Living Polymerization Routes to Siloxane Macromers and Higher Order Silicone Structures

Jonathan Goff,* Edward Kimble, and Barry Arkles

Gelest, Inc., 11 East Steel Road, Morrisville, Pennsylvania 19067
***E-mail: jgoff@gelest.com**

This report describes the synthesis, characterization and physical properties of symmetric silicone macromers, as well as new dual functional macromers, with both asymmetric and symmetric structures. Higher order silicone structures are introduced as convergent-branched silicones synthesized using hydride functional silicone macromer building blocks linked to a cyclic siloxane core. Silicone chain length, endgroup functionality and number of chains attached to the core have been studied to elucidate the physical properties of these higher order silicone structures.

Introduction

Functional siloxane polymers, commonly referred to as reactive silicones, constitute a large class of reactive materials. Siloxanes with vinyl, silanol and hydride substitution have the broadest utilization, serving as the basis for the majority of elastomeric silicone products (*1*). Functional siloxanes combined with organic monomers form "hybrid" polymers, which, while demonstrating utility, have comparatively limited commercial application (*2*). Most siloxane polymers are prepared by ring-opening polymerization with broad molecular weight distributions, which curtail their ability to act as precise structural elements. An alternative is to employ silicone macromers prepared by controlled "living" anionic ring-opening polymerization (AROP). Silicone macromers are defined as silicon containing species with a single functional polymerizeable group, which, although used as monomers, have sufficiently hig molecular weight and internal monomer units to be considered polymeric (*3*).

Monomer requirements for 'living' polymerization technique are more restrictive than standard acid/base catalyzed ring-opening polymerizations, requiring a cyclic siloxane with ring strain. Cyclic trimer monomers, such a hexamethylcyclotrisiloxane (D3), are commonly used. A lithium reagent is used to generate a lithium siloxanolate *in situ* and a polar aprotic solvent is used to form a lose ion pair between the siloxanolate and the lithium counter ion allow for propagation of the siloxane chains. The conditions and time scale of the 'living' AROP must be carefully considered to ensure that the propagation of the polymer chains occurs preferentially over chain scrambling and backbiting reactions. An endcapper is used to react with the siloxanolate once the monomer is consumed to add functionality. Siloxanes made from living polymerizations are reported to have PDIs close to unity. In addition to homopolymer silicones, the AROP technique can produce random or block copolymer structures depending on monomer choice and order of addition to the polymerization (*4, 5*).

Traditional asymmetric silicone macromers with a single functional group synthesized by living polymerizations afford many desirable properties, including, narrow molecular weight distribution, high oxygen permeability, increased polarity and available reactive functionality. They can serve as precise structural elements to prepare hybrid copolymers. The methacrylate functional silicone macromers first reported nearly 25 years ago are representative of the typical structure (*6*):
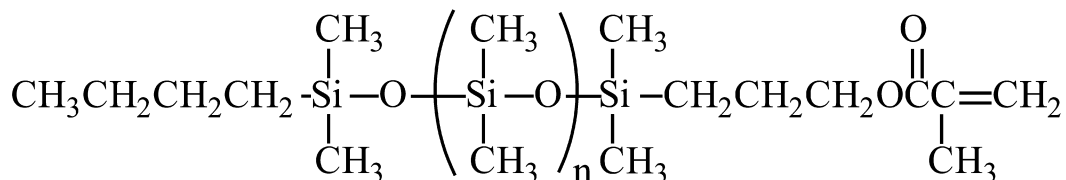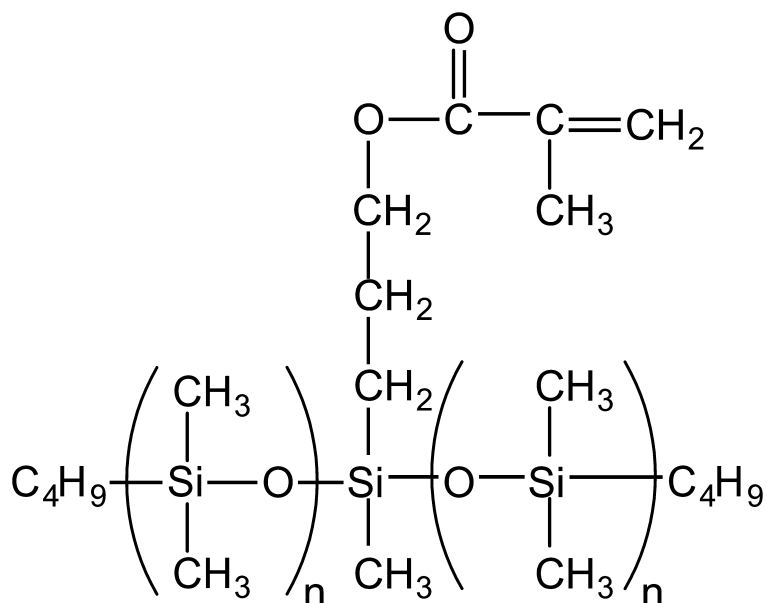

As depicted, the structure indicates the α-butydimethylsiloxy termination derived from the lithium butyldimethylsilanolate initiator, the repeating dimethylsiloxane unit derived from the ring-opening polymerization of the ring-strained hexamethylcyclotrisiloxane and the omega termination or "capping" functionality derived from methacryloxypropyldimethylchlorosilane.

