SYMMETRIC SILICONE MACROMERS

Edward Kimble, Barry Arkles, Rudolph Cameron

Gelest Inc.
11 East Steel Rd.
Morrisville, PA 19067

Introduction

In a variety of applications it is desirable to incorporate siloxane units into other macromolecular structures in order to improve oxygen permeability, release, emollient or low temperature properties associated with silicones. Often a greater degree of hydrophilicity is required in the final polymer composition than can be obtained from linear polysiloxanes and polysiloxane block polymers. Another approach is to introduce discrete monomers in which a small number of branched siloxane groups form a pendant group. The most prominent example of this class of monomer is methacryloxypropyltris(trimethylsiloxy)silane which is readily copolymerized with other acrylate monomers and has facilitated commercial applications in lithographic, wound dressing and rigid gas-permeable contact lens applications.[1] A continuing challenge for methacrylate polymer based structures utilized in pigment dispersion, lithographic and contact lens applications is to further increase those properties generally associated with silicones without sacrificing mechanical properties and without forming microdomains of polysiloxanes, which can compromise both optical and mechanical properties. Silicone macromonomers such as a mono(methacryloxypropyl)-terminated polydimethylsiloxane (MPDMS) or 2-hydroxy-3-methacryloxypropyl terminated polydimethylsiloxane (HMPDMS) are copolymerized with monomers such as methyl methacrylate (MMA), hydroxyethylmethacrylate (HEMA) or dimethylacrylamide (DMA). If the polysiloxane domain is too large, molecular phase separation can occur. This can reduce mechanical properties or in cases such as hydrated copolymers result in compositions that are cloudy and, consequently not suitable for optical applications. On the other hand, reducing the number of siloxane units to prevent phase separation can make desirable properties unachievable. Monomers with high pendant siloxane content, but few trimethylsiloxy terminating groups (which have group contributions with lower surface energies than dimethylsiloxy groups) are preferred. More specifically, siloxane macromonomers containing a polymerizeable group such as methacrylate, acrylate, 3-methacryloxy-2-hydroxypropyl, or vinyl on the alpha or omega terminus of a polydimethylsiloxane and having a Mn of less than 5000 g/mol have achieved successful commercial application.

Most effort on "living" anionic ring opening polymerization (AROP) has been dedicated to forming block polymers as reviewed by Yilgor.[2] Frye and others at Dow Corning[3] made the earliest reports on living AROP. Monomethacryloxypropyl terminated polydimethylsiloxanes (**Figure 1**) produced by "living" AROP were first introduced to the US market in 1987.[4]
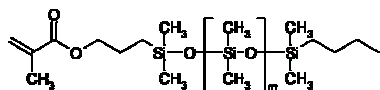

Figure 1. Monomethacryloxypropyl terminated polydimethylsiloxane

A more recent review by Belorgney and Sauvet[5] generally refers to this class of materials as α-monofunctional polysiloxanes. The general technique utilized is to initiate a living polymerization of a ring-strained cyclotrisiloxane with an alkyllithium or alkyldimethylsiloxanolate lithium initiator and after the cyclic siloxane monomer is consumed either feeding different monomers to form block copolymers and finally terminating the reaction by a coupling or capping reaction. In terms of comparison with the prior art monofunctional materials are formed directly or indirectly by a capping reaction, i.e. in the case of methacrylate terminated materials either capping with methacryloxypropyldimethylchlorosilane as described in US Pat. 5,672,671 assigned to Chisso[6] or by first forming a monohydride terminated material by capping with dimethylchlorosilane and then hydrosilylation with allylmethacrylate. Methacrylate functional macromers have reported applications in contact lenses[7], pigment dispersion[8] and hair spray[9].

