

NOTE

Silicone Macromers for Graft Polymer Synthesis

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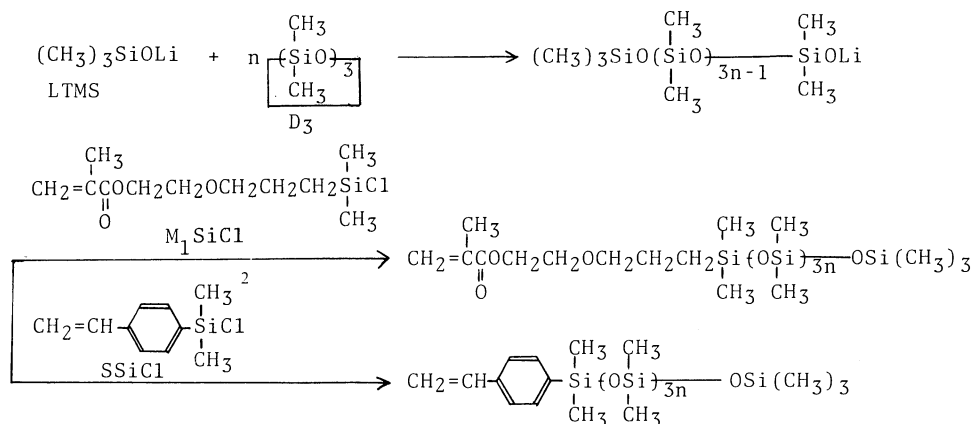
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KEY WORDS Macromer / Graft Polymer / Silicone / Chlorosilane /
Hydrosilylation /

Silicone polymers are industrially produced in large quantity for various purposes depending molecular weight and copolymer composition. Silicones are also noteworthy for their high permeability of gases. However, their thin films are not mechanically strong enough for use as gas permeable membranes. The disadvantage has been overcome by making thin films of block polymers with polycarbonates with excellent results.¹ It would be of interest to synthesize silicone containing graft polymers having hard backbone seg-

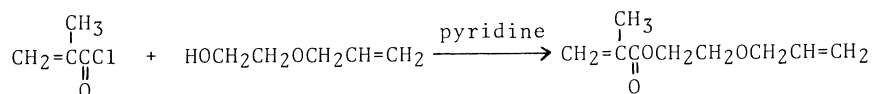
ments from the standpoint of mechanically strong gas permeable membranes of phase separated structures.

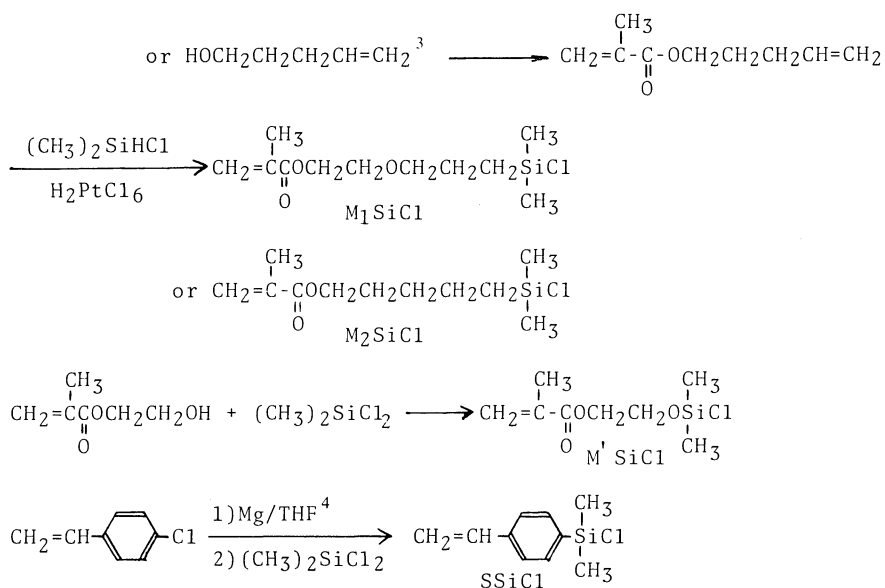
Although there are many methods for preparing graft polymers, the macromer method seems advantageous since the number and length of the grafted branches can be easily controlled. In doing this, two types of silicone macromers, namely styrene and methacrylate types, were synthesized according to Scheme 1.