Methacrylate functional macromers have been commercialized in pigment dispersion, adhesive release, controlled atmosphere food packaging and contact lens applications (*7–11*). To date, however, the utilization of silicone macromers has been limited primarily by economic, but also by structural and compositional considerations. Objectives for silicone macromer design include increasing their solubility range in organic monomers/solvents, retention of desirable siloxane properties without domain formation and improvement of economics (*3*).
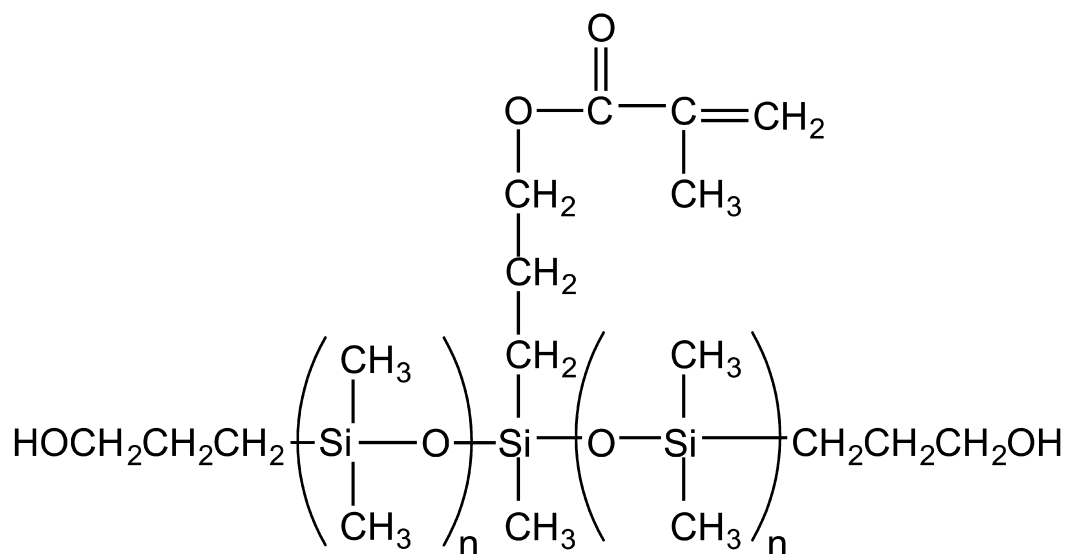
Silicone macromers with symmetric architectures can be readily formed via the anionic ring-opening polymerization of a cyclic trisiloxane and subsequent coupling with a functional dihalogen substituted silane reagent (*3, 12*).
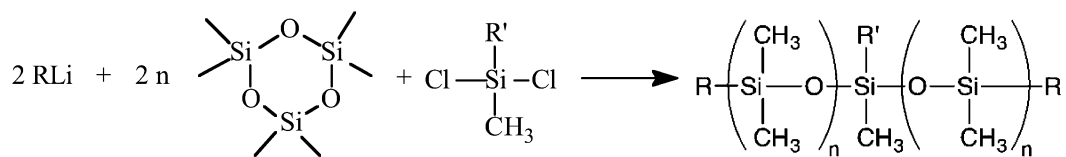
Symmetric macromers, for example, can contain a pendant methacrylate group bisecting the polydimethylsiloxane backbone.

$$\text{C}_4\text{H}_9-\left(\text{Si(CH}_3)_2-\text{O}\right)_n-\text{Si(CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O-CO-C(CH}_3)=\text{CH}_2)-\left(\text{O}-\text{Si(CH}_3)_2\right)_n-\text{C}_4\text{H}_9$$

A second class of functionality can be introduced into macromers by using novel initiators, yielding telechelic polymers in which the second functional class, for example hydroxyl, is at the telechelic polymer termini, which are equidistant from the first functional class (*12*).

$$\text{HOCH}_2\text{CH}_2\text{CH}_2-\left(\text{Si(CH}_3)_2-\text{O}\right)_n-\text{Si(CH}_3)(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O-CO-C(CH}_3)=\text{CH}_2)-\left(\text{O}-\text{Si(CH}_3)_2\right)_n-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$$

This report describes the synthesis, characterization and physical properties of symmetric silicone macromers, as well as new dual functional macromers, with both asymmetric and symmetric structures. Higher order silicone structures are introduced as convergent-branched silicones synthesized using hydride functional silicone macromer building blocks linked to a cyclic siloxane core. Silicone chain length, endgroup functionality and number of chains attached to the core have been studied to elucidate the physical properties of these higher order silicone structures.

Experimental

Materials

Hexamethylcyclotrisiloxane (D_3, 98%), (3,3,3-trifluoropropyl)methylcyclotrisiloxane (97%), dimethylchlorosilane (97%), methyldichlorosilane (97%), trichlorosilane (97%), methacryloxypropyldimethylchlorosilane (95%, inhibited with MEHQ), methacryloxypropylmethyldichlorosilane (95%, inhibited with MEHQ), methacryloxypropyltrichlorosilane (95%, inhibited with MEHQ), platinum-divinyl tetramethyldisiloxane catalyst (Karstedt catalyst, 2.2 wt% Pt), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4vinyl, 97%), 3-methoxypropyl lithium (1.3 M in hexanes) and 3-(t-butyldimethylsiloxy)-1-propyl lithium (1.0 M in cyclohexane) were obtained from Gelest and used as received. n-Butyl lithium (2.6 M in hexanes, Chemetall-Foote), tetrahydrofuran (THF, HPLC grade, J.T. Baker), hexanes (Ashland Chemical), glacial acetic acid (Quaker City), and ethanol (Quaker City) were used without further purification.

Synthesis of Methacrylate Functional Asymmetric Silicone Macromers

An exemplary synthesis of a 1,000 g mol^{-1} monomethacryloxypropyl terminated poly(dimethylsiloxane) asymmetric macromer (MCR-M11) is provided. In the case of a 1,000 g mol^{-1} monomethacryloxypropyl terminated poly(trifluoropropylmethylsiloxane) (MFR-M15) synthesis, (3,3,3-trifluoropropyl)methylcyclotrisiloxane is substituted for hexamethyl-cyclotrisiloxane (D_3). Other molecular weight asymmetric silicone macromers can be synthesized in an analogous manner by adjusting monomer to initiator ratios to control polymer chain length. D_3 (250 g, 1.12 mol) and hexanes (230 mL) were added to a 1 L round bottom flask containing a magnetic stir bar. The flask was purged with nitrogen and the reaction mixture was stirred at room temperature until the D_3 monomer was dissolved. n-Butyllithium (2.6 M, 96.0 mL, 0.250 mol) was added to the reaction flask via addition funnel and the solution was stirred for 1 h, followed by the addition of THF (100 mL) to the solution as polymerization promoter. Upon ~95% conversion of monomer (3 h), the polymer was terminated with a slight excess of methacryloxypropyldimethylchlorosilane (55.2 g, 0.250 mol). The solution was stirred overnight and washed three times with deionized water. The organic layer was dried with $MgSO_4$ and concentrated under vacuum at 80 °C. The resulting MCR-M11 macromer was characterized using ^{1}H NMR and GPC.

Synthesis of Methacrylate Functional Symmetric Silicone Macromers

An exemplary synthesis of a 1,000 g mol^{-1} bis(n-butyl terminated poly-[dimethylsiloxane])methylmethacryloxypropylsilane symmetric macromer (MCS-M11) is provided. In the case of a 1,000 g mol^{-1} bis(n-butyl terminated polytrifluoropropylmethylsiloxane)methylmethacryloxypropylsilane (MFS-M15) synthesis, (3,3,3-trifluoropropyl)methylcyclotrisiloxane is substituted for D_3. Following a living anionic ring opening polymerization procedure previously described for MCR-M11, D_3 (125 g, 0.562 mol) dissolved in

hexanes (224 mL) was initiated with n-butyllithium (2.6 M, 96.0 mL, 0.250 mol) followed by addition of THF (110 mL) to promote propagation of the silicone chains. At 95% consumption of the D_3 monomer (3 h) the lithium siloxanolate chain ends were coupled using a stoichiometric amount of methacryloxypropylmethyldichlorosilane (30.1 g, 0.125 mol). The solution was stirred overnight and washed three times with deionized water (3 X 200 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum at 80 °C. The resulting MCS-M11 macromer was characterized using ^{1}H NMR and GPC.