This report describes low molecular weight polydimethylsiloxanes and fluorinated alkylmethylsiloxanes that have less tendency to form phase separated domains after polymerization than the monoalkyl monofunctional asymmetric macromonomers. They are formed by lithium counter-ion initiated living AROP of cyclosiloxanes with linear ether, cyclic ether or formamide promoters and then terminating with functional groups or coupling the living polymers, forming symmetric rather than asymmetric macromonomers. At similar molecular weights properties such as oxygen permeability are comparable to the asymmetric macromers; the tendency to phase separate is reduced. In addition this report introduces polar initiators such as methoxypropyllithium and t-butyldimethylsiloxypropyllithium which increase the hydrophilicity of the macromer. In the case of the t-butyldimethylsiloxy initiator, the t-butyldimethylsiloxy group can be removed in a subsequent synthetic step to form a hydroxypropyl terminated polymer. These two factors, a bisected rather than terminated pendant and the introduction of a relatively hydrophilic ether or hydroxyl group derived from the initiator has resulted in a new class of siloxane macromers which appear to have utility in a variety of applications.

Experimental

Materials. n-Butyllithium was purchased from Chemetall and used as received. Hexamethylcyclotrisiloxane, methacryoxypropylmethyl-dichlorosilane and 3-(t-butyldimethylsiloxy)-1-propyllithium were obtained from Gelest. Dry solvents were obtained from laboratory supply houses.

Synthesis of Bis[(n-butydimethylsiloxy)polydimethylsiloxy] (methacryloxypropyl)methylsilane (MCS-M11)
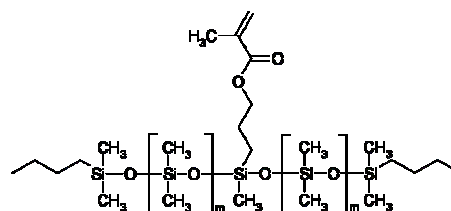

Figure 2. MCS-M11

A 3L, 4-neck flask equipped with an overhead stirrer, pot thermometer, reflux condenser, water bath and addition funnel is blanketed with nitrogen and charged with 292.8g (1.316 mol) of hexamethylcyclotrisiloxane and 374.5g of hexane. A half molar equivalent addition of n-butyllithium (460ml of 1.64M hexane solution) was made rapidly through the addition funnel. An exotherm was observed (18.7° to 37.5°C). Thereafter cooling was used to maintain temperature below 40°C. The mixture was stirred 1 hour and then 107.3g (1.468 mol) of dimethylformamide (DMF) was added at once. A slight exotherm was observed, pot temperature rose from 24.0° to 29.5°C and the mixture stirred for 4 hours. The coupling reaction was accomplished by adding 0.040g of p-methoxyphenol (MEHQ) followed by the addition of 88.5 g of methacryloxypropylmethyldichlorosilane over fifteen minutes. Pot temperature rose from 21.7°- to 33.2°C. The mixture changed from clear to cloudy and was stirred for an additional 18 hours. Water (924g) was added to the reaction mixture with stirring and agitated for 15 minutes. The contents of the flask were separated into aqueous and non-aqueous layers in a separatory funnel. The aqueous layer was discarded. The organic layer was dried over anhydrous sodium sulfate, filtered, transferred to a rotary evaporator and stripped under 10mm Hg vacuum to a maximum pot temperature of 60°C. The resulting oil (367.5g) had a theoretical molecular weight of 1085, a refractive index, 25°C: 1.4174, a density of 0.932 and a viscosity of 9.2 cPs. GPC data (polystyrene st'd without correlation): Mn: 1215, Mw/Mn: 1.24

Synthesis of Bis[(t-butydimethylsiloxypropyl)polydimethylsiloxy](methacryloxypropyl)methylsilane (MCS-MC12)
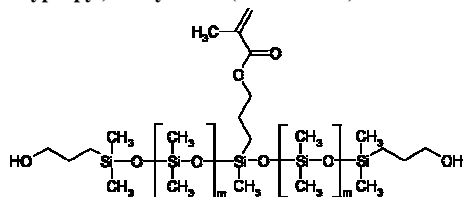

