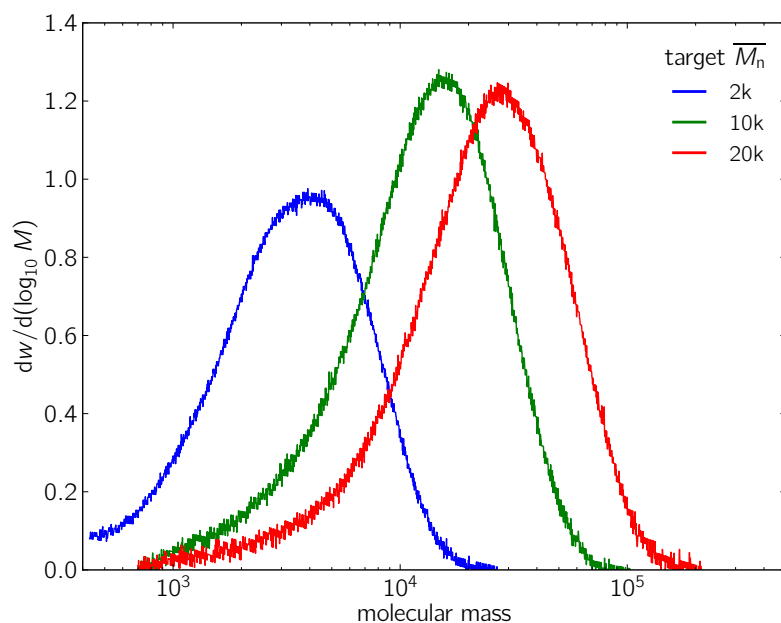
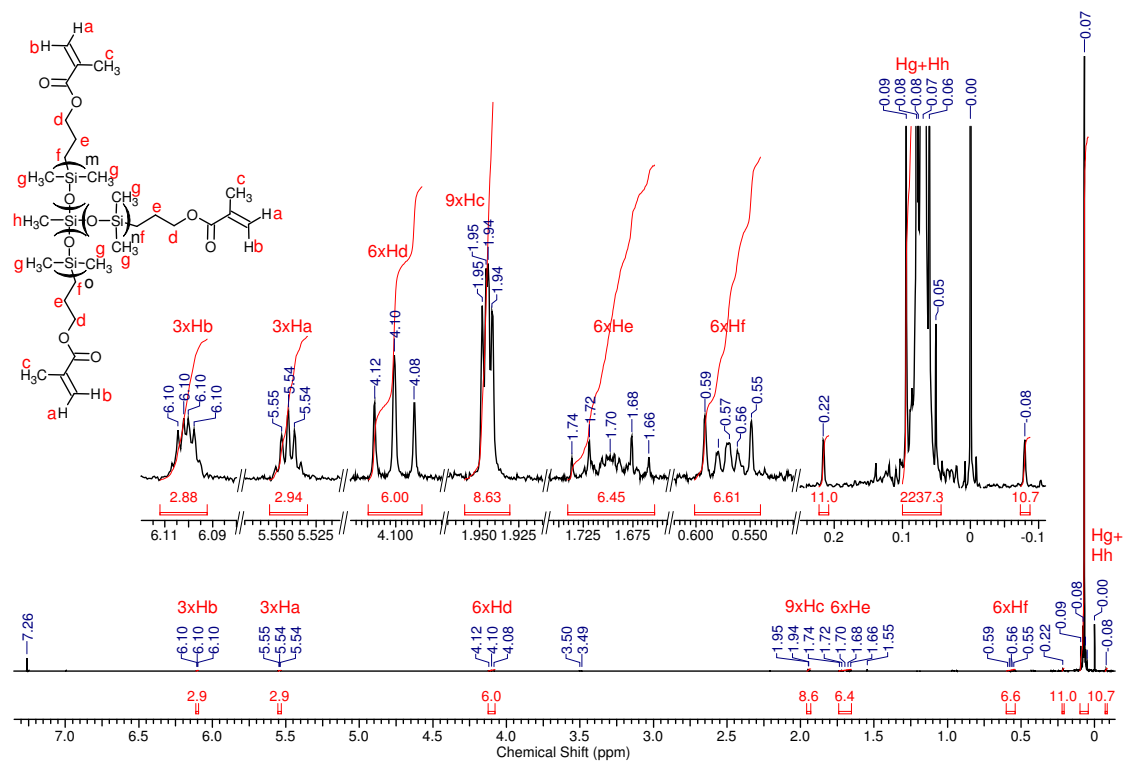Supplementary Figure 1: GPC data for the sequential α,ω-bis(hydrido)PDMS (**1**) synthesis & subsequent hydrosilylation reactions, targeting $\bar{M}_\mathrm{n} \sim 2, 10, 20\,\mathrm{kg\,mol}^{-1}$.