Synthesis of Methacrylate Functional T-Structure Silicone Macromers

A 1,000 g mol^{-1} tris(n-butyl terminated poly[dimethylsiloxane])-methacryloxypropylsilane (MCT-M11) was synthesized using a D_3 anionic ring opening polymerization procedure similar to the synthesis of MCR-M11 and MCS-M11. Once the propagating silicone chains reached the desired length, a stoichiometric amount of methacryloxypropyltrichlorosilane was added to the reaction mixture to couple the lithium siloxanolate chain endgroups. The MCT-M11 was worked up as previously described and characterized using ^{1}H NMR and GPC.

Synthesis of Dual Functional Silicone Macromers

Anionic lithium initiator alternatives to n-butylithium were investigated, including methoxypropyllithium and 3-(t-butyldimethylsiloxy)-1-propyl lithium, for the purpose of introducing hydrophilic chain endgroups in the silicone macromer structure. The synthesis of a targeted 1,000 g mol^{-1} bis(hydroxypropyl terminated poly[dimethylsiloxane])methacryloxypropylmethylsilane (MCS-MC12) is provided. D_3 (85.0 g, 0.382 mol) was dissolved in hexanes (90 mL) in a 1 L roundbottom flask containing a magnetic stir bar with nitrogen purge. The polymerization was initiated with the addition of the silylated or "blocked" initiator, 3-(t-butyldimethylsiloxy)-1-propyl lithium, (1.0 M, 382 mL, 0.382 mol) via addition funnel and the solution was allowed to stir for 1 h. THF (92 mL) was added to the reaction mixture to promote the propagation of the silicone chain ends. Methacryloxypropylmethyldichlorosilane (46.1 g, 0.191 mol) was added to the reaction mixture after 2 h to couple the lithium siloxanolate chain endgroups. The solution was stirred overnight and washed three times with deionized water (3 X 200 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum at 80 °C. The resulting macromer precursor was characterized using ^{1}H NMR and GPC.

The t-butyldimethylsiloxylpropyl endgroups were deblocked using mildly acidic deprotection conditions to form a hydroxypropyl terminated symmetric silicone macromer. MCS-MC12 precursor (70.0 g, 0.073 mol) containing protected hydroxyl groups was dissolved in ethanol (160 mL) in a 500 mL roundbottom flask containing a magnetic stir bar. 10 mL of a 67 wt% aqueous acetic acid solution was added to the reaction mixture. The solution was stirred under nitrogen for 24 h. Water (140 mL) was added to the stirring solution followed by addition of hexanes (200 mL). The solution was allowed to stir for

15 minutes and was transferred to a 1 L separatory funnel. The organic layer was collected and washed with a 5 wt% aqueous sodium bicarbonate solution (200 mL) until the pH was neutral. The organic layer was dried with $NaSO_4$ and concentrated under vacuum at 100 °C with a dry air sparge. Deprotection of the MCS- MC12 endgroups was quantified using various spectral techniques.

Methoxypropyllithium was used as the initiator in a similar procedure to yield monomethoxypropyl-, monomethacryloxypropyl- terminated poly(dimethylsiloxane) (MCR-ME11) and bis(methoxypropyl-terminated poly[dimethylsiloxane])methacryloxypropylmethylsilane (MCS-ME11).

Synthesis of Hydride Functional Branched Silicone Precursors

Asymmetric, symmetric and T structure silicones containing hydride functionality were synthesized using living anionic ring opening polymerization techniques. A characteristic procedure for the synthesis of a 900 g mol^{-1} hydride functional asymmetric silicone is provided. D_3 (200.0 g, 0.900 mol) and hexanes (205 mL) were charged to a 1 L round bottom flask containing a magnetic stir bar. The mixture was stirred for 1 h under nitrogen. n-Butyl lithium (2.6 M, 103.0 mL, 0.270 mol) was charged to the flask via addition funnel and the mixture was stirred for 1 h. THF (90 mL) was added to the flask and the polymerization was monitored during the propagation step. At 95% consumption of D_3 (4 h) an excess of dimethylchlorosilane (27.0 g, 0.285 mol) was added to the solution. The solution was stirred overnight and washed three times with deionized water (3 X 200 mL). The organic layer was dried with $MgSO_4$ and concentrated under vacuum at 80 °C. The resulting precursor to convergent-branched silicone structures (MCR-H07) was characterized using ^{1}H NMR and GPC.

Convergent Branched Silicone Synthesis

A characteristic procedure for the synthesis of a MCR-H07 (α-monobutyl, ω-monohydride terminated polydimethylsiloxne DP=10) convergent-branched silicone is provided. 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4vinyl) (43.40 g, 0.126 mol) and 2.4 g of platinum-divinyl tetramethyldisiloxane catalyst in xylene (2.2 wt% Pt) were charged to a 1 L roundbottom flask containing a magnetic stir bar. The reaction mixture was heated to 90 °C under nitrogen with stirring. A 900 g mol^{-1} hydride functional asymmetric silicone (450 g, 0.50 mol) was added over 2 h to the reaction mixture via addition funnel. The flask temperature was increased to 110 °C and the reaction mixture was allowed to stir for an additional 3 h while monitoring reaction progress by FTIR. The reaction was heated under vacuum at 110 °C for 1 h and filtered over celite. The product was characterized by ^{1}H NMR and GPC.

Characterization

^{1}H NMR spectral analyses of compounds were performed on a 400MHz Jeol NMR using $CDCl_3$ as solvent. A Thermo Nicolet Avatar 360 was used for FTIR

measurements. Viscosities were measured using a Brookfield Viscometer Model DV-II+ at 25.0 °C.

A Viscotek GPC Max VE2001 with a TDA 301 detector equipped with a Viscotek LT5000L mixed medium organic column was used for gel permeation chromatography (GPC) analyses. GPC data were collected in THF at 35 °C. Data were analyzed with a refractive index detector using a calibration made with polystyrene standards. Thermogravimetric Analysis (TGA) of the macromers was performed using a TA Instruments TGA Q50. Samples were equilibrated at 25 °C and the temperature was ramped at 10 °C min-1 to 700 °C in both nitrogen and air atmospheres.

