DUAL FUNCTIONAL SILICONES AS BUILDING BLOCKS FOR HIGHER ORDER SILICONES

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Introduction

Silicone macromers are defined as silicon containing species with a single functional polymerizeable group, which, although used as monomers, have sufficiently high molecular weight and internal monomer units to be considered polymeric. 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. 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. Polydimethylsiloxane macromers with symmetric architectures can be formed via the anionic ring-opening polymerization of a cyclic trisiloxane and subsequent coupling with a functional reagent. The symmetric macromers, for example, can contain a pendant methacrylate group bisecting the polydimethylsiloxane backbone. 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. This paper will present the synthesis of silicone macromers, as well as new dual functional macromers, with both asymmetric and symmetric structures.

Experimental

Materials. Hexamethylcyclotrisiloxane (D_3), (3,3,3-trifluoropropyl)methylcyclotrisiloxane, dimethylchlorosilane, methyldichlorosilane, trichlorosilane, methacryloxypropyldimethylchlorosilane (inhibited with MEHQ), methacryloxypropylmethyldichlorosilane (inhibited with MEHQ), methacryloxypropyltrichlorosilane (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), 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.

Instrumentation. ^{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. Macromer viscosities were measured using a Brookfield Viscometer Model DV-II+ at 25.0 ^{o}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 ^{o}C. Data were analyzed with a refractive index detector using a calibration made with polystyrene standards. Rheological measurements were carried out using a TA Instruments AR2000 equipped with a TA Instruments Environmental Test Chamber at 25 ^{o}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}).

Synthesis of Silicone Macromers. The synthesis of asymmetric silicone maromers has been reported earlier[1]. 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. Hydride functionality on the silicone is achieved by substituting methyldichlorosilane for methacryloxypropylmethyldichlorosilane. 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 Dual Functional Silicone with Hydrophilic Endgroups. The synthesis of a targeted 1,000 g mol^{-1} bis(hydroxypropyl terminated poly[dimethylsiloxane])methacryloxypropylmethylsilane (MCS-MC12) is provided. 3-(t-butyldimethylsiloxy)-1-propyl lithium was substituted for n-butyllithium, and a previously described anionic ring opening polymerization for symmetric silicone macromers was performed. The resulting macromer precursor was characterized using ^{1}H NMR and GPC.

The t-butyldimethylsiloxylpropyl endgroups were deblocked using acidic deprotection conditions to form hydroxypropyl termination of the 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.

Results and Discussion

Asymmetric Silicone Macromers. Living anionic ring opening (ROP) polymerization techniques were utilized in the synthesis of methacrylate functional silicone macromers with different architectures. This approach uses an alkyl lithium reagent as an initiator, and requires a cyclic siloxane monomer with ring strain, such as D_3, and a polar aprotic solvent to drive propagation of the siloxane chains. Molecular weights of the silicone macromers were controlled by adjusting the monomer to initiator ratios, leading to controlled silicone chain lengths with a polydispersity index (PDI) near unity. Equimolar amounts 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.

The simplest methacrylate functional silicone macromer, MCR-M11 (**Figure 2**), is a well-defined polymer with a single functional group, asymmetric architecture and a controlled branch length. Asymmetric silicone macromers have four main components that can be altered to yield materials with different bulk properties and functionalities. These include 1) intiator, 2) main chain polymer backbone structure, 3) endgroup functionality and 4) molecular weight of the macromer. Investigating methacrylate functional silicone macromers, endgroup functionality and targeted polymer molecular weight (1,000 g mol^{-1}) were held constant. An example of main chain structure modification using the asymmetric silicone macromer architecture involved the use of trifluropropyltrimethylcyclotrisiloxane monomer, introducing a trifluoropropyl side group on each repeat unit in the polymer backbone. The resulting macromer, MFR-M15 (**Figure 1**), has an increased polarity, decreased refractive index (RI) and a decreased solubility in hydrocarbon solvents due to the influence of the trifluoropropyl groups. These modifications help achieve the silicone macromer objective of increased solubility ranges, but the siloxane domain formation reduction objective is unaddressed. To achieve this objective, silicone macromer architecture modifications must be introduced in conjunction with main chain and initiator modifications.