Supplementary Figure 2: GPC data for α,ω-bis(methacryl)PDMS (**3**) from the 1 pot, 2 stage reactions, targeting $\bar{M}_\mathrm{n} \sim 2, 10, 20\,\mathrm{kg\,mol}^{-1}$.

Supplementary Figure 3: ^{1}H NMR spectrum of α,ω-bis(methacryl)PDMS (**3**) synthesised by a 1 pot, 2 stage reaction, target $\bar{M}_n$ 10,000 g mol^{-1}, actual $\bar{M}_n$ 22,900 g mol^{-1}.

Supplementary Figure 4: ^{1}H NMR spectrum of the crude reaction product of 1,3-bis(methacryl)disiloxane (**2**) synthesis, NB. contains residual unreacted allyl methacrylate (allylMA), only peaks expected to be due to modified siloxane product have been integrated.
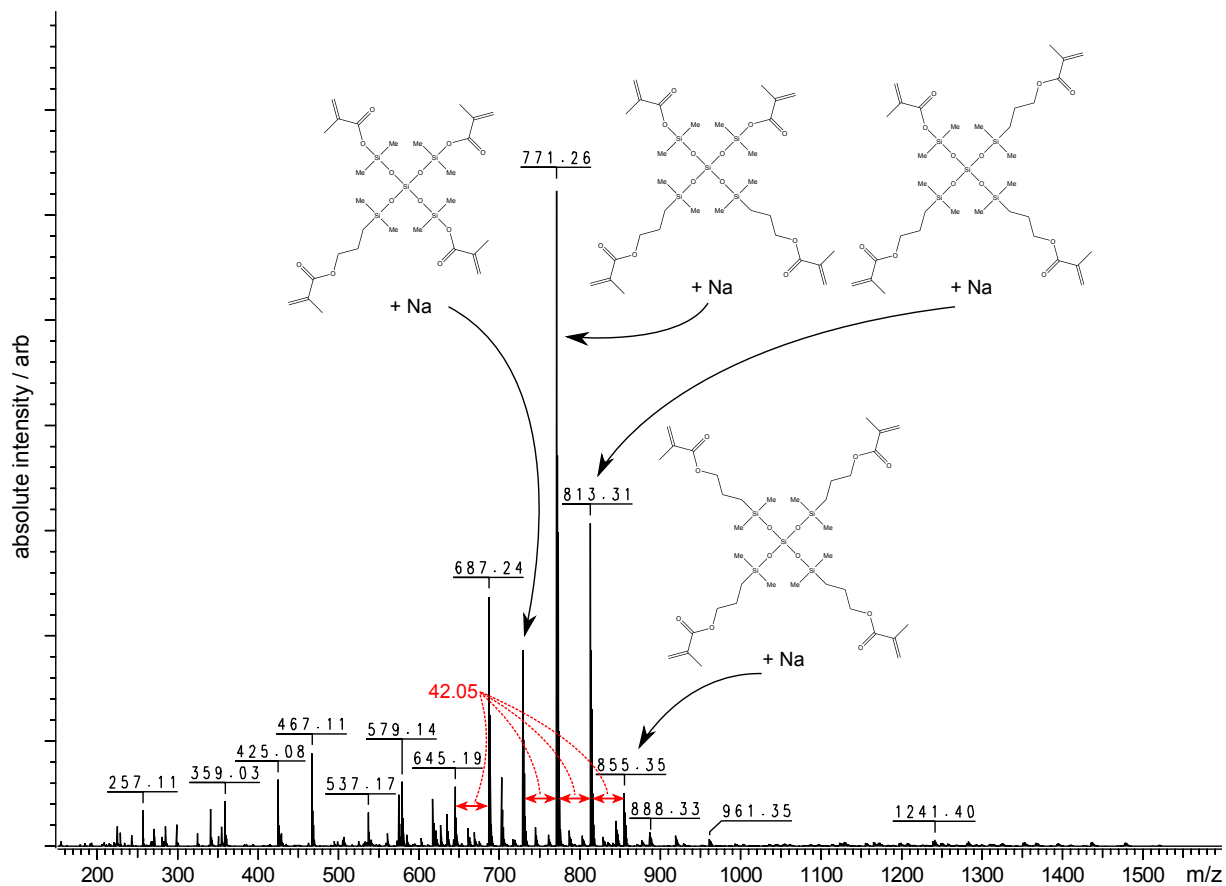
Supplementary Figure 5: ^{1}H NMR spectrum of methyltris(methacryl)PDMS (**6**), target $\bar{M}_\mathrm{n}$ 15, 000 g mol^{-1}, actual $\bar{M}_\mathrm{n}$ 28, 050 g mol^{-1}.