Rheological measurements were carried out using a TA Instruments AR2000 equipped with a TA Instruments Environmental Test Chamber at 25 °C using 40 mm stainless steel parallel plates. Samples were analyzed using a steady state flow experiment, where viscosity was measured as a function of shear rate (0.01-500 s^{-1}).

Results and Discussion

Description of Polymer Designations

In order to provide a concise description of the macromer systems discussed, the following designation was adopted: The first two letters MC indicate macromer M structure with a C conventional dimethylsiloxane repeat unit. The third letter indicates whether it is asymmetric R, symmetric S or T for "T-structure." Functionality and viscosity of the macromer are indicated after a hyphen as follows: 1) letters indicate functionality where M is methacrylate, H is hydride, C is carbinol, V is vinyl, E is methoxy; and 2) numbers are the viscosity ranges of the macromer in powers of 10 followed by the first significant figure. For example MCR-H25 indicates a macromer, an asymmetric architecture with hydride functionality and a viscosity of 10^2 x 5 or 500 cSt. For branched silicones the core or hub is designated, followed by the number of branchpoints or spokes at the hub and the DP of the spokes. These designations are provide a facile method of discussing comparative structures, but are not intended to be detailed descriptions of the polymer structures.

Methacrylate Functional Silicone Macromers

The synthesis of methacrylate functional silicone macromers requires a well-defined polymerization approach. Macromolecular design objectives for silicone macromers include increasing their solubility in polar monomers or solvents, retention of desirable siloxane properties and improvement of economics (*3*, *12*). Due to the lack of controlled chain length and inability to have a single functional group on a silicone, chain growth equilibration polymerizations of silicones are unsuitable for the synthesis of silicone macromers. Chain growth equilibration polymerization of cyclic siloxanes is widely used approach for the synthesis of functional silicones in industry (*13*). This approach utilizes a disiloxane endcapper reagent and an acid or base catalyst with no restrictions

on the ring size of the cyclic siloxane monomer. Silicone polymer growth is achieved by the insertion of the monomer into an active chain center, leading to an equilibrium consisting of approximately 85% functional silicone and a remainder of cyclics and oligomeric siloxanes (Scheme 1). Functional silicones synthesized via this polymerization technique have broad molecular weight distributions with a polydispersity index (PDI) typically ≥ 2.
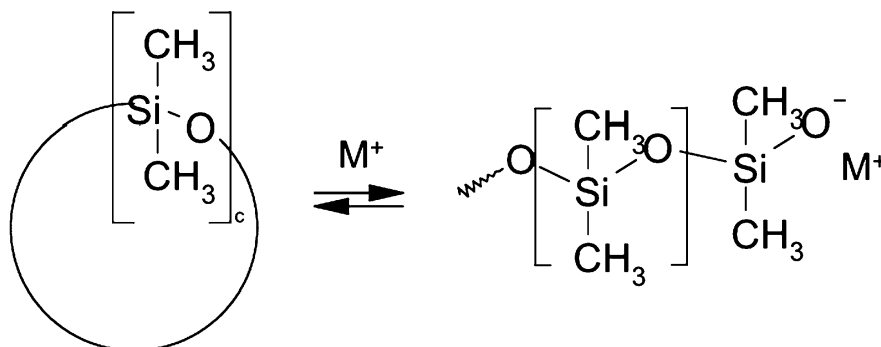
Scheme 1. Base catalyzed chain growth equilibration of cyclic siloxanes. [c = 3, 4, 5, 6, etc.; $M^+ = Na^+, K^+, Cs^+, R_4N^+$, etc.]

Silicones derived from chain growth equilibration techniques are limited by the polymer architectures achievable using a disiloxane endcapper. Acrylate functional silicones synthesized by chain growth equilibrations (e.g. bis(methacryloxypropyl) terminated polydimethylsiloxane and bis(acryloxy-hydroxypropoxypropyl) terminated polydimethylsiloxane) have a telechelic structure, which does not fit the definition of a macromer structure (Figure 1).
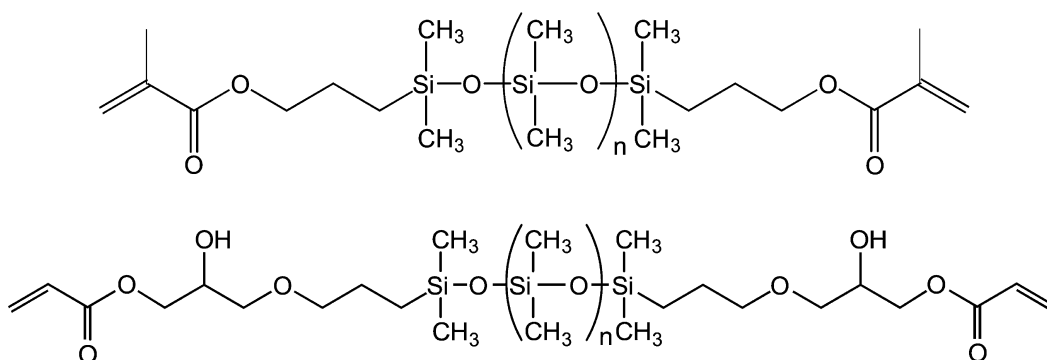

Figure 1. Acrylate functional silicone telechelic structures synthesized by chain growth equilibration techniques. Bis(methacryloxypropyl) terminated PDMS (top) and bis(acryloxyhydroxypropoxypropyl) terminated PDMS (bottom).

The limitations of the chain growth approach led to investigation of other polymerization techniques. Living anionic ring opening (AROP) polymerization techniques were found to be suitable for the synthesis of methacrylate functional

