SILICONE ELASTOMERS BY STEP-GROWTH POLYMERIZATION OF MONODISPERSE DUAL FUNCTIONAL SILICONES

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Introduction

Silicones formed via the living anionic ring-opening polymerization of a cyclic trisiloxane historically contain a single functional group. These asymmetric silicones afford the advantages of precise molecular weight control, narrow molecular weight distribution, and absence of low molecular weight impurities when compared to dual functional silicones synthesized by chain-growth equilibration methods. A new class of dual functional silicones synthesized from a living polymerization approach has been developed. These materials allow for post-polymerization reactions previously limited to their chain-growth silicone analogues. With appropriate functionality, they can undergo radical, vinyl-addition or ROMP polymerization and cure. Functionality of the polymer endgroups can be tuned to produce symmetric and asymmetric dual functional silicones. This paper focuses on the synthesis of monovinyl, monohydride terminated polydimethylsiloxanes. These monodisperse asymmetric dual functional silicones conform to the general structure of an A-B step-growth monomer. A low temperature platinum-catalyzed intermolecular hydrosilylation step-growth process of these materials leads to high molecular weight silicones with elastomeric properties

Experimental

Materials. Hexamethylcyclotrisiloxane (D_3), vinyldimethylchlorosilane, platinum-divinyltetramethyldisiloxane catalyst (Karstedt catalyst, 2.2 wt% Pt), and 1,3,5,7-tetramethylcyclotetrasiloxane (D'_4) were obtained from Gelest and used as received. Methyllithium (3.2 M in diethoxymethane, Chemetall-Foote), tetrahydrofuran (THF, HPLC grade, J.T. Baker), and hexanes (Ashland Chemical) 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°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. Dynamic mechanical analysis (DMA) of the silicone elastomer films was performed using a TA Instruments DMA Q800.

Rheological measurements were carried out using a TA Instruments AR2000 equipped with a TA Instruments Environmental Test Chamber at 50°C using 750 mm stainless steel parallel plates. Samples of dual functional silicone mixed with Pt catalyst were analyzed using an oscillating time sweep experiment, where viscosity was measured as a function of time at a frequency of 1Hz with constant % strain (0.05).

Synthesis of Monovinyl, Monohydride Terminated PDMS. An exemplary synthesis monovinyl, monohydride terminated PDMS with 10 D units is provided. Other molecular weight asymmetric dual funtional silicones can be synthesized in an analogous manner by adjusting monomer to initiator ratios to control polymer chain length. Dimethyllithium silanolate (0.321 mol) in hexanes (400 mL) was synthesized in an analogous procedure from Shintai et al.[1] D_3 (240 g, 1.08 mol) was added to the reaction mixture, followed by the addition of THF (150 mL) to the solution as polymerization promoter. Upon ~95% conversion of monomer, the polymer was terminated with a slight excess of vinyldimethylchlorosilane (39.6 g, 0.328 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 asymmetric dual functional silicone was characterized using ^{1}H NMR and GPC.

Step Growth Polymerization of Monovinyl, Monohydride Terminated PDMS. A representative procedure of the step growth polymerization of a D10 monovinyl, monohydride Terminated PDMS resulting in a silicone elastomer is provided. D10 monovinyl, monohydride terminated PDMS (10 g, 0.01 mol) and platinum-divinyl tetramethyldisiloxane catalyst (2 drops) were added to a scintillation vial and the mixture was mixed vigorously by shaking for 5 minutes. The mixture was poured into an aluminum pan and placed into an oven set at 50°C for 20 minutes. A silicone film with elastomeric properties was recovered and characterized by DMA and TGA.

Results and Discussion

Monovinyl, Monohydride Terminated PDMS. Living anionic ring opening polymerization techniques were utilized to synthesize the new class of dual functional silicones presented. This approach afforded precise control over the stoichiometry of the endgroups with no low molecular weight cyclic or oligomeric impurities and a molecular weight distribution near unity. **Figure 1** shows a representative ^{1}H NMR spectrum of a D10 monovinyl, monohydride terminated PDMS, confirming a 1:1 stoichiometry of vinyl to hydride endgroups.

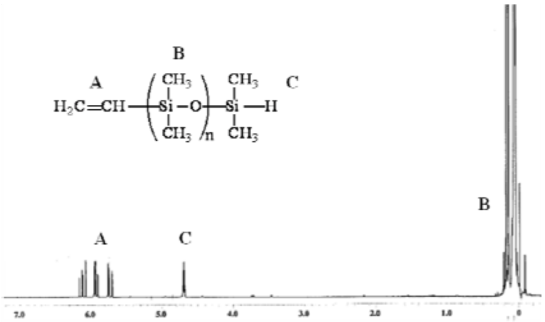


Figure 1. ^{1}H NMR characterization of a monovinyl, monohydride terminated PDMS (D_p = 10).