Scheme 1. Synthetic scheme of silicone macromers.

The two types of chlorosilane terminating agents were synthesized according to Scheme 2.

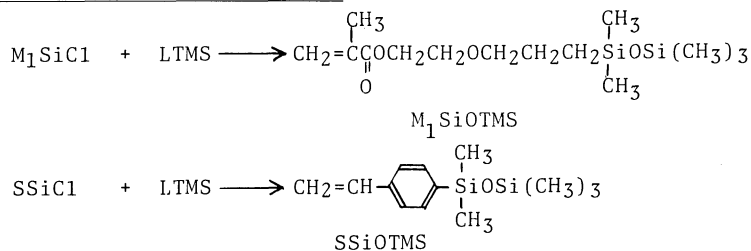




Scheme 2. Synthetic scheme of chlorosilane terminating agents.

These chlorosilane end-capping agents were reacted with lithium trimethylsilylanolate (LTMS), as model reactions, to study reactivity toward living ends. It was found that both the end-capping agents

reacted instantaneously and quantitatively with LTMS at ambient temperature, as evidenced by ^1H NMR.



The polymerization of D_3 was initiated by LTMS and terminated with trimethylsilyl chloride in THF. Polymers of molecular weight as high as 10,000 with narrow molecular weight distributions could be obtained by living anionic polymerization.

Since the degree of polymerization could be controlled by simply changing the monomer/initiator ratio, and both the terminating agents reacted quantitatively with LTMS, silicone macromers having specified molecular weights were synthesized by terminating the living polydimethylsiloxane with SSiCl or MSiCl (M_1SiCl or M_2SiCl). The results for this are shown in Table I.

In experiments of the S and M series, experimental molecular weight values by various methods

coincided quite well with those calculated; the molecular weight distribution was considerably narrow. The functionality of macromers estimated by VPO and UV fell in the region 0.97–1.12. Thus, the well defined silicone macromers of styrene and methacrylate type (macro-St and macro-MA) were obtained. But termination by $\text{M}'\text{SiCl}$ gave polymers having abnormally high molecular weights as estimated by UV. This implies that the functionality of the macromer is much lower than unity (0.38). The reason for this may possibly be that bonding between the prepolymer and end-capping agent (C–O–Si bond), following its formation is unstable and cleaved in the purification step. The $\text{CH}_2\text{OSi}(\text{CH}_3)_2\text{O}$ bond is known to


Table I. Synthesis of silicone macromers^a

No.	[D ₃]	[LTMS]	Polym'n	Conversion ^b	Yield ^c	M _n , VPO ^e	M _n , GPC ^f	M _w , GPC ^f	M _w /M _n	M _n , UV ^g
	mol l ⁻¹	mol l ⁻¹	Time/h	%	%					
IS	0.911	0.0663	15	93	79	3,100	3,000	3,300	1.10	3,050
1M	0.911	0.0663	15	93	75	3,200	3,200	3,600	1.14	3,100
2S	0.983	0.0432	17	93	86	5,000	5,200	5,600	1.08	5,400
2M	0.983	0.0432	17	93	80	5,000	5,300	5,700	1.08	5,600
3S	0.980	0.0282	20	94	83	7,500	7,500	8,100	1.08	8,200
3M	0.980	0.0282	20	94	80	7,600	7,600	8,400	1.11	8,400
4M' ^h	0.970	0.0311	20	92	80	6,700	—	—	—	17,300

^a Polymerized at 0°C, and terminated by chlorosilane terminating agents. S series were terminated by SSiCl and M series by M₁SiCl.

^b Determined from the disappearance of D₃ by gas chromatography.

^c Yield after reprecipitation from THF into methanol. Both methanol soluble and insoluble fractions had similar molecular weight.