silicone macromers with different architectures. This approach uses an alkyl lithium reagent as an initiator, a cyclic siloxane monomer with ring strain, such as D_3, and a polar aprotic solvent to drive propagation of the siloxane chains (Scheme 2) (13–16). A combination of monomers may be used to produce block copolymers from the living AROP approach (4). Molecular weight was controlled by adjusting the monomer to initiator ratios, leading to controlled silicone chain lengths with PDIs near unity. Equimolar amount of chlorosilane to lithium siloxanolate was used to obtain the targeted methacrylate functional silicone macromer architectures and reduce the high molecular weight methacrylate impurities associated with the addition of excess chlorosilane.
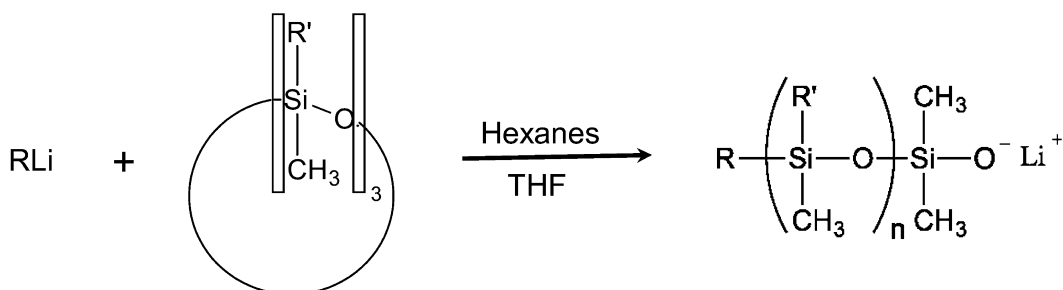
Scheme 2. AROP of cyclic trisiloxanes yields propagating silicone chains with 'living' lithium siloxanolate chain ends. Use of a functional chlorosilane (e.g. methacryloxypropyldimethylchlorosilane) to endcap the chain ends yields a silicone macromer structure. [R = CH₃-, n-butyl-, C₄H₉Si(CH₃)₂O(CH₂)₃-, CH₃O(CH₂)₃- ; R' = CH₃-, CF₃(CH₂)₂-]

The simplest methacrylate functional silicone macromer, MCR-M11, is a well- defined polymer with a single functional group, asymmetric architecture and a controlled branch length. Silicone macromers have four main components that can be altered to yield materials with different bulk properties and functionalities: 1) initiator selection, 2) polymer backbone structure, 3) endgroup functionality and 4) molecular weight of the macromer. In the initial investigation into methacrylate functional silicone macromers, endgroup functionality and number of siloxane units (DP=10) were held constant. Polymer backbone structure modification of asymmetric silicone macromers utilized trifluropropyltrimethylcyclotrisiloxane monomer, introducing a polar 3,3,3-trifluoropropyl side group on each repeat unit in the polymer backbone. The resulting macromer, MFR-M15, had an increased polarity, decreased refractive index (RI) and a decreased solubility in hydrocarbon solvents due to the influence of the trifluoropropyl groups. Main chain structure modification addresses the silicone macromer objective of increased solubility ranges, but the reduction of siloxane domain formation objective is unaddressed. Domain formation is associated with polymer block size. To achieve a reduction in block size while maintaining siloxane content, silicone macromer architecture modifications were investigated in conjunction with main chain and initiator modifications.

Modifying the silicone macromer to have a symmetric architecture with central methacrylate functionality and dimethylsiloxane (MCS-M11) or

trifluoropropylmethylsiloxane (MFS-M15) backbone units decreased the relative block size of the siloxane compared to asymmetric macromers of similar molecular weight (~1,000 g mol^{-1}). Structural analysis of the symmetric silicone macromers by ^{1}H NMR revealed a 2:1 stoichiometry between the n-butyl endgroups and the central methacryloxypropyl group, indicating a well-defined architecture (Figure 2).

The macromolecular design approach utilized for methacrylate functional silicone macromers allows for a maximum of three silicone pendant chains per methacrylate functional group. A 1,000 g mol^{-1} T-structure silicone macromer (MCT-M11) architecture further reduces the relative siloxane block size compared to their asymmetric and symmetric counterparts. At high molecular weights, the economics are favorable for T-structures, however, the economics of producing such materials at low molecular weights are unfavorable due to the required stoichiometry of three moles of initiator to produce one mole of macromer. Figure 3 illustrates the different methacrylate functional silicone macromer architectures synthesized.

In addition to silicone backbone and architecture modification, the initiator can be modified to add reactive or polar chain endgroups to the macromers. Polar functionalities are of specific interest for the methacrylate functional silicone macromers, leading to research effort to develop novel living AROP initiators. 3-Methoxypropyl lithium and 3-(t-butyldimethylsiloxy)-1-propyl lithium were investigated for the methacrylate functional silicone macromer series, leading to methoxypropyl and hydroxypropyl chain endgroups respectively (*3*, *12*). Symmetric silicone macromers with polar chain endgroups, such as MCS-MC12 and MCS-ME11, combine reduced siloxane block size with the presence of hydrophilic endgroups to help achieve the objective of increased macromer solubility in polar solvents or monomers.

Table 1 shows the characterization data for the series of DP=10 methacrylate functional silicone macromers synthesized via living AROP techniques. NMR and GPC analysis showed good agreement between molecular weights with monomodal peaks and low molecular weight distributions (PDI), indicating precise control over the design of silicone macromer architecture and chain length to obtain desired properties.

The effect of backbone and architecture macromer modification on solubility in dimethylacrylamide (DMA) and hydroxyethylmethacrylate (HEMA) is illustrated in Table 2. MCS-M11 has increased solubility in the polar monomers compared to the asymmetric MCR-M11. The decreased siloxane block size reduces the tendency towards phase separation, leading to an increased solubility in polar monomers. Introducing methoxypropyl endgroups in an asymmetric architecture (MCR-ME11) also increased the solubility of the macromer in polar monomers. The contribution of a polar endgroup did not modify the solubility profile of the macromer as significantly as the reduced block size of the symmetric architecture. Backbone modification of the symmetric macromer to contain trifluoropropyl pendant groups also had a drastic effect on solubility, leading to complete miscibility of MFS-M15 in DMA and a doubling of solubility in HEMA compared to MCR-M11.
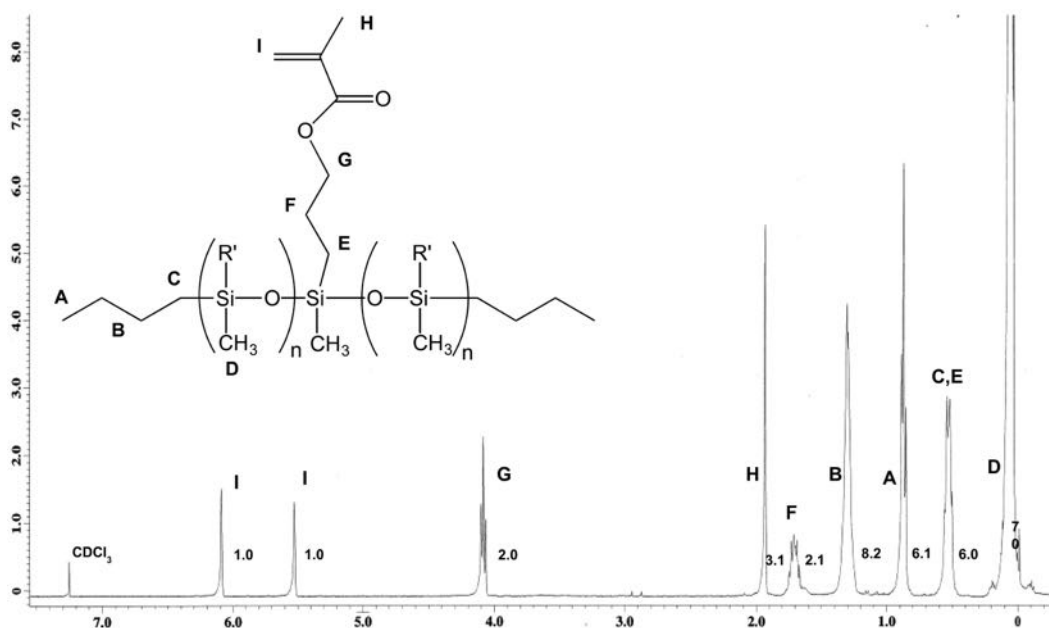
Figure 2. ^1H NMR analysis of MCS-M11 synthesized via living anionic ring opening polymerization shows a well-defined structure with no impurities.