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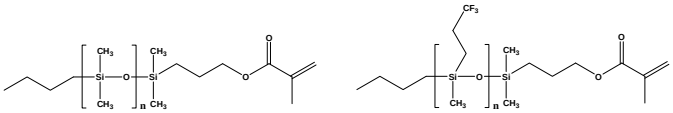

Figure 1. Structure of MCR-M11 (left) and MFR-M15 (right).

Symmetric Silicone Macromers. Modifying the silicone macromer to have a symmetric architecture with central functionality and dimethylsiloxane (MCS-M11) or trifluoropropylmethylsiloxane (MFS-M15) backbone units decreases the relative block size of the siloxane compared to asymmetric macromers of similar molecular weight (~1000 g mol^{-1}) (**Figure 2**). This decreased siloxane block size reduces the tendency towards phase separation, which leads to an increased solubility in polar monomers. The effect of backbone and architecture macromer modification on solubility in dimethylacrylamide (DMA) and hydroxyethylmethacrylate (HEMA) is illustrated in **Table 1**. MCS-M11 has double the solubility in the polar monomers compared to the asymmetric MCR-M11, due to a reduced siloxane block size. Backbone modification of the asymmetric macromer to contain trifluoropropyl pendant groups also has a drastic effect on solubility, leading to complete miscibility of MFR-M15 in DMA.

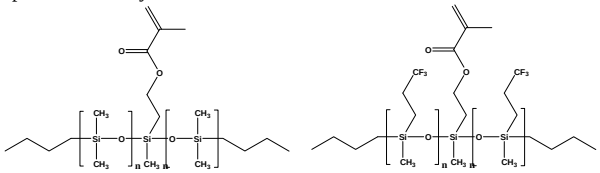

Figure 2. Structure of MCS-M11 (left) and MFS-M15 (right).

Table 1. Solubility of methacylate functional silicone macromers in polar monomers.

Silicone Macromer	Solubility of macromer in DMA	Solubility of macromer in HEMA
MCR-M11	4%	1%
MCS-M11	8%	2%
MFR-M15	100%	2%

Table 2 shows the characterization data for the methacrylate functional asymmetric and symmetric silicone macromers synthesized from living polymerization techniques. NMR and GPC analysis showed good agreement between molecular weights with low molecular weight distributions, allowing for precise control over the design of silicone macromers to obtain the desired properties.

Table 2. Characterization data of methacrylate functional silicone macromers.

Silicone Macromer (# D units ~10)	M_n GPC (g mol^{-1})	PDI	Viscosity (cSt)
MCR-M11	1000	1.3	11
MFR-M15	1300	1.2	55
MCS-M11	1210	1.2	9
MFS-M15	970	1.2	44

Dual Functional Silicones. In addition to modification of the backbone and architecture, the initiator can be modified to add functionality, leading to dual functional silicones (**Figure 3**). Symmetric dual functional silicones, such as MCS-MC12, help achieve the objective of increased solubility in polar solvents/monomers due to reduced siloxane block size and presence of hydrophilic endgroups.

Dual functional symmetric macromers can be viewed as the simplest structural elements of hyperbranched and dendritic structures. Incorporating this macromolecular design approach into higher silicone architectures produces materials with unique structure-property relationships. Specific functionalization can lead to new ROMP reactive silicones. Asymmetric dual functional silicones are heterobifunctional species that can lead to step-growth reactive silicones.

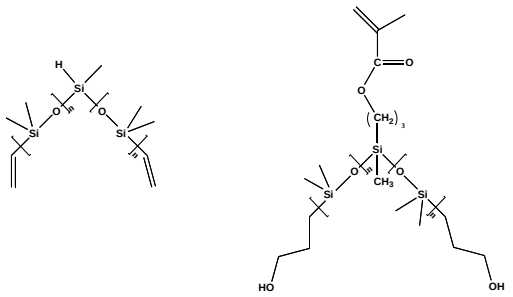

Figure 3. Structure of dual functional symmetric polydimethylsiloxane macromers (MCS-MC12 on right).

Conclusions

Synthesis of silicone macromers with different backbones, architectures, and endgroup functionalization allows for control of the material's solubility in different polar systems while retaining desirable silicone macromer properties. Dual functional silicones allow for development of new classes of silicone monomers based on tunable functionalities.

References

(1.) Arkles, B. Kimble, E., US Pat. 7,947,091, **2011.**