Poly(dimethylsiloxane) macromonomers having both alkenyl and polymerizable groups. Application to crosslinkable copolymers

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Novel poly(dimethylsiloxane) macromonomers containing both alkenyl and acrylic or other radical-polymerizable groups have been prepared by polymerizing D_3 using a partially lithiated alkenyl siloxanol as an initiator, followed by end-capping with chlorosilanes having radical-polymerizable groups. By copolymerizing these macromonomers with comonomers (MMA and styrene), crosslinkable copolymers have been obtained. They are soluble in organic solvents and thermoplastic before crosslinking, and can be crosslinked via both hydrosilylation and photoactivated thio-ene reactions to give insoluble and non-melting materials.

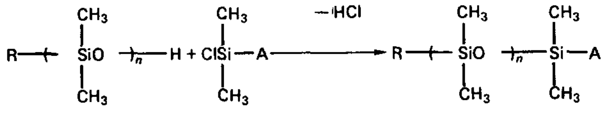
(Keywords: poly(dimethylsiloxane); macromonomer; copolymer; crosslink; hydrosilylation; thio-ene reaction; photodelineation)

INTRODUCTION

Poly(dimethylsiloxane) macromonomers (PDMS-M) with controlled chain length and polymerizable functionality such as acrylic or vinyl groups have been prepared and applied to the synthesis of various graft copolymers[1-3]. Such copolymers are reported to have interesting properties originating from the unique nature of the siloxane bond and the surface characteristics of poly(dimethylsiloxane). Only terminally monofunctional macromonomers, however, have been obtained by the traditional anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) using butyllithium or lithium trimethylsilanolate as an initiator, followed by end-capping with chlorosilanes having polymerizable groups.

We have recently reported a novel preparation method of PDMS-M using a partially lithiated alkenyl siloxanol as an initiator. This approach gives PDMS-M having an alkenyl functionality at one end[4]. By combining this method and the conventional end-capping method, PDMS-M with both alkenyl and acrylic or other radical-polymerizable groups have been prepared (*Scheme 1*).

Scheme 1

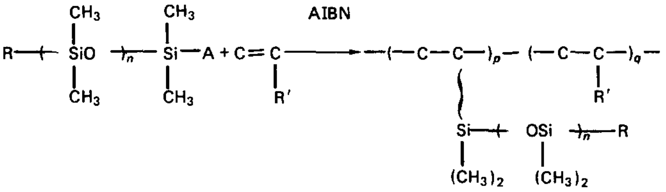


$$R\text{-}[Si(CH_3)_2O]_n\text{-}H + ClSi(CH_3)_2\text{-}A \xrightarrow{-HCl} R\text{-}[Si(CH_3)_2O]_n\text{-}Si(CH_3)_2\text{-}A$$

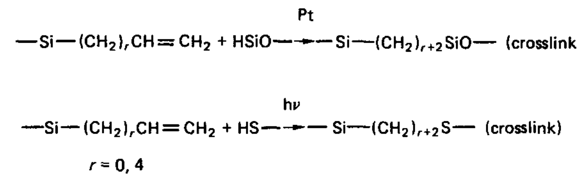
where R = vinyl, hexenyl and A = 3-methacryloxypropyl, 4-vinylphenyl.

Since the vinyl group or hexenyl group attached to a silicon atom is resistant to radical polymerization where the initiator is azobisisobutyronitrile (AIBN)[5] (*Scheme 2*), we have succeeded in crosslinking the copolymers by both hydrosilylation and thio-ene photoactivated reactions of the unreacted alkenyl groups (*Scheme 3*).

Scheme 2



Scheme 3



$$-Si-(CH_2)_rCH{=}CH_2 + HSiO- \xrightarrow{Pt} -Si-(CH_2)_{r+2}SiO- \text{ (crosslink)}$$

$$-Si-(CH_2)_rCH{=}CH_2 + HS- \xrightarrow{h\nu} Si-(CH_2)_{r+2}S- \text{ (crosslink)}$$

$$r = 0, 4$$

This paper describes the preparation of the hetero-difunctional PDMS-M, the copolymerization with vinyl monomers, the crosslinking of the copolymers and the possibility of photolithographic use.

EXPERIMENTAL

Materials. D_3 was distilled under reduced pressure, dissolved in toluene/dimethylsulphoxide (1/1/0.02 weight ratio) and dried over molecular sieves which had been activated at 350°C for 3 h. Vinyl- or hexenyldimethylsiloxy-tris(dimethylsiloxane)-ol, 3-(methacryloxypropyl)-dimethylchlorosilane and 4-(vinylphenyl)-dimethylchlorosilane were prepared by known methods[2,4,6]. Methyl methacrylate (MMA) and styrene were distilled and stored over activated molecular sieves. AIBN and n-

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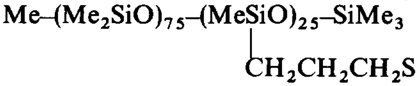
butyllithium (n-BuLi; in hexane) were used as purchased. Other materials were of commercial source and dried over molecular sieves.