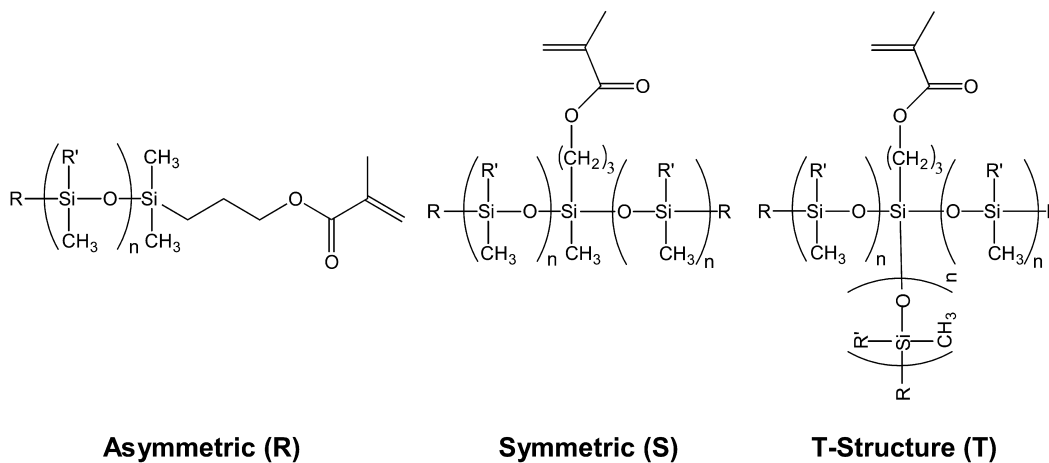**Asymmetric (R)**   **Symmetric (S)**   **T-Structure (T)**

Figure 3. Asymmetric (MCR-M11/MFR-M15/MCR-ME11), Symmetric (MCS-M11/MFS- M11/MCS-MC12/MCS-ME11), and T Structure (MCT-M11) Silicone Macromer Structures. [R = CH$_3$-, n-butyl-, HO(CH$_2$)$_3$-, CH$_3$O(CH$_2$)$_3$-; R' = CH$_3$-, CF$_3$(CH$_2$)$_2$-]

Table 1. Characterization data of methacrylate functional silicone macromers.

Methacrylate Functional Silicone Macromer ($D_p \sim 10$)	Chain Endgroup	Backbone Structure	M_n GPC (g mol-1)	Reported PDI[a]	Viscosity (cSt)
MCR-M11 (asymmetric)	n-butyl	Si(CH$_3$)$_2$O	1050	1.3	11
MFR-M15 (asymmetric)	n-butyl	Si(CF$_3$[CH$_2$]$_2$Me)O	1300	1.2	55
MCR-ME11 (asymmetric)	methoxypropyl	Si(CH$_3$)$_2$O	900	1.2	13
MCS-M11 (symmetric)	n-butyl	Si(CH$_3$)$_2$O	1250	1.2	9
MFS-M15 (symmetric)	n-butyl	Si(CF$_3$[CH$_2$]$_2$Me)O	970	1.2	44
MCS-ME11 (symmetric)	methoxypropyl	Si(CH$_3$)$_2$O	840	1.2	9
MCS-MC12 (symmetric)	hydroxypropyl	Si(CH$_3$)$_2$O	1100	1.3	17
MCT-M11 (T-structure)	n-butyl	Si(CH$_3$)$_2$O	990	1.4	9

[a] PDIs from GPC are reported without deconvoluting macromer peak from solvent and low MW (e.g. inhibitor) interference.

Table 2. Solubility study of macromers with polar monomers and water.

Macromer	Solubility in DMA (wt%)	Solubility in HEMA (wt%)	H₂O Haze Point (ppm)
MCR-M11	4	1	1500
MCS-M11	8	2	3500
MCR-ME11	5	2	3000
MFS-M15	100	2	9000

Comparing the solubility of the macromers in water, a trend similar to the solubility in polar monomers was observed (Table 2). The reported haze points of the macromer in water increased when architecture, chain endgroup and backbone modifications were introduced in the silicone macromer structure. A combination of these modifications could be employed to further improve the solubility range of the silicone macromers.

Hydride Functional Silicone Macromers

Living AROP macromolecular design approach can produce macromer building blocks for higher order silicone structures. From this perspective, hydride functional silicone macromers can be viewed as the simplest structural element of a branched silicone structure (Figure 4). Convergent-branched silicones were synthesized by linking the hydride functional silicone macromers to a cyclic siloxane core via hydrosilylation chemistry.
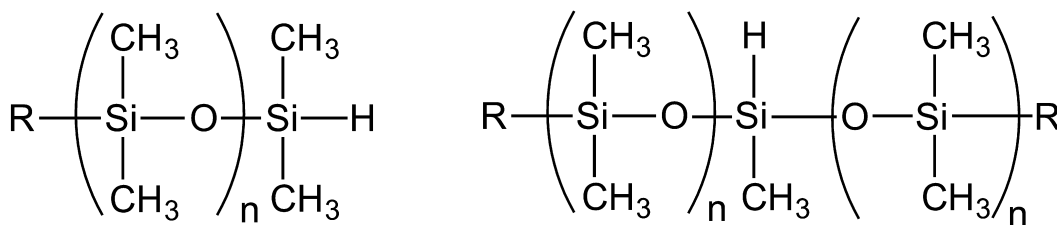

Figure 4. Asymmetric (MCR-H; left) and symmetric (MCS-H; right) hydride functional silicone macromers. [R = CH₃-, n-butyl-, C₄H₉Si(CH₃)₂O(CH₂)₃-, CH₂=CH-]