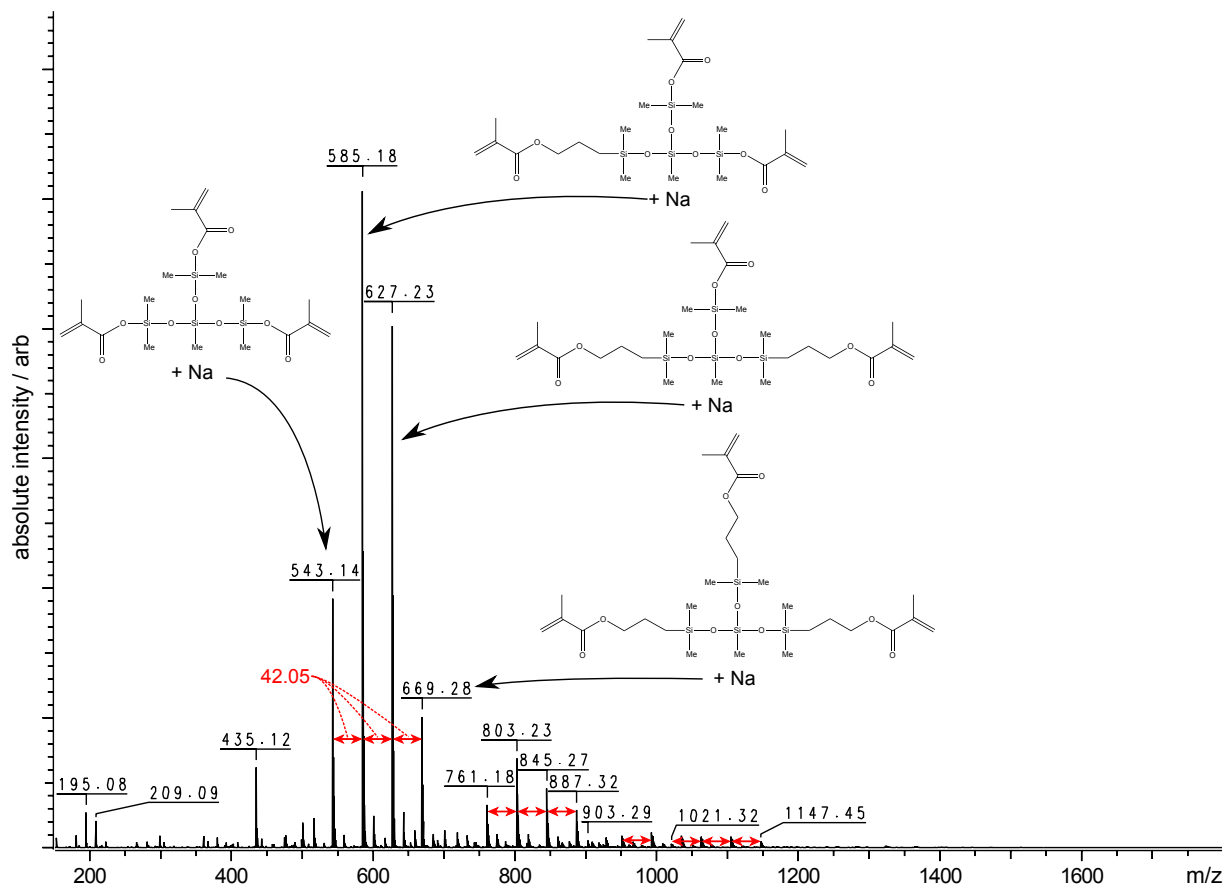
Supplementary Figure 6: ESI-MS spectrum of the crude reaction product of hydrosilylation reaction between methyltris(dimethylsiloxy)silane and allyl methacrylate (intended product: methyltris(methacryl)siloxane (**5**)).