^d Calculated by $M_n, \text{ calcd} = \frac{[\text{D}_3]}{[\text{LTMS}]} \times \frac{\text{conversion}}{100} \times 222 + 250$ (molecular weight of (CH₃)₃SiO——CH=CH₂ for S series



^e Determined by VPO.

^f Correlated to standard polystyrene.

^g ϵ of each macromer was assumed to be same with that of M₁SiOTMS or SSIOTMS, respectively.

^h 4M' was terminated by M'SiCl.

Table II. Copolymerization of macromers

No.	Macromer	Comonomer	AIBN	Time	Yield	Siloxane component in graft polymer/wt%	M_n , GPC ^a	M_n , mo ^b
	wt%	wt%	mol%	h	%			
1	Macro-MA ^c 21.1	MMA 78.9	0.30	15	76	21	40,100	85,700
2	Macro-St ^d 15.8	St 84.2	0.33	136	80	15	32,000	42,900

^a Correlated to standard polystyrene.

^b Determined by membrane osmometry.

^c M_1SiCl terminated macromer 2M was used.

^d $SSiCl$ terminated macromer 1S was used.

be easily cleaved by hydrolysis.

The macromers, macro-St and macro-MA, were converted into graft polymers by copolymerizing with styrene and methyl methacrylate, respectively, as shown in Table II.

In copolymerization, both macromers showed almost the same reactivity as that of the corresponding monomers. The number of branches was roughly estimated as 3.2 and 2.2 for No. 1 and No. 2, respectively.

EXPERIMENTAL

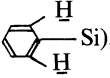
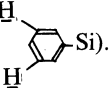
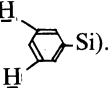
3-(2-Methacryloyloxyethoxy)propyldimethylchlorosilane [M_1SiCl]

To a prewarmed (60°C) mixture of 2-allyloxyethyl methacrylate (5.11 g, 30 mmol), *p*-*t*-butylcatechol (0.10 g) and chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 0.052 g, 0.1 mmol) in 2-propanol (0.5 ml) contained in a round bottom flask equipped with a Dewar condenser, dimethylchlorosilane (3.41 g, 36 mmol) was added dropwise at a speed sufficient to bring about a gentle reflux of dimethylchlorosilane within a period of 30 min. The reaction mixture heated at the above temperature for an additional 3 h stirring. The product M_1SiCl was obtained by distillation directly from the reaction mixture, bp 80°C (0.1 mmHg), 2.15 g (27%). Calcd for $C_{11}H_{21}O_3SiCl$: C, 49.89%; H, 7.99%; O, 18.12%; Si, 10.61%; Cl, 13.39%. Found: C, 50.15%; H, 8.11%; Cl, 13.08%. ¹H NMR ($CDCl_3$) δ 0.40 (s, 6H, Si(CH₃)₂), 0.66–1.12 (m, 2H, SiCH₂), 1.40–1.95 (m, 2H, CH₂), 1.96 (m, 3H, CCH₃), 3.34–3.70 (m, 4H, CH₂OCH₂), 4.16–4.47 (m, 2H, CO₂CH₂), 5.57 (m, 1H, CH=), and 6.13 ppm (s, 1H, CH=).

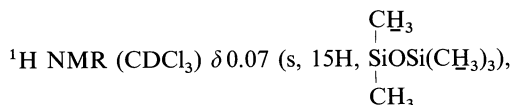
5-Methacryloyloxypropyldimethylchlorosilane [M_2SiCl]

This compound was synthesized from 4-pentenyl methacrylate in a manner similar to that for obtaining M_1SiCl . bp 92°C (0.9 mmHg), 75% yield. Calcd for $C_{11}H_{21}O_2SiCl$: C, 53.10%; H, 8.50%; O, 12.86%; Si, 11.29%; Cl, 14.25%. Found: C, 53.40%; H, 8.72%; Cl, 14.10%. ¹H NMR ($CDCl_3$) δ 0.38 (s, 6H, Si(CH₃)₂), 0.62–1.02 (broad, 2H, CH₂Si), 1.17–1.83 (m, 6H, (CH₂)₃), 1.92 (m, 3H, CCH₃), 4.51 (t, 2H, $J=7.0$ Hz, OCH₂), 5.60 (m, 1H, CH=), and 6.08 ppm (m, 1H, CH=).