Degree of branching in the higher order silicone structures can be controlled by modifying the architecture of the hydride functional silicone macromer (asymmetric vs. symmetric). Convergent higher order silicone structures can be generated utilizing D₄vinyl as the cyclic siloxane as a core and reacting with a macromer (Figure 5). Reacting an asymmetric monohydride functional macromer, which can be visualized as possessing a single siloxane pendant, generates a structure with four monospokes. Reacting a symmetric monohydride functional macromer, which can be visualized as possessing two siloxane pendants, generates a structure with four dispokes. T-structure hydride functional

silicone macromers, which would in principle lead to a trispoke structure, were investigated, but was abandoned for economic reasons and the inability to quantitatively hydrosilylate the macromer onto the cyclic siloxane core.
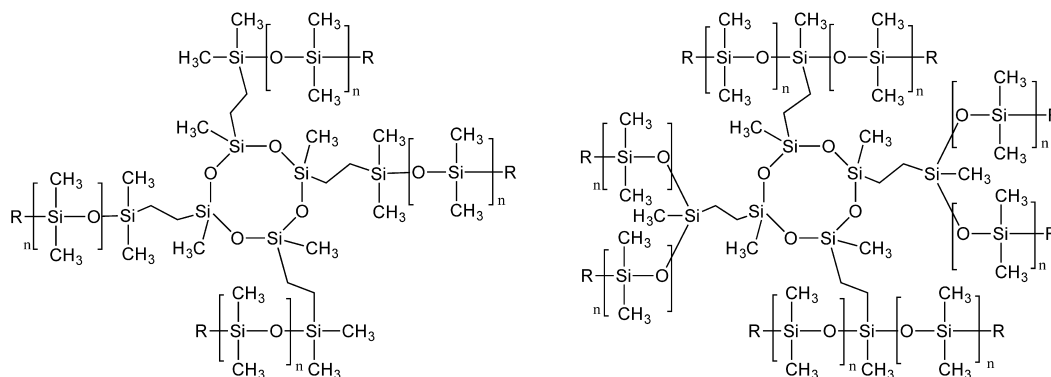

Figure 5. Monospoke (left) and dispoke (right) convergent-branched silicones with a D₄Vinyl hub. [R = CH₃-, n-butyl-, HO(CH₂)₃-, CH₃O(CH₂)₃-]

Previously described initiator modification techniques were employed to synthesize dual functional silicones with functional endgroups (e.g. protected siloxylpropyl or vinyl) (*12*, *17*). A series of hydride functional silicones were synthesized for use as precursors for convergent-branched silicone structures (Table 3). The number of D units per siloxane block was held constant between asymmetric and symmetric architectures to allow for direct comparison of branching effects between the higher order silicone structures. Good molecular weight agreement was observed between GPC, NMR and our targeted molecular weights. Low PDIs are indicative of controlled living polymerization technique. The recorded viscosities of the hydride functional silicone macromers were typical of silicones of their respective MWs.

Convergent Branched Silicones

Assembled silicone macromer structures attached to metal oxide cores have been reported in literature (*18*, *19*). A similar approach with hydride functional silicone macromers would allow access to convergent, branched architectures with a variety of cores (*20*). Higher order silicones were synthesized by attaching the hydride functional silicone building blocks to a cyclic siloxane core (D₄Vinyl) in a convergent approach using hydrosilylation chemistry. The structure of the convergent-branched silicones can be tailored for number of branches and functionality on the branch termini via design of the hydride functional silicone macromer precursors (Figure 5). Deblocking the t-butyldimethylsiloxypropyl endgroups of the precursor macromer under acidic conditions after the hydrosilylation step revealed hydroxypropyl termination on the branch termini.

Table 3. Characterization data of hydride functional silicone precursors for branched silicone structures.

Hydride Functional Silicone Macromer	Chain Endgroup	# D Units/PDMS Block	Targeted MW (g mol⁻¹)	Mn GPC (g mol⁻¹)	PDI	Viscosity (cSt)
MCR-H07 (asymmetric)	n-butyl	10	900	1090	1.2	7
MCR-H11 (asymmetric)	n-butyl	20	1,560	1,530	1.3	13
MCR-H14 (asymmetric)	n-butyl	50	3,800	4,080	1.2	43
MCR-HC12 (asymmetric)	siloxypropyl	20	1,640	1,850	1.3	17
MCS-H14 (symmetric)	n-butyl	20	3,140	3,220	1.2	44
MCS-H21 (symmetric)	n-butyl	50	7,600	8,200	1.2	104
MCS-HC14 (symmetric)	siloxypropyl	20	3,300	3,700	1.3	45

Table 4. Characterization data of the convergent branched silicones.

Convergent Branched Silicone (D₄Vinyl Hub)	Chain Endgroup	# D Units/Branch	Targeted MW (g mol⁻¹)	Mₙ GPC (g mol⁻¹)	PDI	Viscosity (cSt)
MCR-H07 (monospoke)	n–butyl	10	4,700	4,400	1.4	37
MCR-H11 (monospoke)	n–butyl	20	6,400	6,050	1.4	66
MCR-H14 (monospoke)	n–butyl	50	16,700	16,900	1.7	236
MCR-HC12 (monospoke)	hydroxypropyl	20	8,000	9,850	2.5	165
MCS-H14 (dispoke)	n–butyl	20	12,500	10,500	1.4	91
MCS-H21 (dispoke)	n–butyl	50	33,500	33,400	1.8	329
MCS-HC14 (dispoke)	hydroxypropyl	20	16,300	11,400	2.8	400

Molecular weight characterization and solubility properties of these materials were studied. Molecular weight characterization showed good agreement with the theoretical MW (Table 4). The PDI of the higher order silicones increased from the precursor monohydride functional macromers. The observed broadening of molecular weight distribution increased with molecular weight and number of the silicone branches in the assembled higher order structure. The broadening of the molecular weight distribution is attributable to the efficiency of hydrosilylation of the precursors onto the D_4Vinyl hub.

Solubility of water in the branched structures, while retaining the core silicone properties, can be increased with hydrophilic termination of the silicone branches (Table 5). The solubility differences between n-butyl terminated silicones and hydroxypropyl silicones were studied. In the case of monospoke DP=20 branched materials, the solubility of water was doubled from butyl to hydroxypropyl termination. The observed increase in solubility of water was not as dramatic for the dispoke branched materials. It was observed that the hydroxypropyl terminated materials had significantly greater ability to disperse in aqueous phases.

Table 5. Solubility study of higher order silicones with water.