Supplementary Figure 7: ESI-MS spectrum of the crude reaction product of hydrosilylation reaction between tetrakis(dimethylsiloxy)silane and allyl methacrylate (intended product: tetrakis(methacryl)siloxane (**8**)).
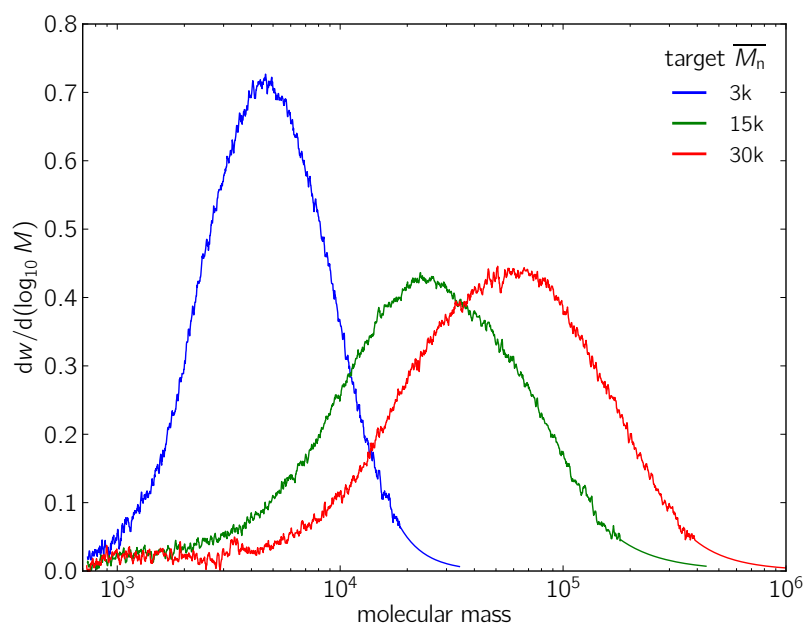
Supplementary Figure 8: GPC data for the three-armed methyltris(methacryl)PDMS (**6**), targeting $\bar{M}_\mathrm{n} \sim 3, 15, 30\,\mathrm{kg\,mol}^{-1}$.
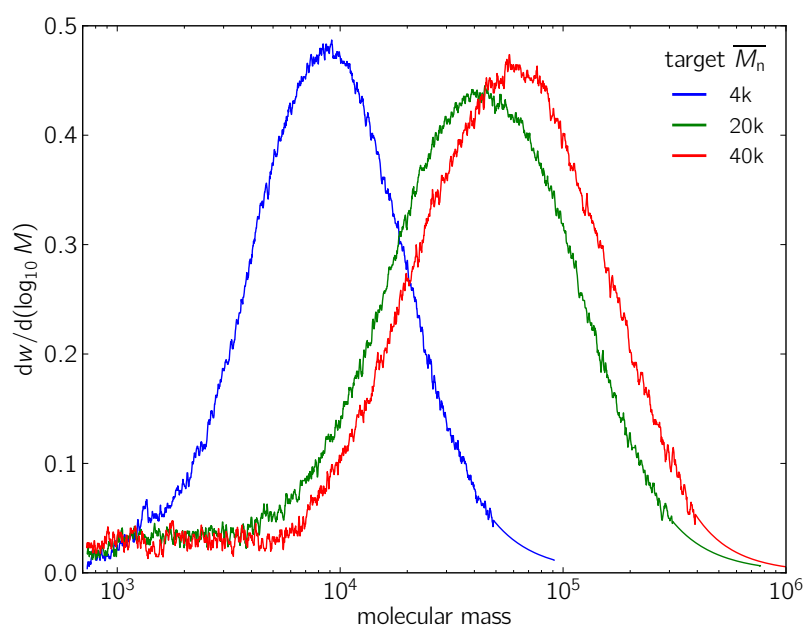
Supplementary Figure 9: GPC data for the four-armed tetrakis(methacryl)PDMS (**9**), targeting $\bar{M}_\mathrm{n} \sim 4, 20, 40\,\mathrm{kg\,mol}^{-1}$.