Figure 3. MCS-MC12

A 3L 4 neck flask equipped with an overhead stirrer, pot thermometer, reflux condenser, water bath and addition funnel was blanketed with nitrogen and charged with 65.3g (0.2935 mol) of hexamethylcyclotrisiloxane and 255.6g of cyclohexane. A molar equivalent addition of 3-(t-butyldimethylsiloxy)-1-propyllithium (310 ml of 0.93M cyclohexane solution) was made rapidly through the addition funnel. An exotherm was observed (20.5° to 30.5°C). Thereafter cooling was used to maintain temperature below 40°C. The mixture was stirred 1 hour and then 42.8g (0.5855 mol) of dimethylformamide (DMF) was added at once. A slight exotherm was observed, pot temperature rose from 22.0° to 26.2°C. and the mixture stirred for 4 hours. The coupling reaction was accomplished by adding 0.040g of p-methoxyphenol (MEHQ) followed by the addition of 34.9 g of methacryloxypropylmethyldichlorosilane over fifteen minutes. Pot temperature rose from 18.4° to 31.3°C. The mixture changed from clear to cloudy and was stirred for an additional 16 hours. Water (368.5g) was added to the reaction mixture with stirring and agitated for 90 minutes. The contents of the flask were separated into aqueous and non-aqueous layers in a separatory funnel. The aqueous layer was discarded. The organic layer was dried over anhydrous sodium sulfate, filtered, transferred to a rotary evaporator and stripped under 10mm Hg vacuum to a maximum pot temperature of 60°C. The resulting oil (129.5g) had a theoretical molecular weight of 960, a refractive index, 25°C: 1.4320, density of 0.906 and a viscosity of 17.2 cPs. GPC data (polystyrene st'd without correlation): Mn: 1126, Mw/Mn: 1.139

A 500mL 3 neck flask equipped with a magnetic stirrer, pot thermometer, reflux condenser, heating mantle, and addition funnel was blanketed with nitrogen and charged with 180mL of a solution prepared from 29g concentrated hydrochloric acid and 971g of ethanol. 50mL of the product of Example 5 were charged to the addition funnel and added to the pot over a period of 16 minutes. The mixture turned hazy initially, and then cleared during the addition. The mixture was stirred at 20-25°C for 1 hour and 4.8g of sodium bicarbonate was added to neutralize the mixture. The resulting salts were filtered off, and the filtrate was stripped in a rotary evaporator under 10mmHg vacuum and a maximum temperature of 70° C, removing ethanol and t-butyldimethylsilanol, and then filtered. The resulting oil (40.8g) showed a peak in the FT-IR at 3347 cm⁻¹ corresponding to the hydroxyl group formed on the endcaps of the PDMS chain.

The series of macromers synthesized by this general method is summarized in **Table 1**.

Table 1. Methacryloxypropyl Containing Macromers

Code	Structure	α-termination	ω-termination	Siloxane Unit	Visco., cSt.	Mn	Refractive Index, 25°C	Denisty, g/mL
MCR-M11	asymmetric	n-butyl	methacryloxy-propyl	dimethyl	8-10	800-1000	1.410	0.96
MCR-M17	asymmetric	n-butyl	methacryloxy-propyl	dimethyl	70-80	4500-5500	1.406	0.97
MFR-M15	asymmetric	n-butyl	methacryloxy-propyl	trifluoropropyl-methyl	55-65	1500-1700	1.396	1.16
MCS-M11	symmetric	n-butyl	n-butyl	dimethyl	7-9	800-1000	1.417	0.93
MFS-M15	symmetric	n-butyl	n-butyl	trifluoropropyl-methyl	45-55	800-1000	1.398	1.09
MCS-MC12	symmetric	hydroxy-propyl	hydroxy-propyl	dimethyl	18-22	800-1000	1.432	0.94