Convergent Branched Silicone (D₄Vinyl Hub)	Chain Endgroup	# D Units/ Branch	H₂O Haze Point (ppm)
MCR-H11 (monospoke)	n-butyl	20	300
MCR-HC12 (monospoke)	hydroxypropyl	20	600
MCS-H14 (dispoke)	n-butyl	20	290
MCS-HC14 (dispoke)	hydroxypropyl	20	530

Rheological studies were performed on higher order and linear, chain growth equilibration silicones to highlight the differences in behavior. Comparing the viscosity as a function of shear rate, a shear-thinning region of non-Newtonian behavior was observed for all convergent-branched silicones. The curves reached a Newtonian plane at higher shear rates. The viscosity at specific shear rates increased with MW and number of spokes extending from the core. The predicted behavior of these materials, like dendrimers, should be Newtonian (20). However, little difference in rheological behavior is observed between these convergent-branched silicones and linear silicones for the lower molecular weight materials (Figure 6). This corresponds to theoretical models where the reptation component is reduced and the gyration component is maintained (21).

Deviation in rheological behavior was observed between the higher molecular weight (33,000 g mol⁻¹) dispoke branched silicone and linear silicone (40,000 g mol⁻¹) (Figure 7). An explanation for this phenomenon is that silicone chains begin to entangle at higher molecular weights. The 33,000 g mol⁻¹ dispoke branched silicone contains relatively short DP=50 pendants and will not chain entangle.
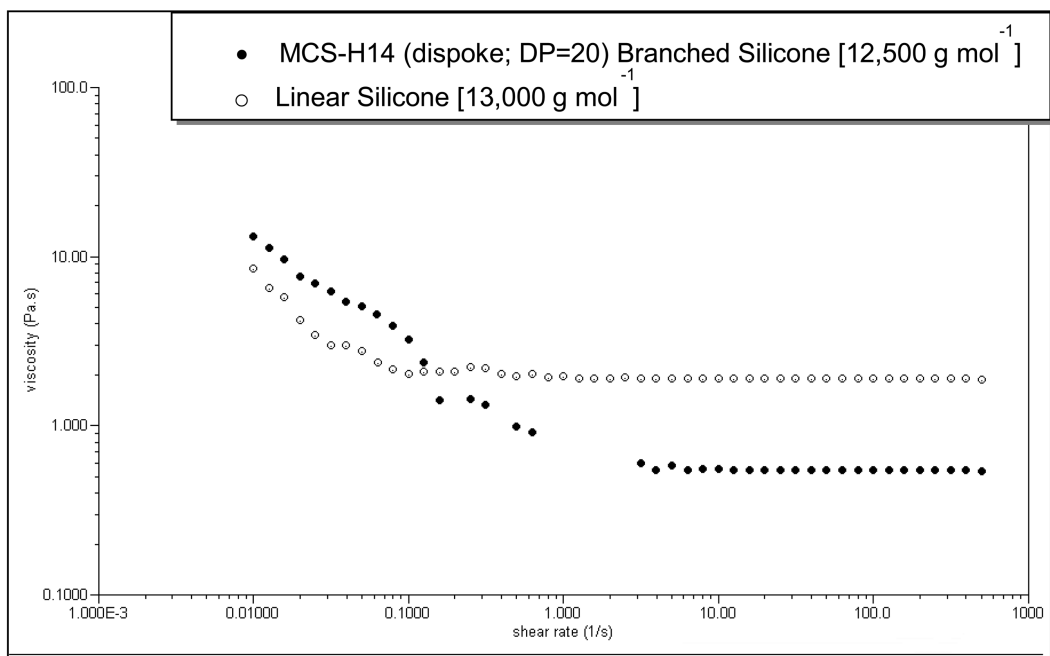
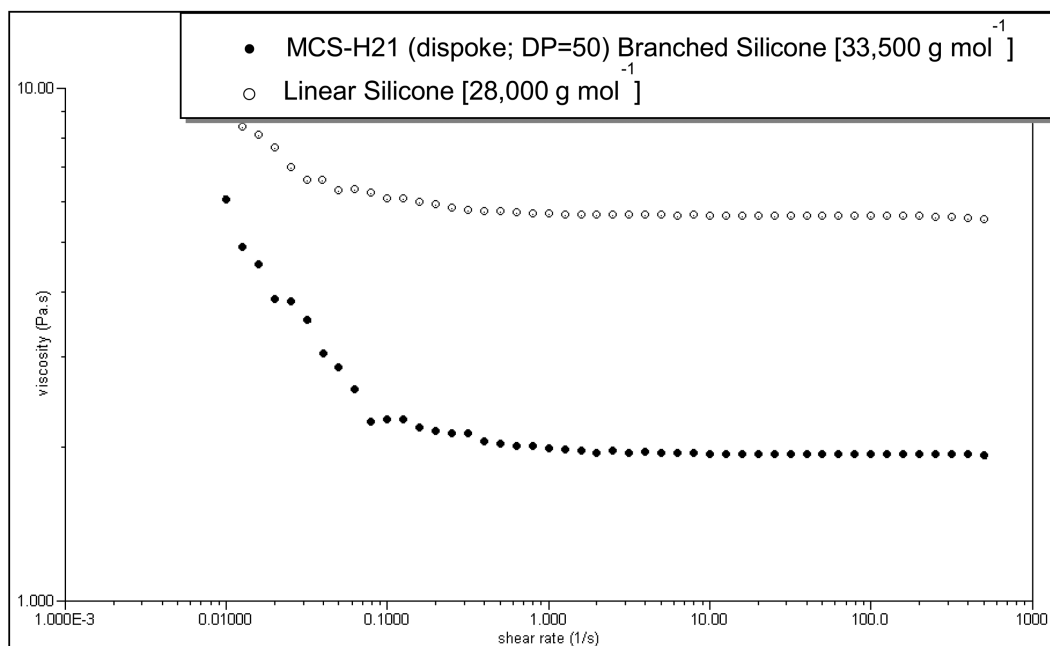*Figure 6. Rheological comparison of lower molecular weight branched silicone and linear silicone materials.*

Figure 7. Rheological comparison of higher molecular weight branched silicone and linear silicone materials.

Conclusions

The structures of silicone macromers have been significantly elaborated. By utilization of a "coupling" rather than "capping" approach to living polymerization, symmetric and T-structures are readily available. The interruption the dimethylsiloxane backbone at a central point formed during the coupling reaction reduces the opportunity for domain formation and phase separation compared to asymmetric monomers of equivalent molecular weight. Utilization of polar and blocked initiators can further modify compatibility with organic monomers. The revealed deblocked initiator segments provide access to dual-functional siloxanes. These materials have telechelic functionality with a different central functionality, allowing them to behave as building blocks for higher order structures, for example convergent-branched silicones with cyclic siloxane cores.

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