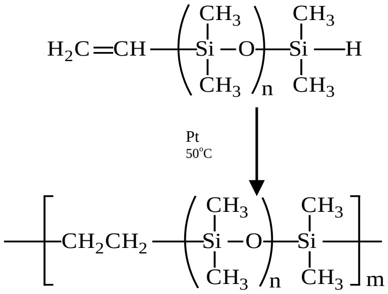
The monovinyl, monohydride terminated PDMS has an A-B step-growth monomer structure. This dual functional silicone has the capability of undergoing a step-growth polymerization process with no crosslinking or early termination, due to the 1:1 stoichiometry and lack of low molecular weight impurities. A series of monovinyl, monohydride terminated silicones were synthesized with varying chain lengths (D_p = 10 - 50) to study the effect of PDMS block size on cure rate, rheology, thermal transitions, and mechanical properties on the resulting silicone elastomers (**Table 1**).

Table 1. Characterization data of monovinyl, monohydride terminated PDMS step growth monomers.

# of D Units Targeted in Dual Funtional Silicone	NMR M_n	GPC M_n	PDI	Viscosity (cSt)
10	1,090	1,130	1.3	13
50	4,500	4,100	1.2	47

Silicone Elastomer by Step-Growth of Silicone Monomer. A platinum-catalyzed intermolecular hydrosilylation step-growth polymerization of the monovinyl, monohydride terminated PDMS monomers leads to long chain silicones with $M_n >> 100{,}000$ g mol^{-1} and molecular weight distributions < 2 (**Figure 2**). The silicones resulting from this step-growth process display elastomeric properties. Early studies suggest that the concentration of platinum catalyst present in the step-growth polymerization can affect the degree of polymerization of the monomer. Rheological studies have been performed to determine the effect of temperature and platinum concentration on the step-growth polymerization of the monovinyl, monohydride terminated PDMS monomers (**Figure 3**).

These results contrast strongly with those of Shintai in which oligomers which monovinyl, monohydride terminated monomers with less than 3 D units resulted in polymers with molecular weights not exceeding 5400 daltons, which corresponds to slightly viscous oils rather than elastomers. Factors which may have contributed to the inability of Shintai to achieve the higher molecular weights we report may be that the lower molecular weight monomers have a significantly greater probability of forming cyclic species or that the loss of even a small portion of the hydride termination, perhaps due to oxidation or reaction with water results in the conversion of these monomers to chain termination species.



$$H_2C{=}CH-\left(Si(CH_3)_2-O\right)_n-Si(CH_3)_2-H \xrightarrow[50^{o}C]{Pt} \left[-CH_2CH_2-\left(Si(CH_3)_2-O\right)_n-Si(CH_3)_2-\right]_m$$

Figure 2. Step-growth polymerization of monovinyl, monohydride terminated PDMS catalyzed by platinum catalyst.

Silicone elastomers formed by a step-growth approach generate materials with elastomeric properties without apparent crosslinking as evidenced by DMA. Step-growth formation of silicone elastomers from dual functional silicones offer high-speed cure rates, tunable monomers (MW and backbone structure), no low molecular weight material, resistance to reversion, and high thermal stability (< 2 wt% loss at 450^{o}C by TGA).

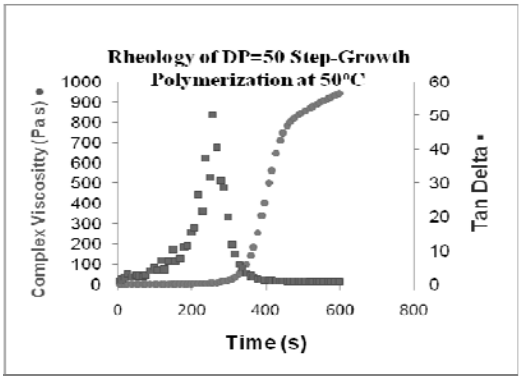


Figure 3. Cure rate rheological study of a D50 monovinyl, monohydride terminated PDMS step-growth process catalyzed by platinum at 50^{o}C.

Conclusions

A new class of dual functional silicones has been synthesized using living anionic ring opening polymerization techniques. An asymmetric silicone containing both vinyl and hydride termination can undergo a step-growth process when catalyzed by platinum, resulting in a silicone elastomer. The resulting elastomer affords many advantages over traditional silicone elastomers.

References

(1) Shintai, K., et al, *Polymer Bulletin*, **1996**, *37*, 705

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