p-Vinylphenyldimethylchlorosilane ($SSiCl$)

p-Vinylphenylmagnesium chloride² (0.2 mol, in 120 ml THF) was added dropwise to dimethyldichlorosilane (51.7 g, 0.4 mol). Following this, the reaction mixture was refluxed for 30 min. Ether (100 ml) was added to the resulting system, and the formed salt was filtered off in a dry-box. The product $SSiCl$ was obtained directly from the reaction mixture by distillation, 60–65°C (0.5 mmHg), 20 g (51%). bp 63°C (0.01 mm) (lit. 2) 62–63°C (0.01 mmHg). ¹H NMR ($CDCl_3$) δ 0.66 (s, 6H, Si(CH₃)₂), 5.23 (q, 1H, $J_1=2.0$ Hz, $J_2=10.0$ Hz, $\begin{matrix} H \\ | \\ C=C \\ | \\ H \end{matrix}$), 5.88 (q, 1H, $J_1=2.0$ Hz, $J_2=18.0$ Hz, $\begin{matrix} H \\ | \\ C=C \\ | \\ H \end{matrix}$), 6.66 (q, 1H, $J_1=10.0$ Hz, $J_2=18.0$ Hz, $\begin{matrix} H \\ | \\ C=C \\ | \\ H \end{matrix}$), 7.33 (d, 2H, $J=8.0$ Hz, ) and 7.50 ppm (d, 2H, $J=8.0$ Hz, ) and 7.50 ppm (d, 2H, $J=8.0$ Hz, ).

3-(2-Methacryloyloxyethoxy)propylpentamethyl-
disiloxane ($M_1SiOTMS$)



0.33—0.67 (m, 2H, SiCH_2), 1.00—1.82 (m, 2H, CH_2), 1.94 (m, 3H, CCH_3), 3.30—3.80 (m, 4H, CH_2OCH_2), 4.13—4.30 (m, 2H, CO_2CH_2), 5.51 (m, 1H, CH=), and 6.10 ppm (s, 1H, CH=).


p-Vinylphenylpentamethyl-*disiloxane* ($SSiOTMS$)

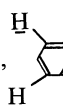
$^1\text{H NMR (CDCl}_3) \delta 0.11 \text{ (s, 9H, Si(CH}_3\text{)}_3$), 0.33

(s, 6H, $-\text{SiO}$), 5.20 (q, 1H, $J_1=2.0 \text{ Hz}$, $J_2=10.0 \text{ Hz}$,

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ / \\ \text{H} \end{array}$, 5.80 (q, 1H, $J_1=2.0 \text{ Hz}$, $J_2=18.0 \text{ Hz}$,

$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ / \\ \text{H} \end{array}$, 6.66 (q, 1H, $J_1=10.0 \text{ Hz}$, $J_2=18.0 \text{ Hz}$,

$\text{C}=\text{C} \begin{array}{c} \text{H} \\ | \\ \text{H} \end{array}$), 7.30 (d, 2H, $J=8.0 \text{ Hz}$, , and

7.48 ppm (d, 2H, $J=8.0 \text{ Hz}$, ).

Macromers

The living polydimethylsiloxanes in Table I were reacted with 10% excess of MSiCl or SSiCl at -78°C . The formed macromers were purified by reprecipitation from THF into methanol.

Graft Polymers

The graft polymers were purified by fractional reprecipitation from THF into ether (M series) or from THF into methanol (S series). The absence of the macromer was evidenced by GPC. The composition of graft polymers was estimated by $^1\text{H NMR}$. The molecular weight was determined by GPC and membrane osmometry. The molecular weight by GPC was considerably lower than that determined by membrane osmometry. Membrane osmometry should provide accurate molecular weight determinations for branched polymers.

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