Results and Discussion

Symmetric silicone macromers are formed by a coupling reaction which in essence doubles molecular weight of the living prepolymer. In contrast, asymmetric silicone macromers are formed by a capping reaction of the living prepolymer which terminates the reaction at the same time it provides functionality. The synthesis of the symmetric silicone macromers is facile and offers a path for elaboration of silicone macromer structure. Importantly, it allows significant contributions of chain termini to the physical properties of the macromers not simply by doubling the availability, but by bringing them into closer proximity with regions of high siloxane concentration. In other words, the symmetric macromers can be visualized as centering the polar polymerizeable functionality on the polydimethylsiloxane and "bisecting" the polydimethylsiloxane chain rather than terminating it, thus creating pendants at half the molecular weight. The reduction of tendency for phase separation of the symmetric silicone macromers in comparison to the asymmetric silicone macromers is thought to be due to the fact that the dimethylsiloxane blocks are approximately half the size at equivalent molecular weights. As molecular weight increases, the reduction in phase separation of the symmetric macromers compared to the asymmetric macromers is expected to decrease and ultimately be eliminated since the minimum number of siloxane groups that induce phase separation will be exceeded. The utilization of initiators which are polar or can be converted to hydroxyl groups markedly increases solubility of the silicone macromers with the polar monomers DMA and HEMA and increases the solubility of water in mixed macromer – monomer systems.

An indication of the relative polarity and hydrophilicity of the symmetric and asymmetric macromers was obtained in a series of solubility studies, first with other common monomers and second with water. **Table 2** shows that changing the structure from asymmetric to symmetric doubled the solubility of these macromers in polar monomers. The structure change also leads to a higher solubility of water in the siloxane (**Table 3**). Changing the substitution on the backbone from dimethyl to (trifluoropropyl)methyl further increases of water in the siloxane and leads to complete miscibility with DMA.

Table 2. Solubility of Macromers in DMA & HEMA

Macromer	DMA	HEMA
MCR-M11	4%	1%
MCS-M11	8%	2%
MFR-M15	100% (miscible)	2%

Table 3. Solubility of Water in Silicone Macromers

Macromer	H₂O Solubility
MCR-M11	2000 ppm
MCS-M11	3500 ppm
MFR-M15	9000 ppm

Table 4. Solubility of Water in Mixed Silicone Macromer – Monomer Systems

Macromer	100%	50% DMA	50% HEMA
MCS-M11	<1%	not miscible	not miscible
MFR-M15	<1%	not miscible	not miscible
MCS-MC12	10%	5.60%	11.10%

Conclusions

Elaboration of traditional silicone macromer structures from asymmetric to symmetric backbone and formation of macromers with terminal hydroxyl groups offer new building blocks for hydrophilic polymer systems with unique permeability, surface energy, thermal and mechanical properties .

References
(1) B. Arkles, Chemtech, **1983**, *13*, 542.
(2) I. Yilgor, Polymer Science, **1988**, *86*, 28-30.
(3) C. Frye, J. Org. Chem., **1970**, 35, 1308.
(4) R. Anderson, B. Arkles, G, Larson, Silicon Compounds Register & Review, 4th edition, **1987** p.271. Bristol, PA.)
(5) G. Belorgney and G. Sauvet in "Silicon Containing Polymers" R. G. Jones ed Kluwer, **2000**, p 43-78
(6) T. Nakano, K. Tsuchiya, S. Yoshimatsu, T. Fuchigami, "Process for Producing Diorganopolysiloxane", US Pat. 5,672,671, September 30, 1997.
(7) D. Vanderlaan, D. Turner, M. Hargiss, A. Maiden, R. Love, J. Ford, R. Steffen, G. Hill, U.S. Pat. 6,943,203, September 13, 2005
(8) J. Sun, B. Beach, U.S. Pat 6,991,884, January 31, 2006
(9) K. Hayama, K. Narazaki, S. Kawagichi, U.S. Pat. 5,166,276, November 24, 1992.