Preparation of PDMS-M. Into a dry 500 ml flask containing $H_2C{=}CH(Me_2)Si{-}(OMe_2Si)_3{-}OH$ (24.6 g, 81 mmol), n-BuLi in hexane (0.3 ml, 0.48 mmol) was added dropwise with stirring under dry nitrogen. Immediately after the n-BuLi was added, D_3 in toluene/DMSO (200 g, 0.9 mol) was added as quickly as possible. Stirring was continued at room temperature (about 32°C in the flask) under dry nitrogen until the conversion of D_3, measured by gas liquid chromatography (g.l.c.), reached 75.4% (4 h). The reaction was terminated by adding dry ice (5 g) and water (0.02 g). $H_2C{=}CH(Me_2)Si{-}(OMe_2Si)_{28}{-}OH$ ($VD_{28}OH$) was obtained by stripping off the solvents and unreacted D_3, followed by filtering off the precipitate. The M_n and M_w/M_n by gel permeation chromatography (g.p.c.) were 2500 (calculated 2190) and 1.25, respectively. The vinyl content measured by iodometry was 1.24 wt% (calculated 1.24).

Into a dry 300 ml flask were added $VD_{28}OH$ (120 g, 54.8 mmol), triethylamine (8.1 g, 80 mmol) and toluene (150 ml), and the flask was immersed in an ice bath. With stirring 3-(methacryloxy)propyl-dimethylchlorosilane (13.2 g, 60 mmol) was added dropwise so that the temperature did not exceed 5°C. White precipitate appeared within a short period of time. The mixture was stirred for 5 h, and methanol (0.32 g, 10 mmol) was added in order to convert unreacted chlorosilane into methoxysilane. Finally, the precipitate was filtered off and the solvent, methoxysilane and unreacted materials were stripped off using a wiped film evaporator to obtain $H_2C{=}CH(Me_2)Si{-}(OMe_2Si)_{28}{-}OSi(Me_2){-}(CH_2)_3OCOC(Me){=}CH_2$ ($VD_{28}Ma$). Other PDMS-M macromonomers were prepared in a similar way.

Copolymerization. Known amounts of PDMS-M, comonomer and toluene were put into a dry 100 ml flask. AIBN was added to the mixture, which was then heated with stirring under dry nitrogen. The conversion of the comonomer was periodically monitored by g.l.c. The polymerization was terminated by pouring the reaction solution into excess methanol to give the copolymer as precipitate. The precipitate was dissolved in acetone and the solution was filtered to remove the gel. After stripping off the solvent, the copolymer was purified by extraction with hexane, 2-propanol or ethanol, according to the solubility of the copolymer.

Crosslinking (hydrosilylation). In a dry vial, specified amounts of VM28/20 (see the sample code explanation below), toluene and $(Me_2HSiO)_4Si$ (SiH/alkenyl = 1.2/1 molar ratio) were mixed. The complex of Pt with 1,3-divinyl-tetramethyldisiloxane (Pt: 35 ppm to the copolymer) was added to the solution. The mixture was thoroughly mixed and transferred to a Teflon dish and air-dried. By heating the dish at 100°C for 1 h, a cured film was obtained.



Crosslinking (photocure). In a dry vial, specified amounts of VM28/20, methyl ethyl ketone, $Me{-}(Me_2SiO)_{75}{-}(\underset{\displaystyle CH_2CH_2CH_2SH}{\underset{|}{MeSiO}})_{25}{-}SiMe_3$ (SH/vinyl = 1.2/1 molar ratio) and photoinitiator (Irgacure 651, 4 wt% of the solid) were mixed thoroughly. The mixture was spin-coated onto a silicon wafer and air-dried. Photo-irradiation (405 nm) was done on a mask aligner (Canon PLA-500). The pattern was developed with acetone as a developer.

Measurements. 400 MHz ^1H n.m.r. spectra were recorded on a Jeol JNM-GX400 spectrometer. G.p.c. measurements were done on a Tosoh HLC-802A chromatograph equipped with TSK G3000H8/4000H8/5000H6/6000H6 columns. PDMS-M and its copolymers with MMA were analysed using toluene as eluent under refractive index detection; the copolymers with styrene were analysed using $CHCl_3$ as eluent under u.v. detection. Calibration was done using standard PDMS for PDMS-M samples and standard polystyrenes for the copolymers. Si contents were measured on a Hitachi Z-8000 polarized Zeeman atomic absorption spectrometer. Alkenyl group contents were measured by iodometry on a Hiranuma Comtite-7 titrator. Melting temperatures of the copolymers were determined by microscopic visual observation using a Mettler FP80/82 hot stage. Dynamic viscoelasticity was measured on a Rheometrics Dynamic Analyzer-700 equipped with parallel plates; the vibrating frequency was 10 rad s^{-1} and the strain was 1.0%

RESULTS AND DISCUSSION

Preparation of PDMS-M

Table 1 lists the four PDMS-M samples prepared in this study (*Scheme 1*). The vinyl contents of the precursors (before end-capping with chlorosilanes) are in good agreement with the calculated values. The values of M_n(calc) were calculated not from the molecular formulae in the footnotes of *Table 1* but from the actual conversion of D_3 in the polymerization. By comparing the g.p.c. data before and after the reaction with difunctional SiH-containing polysiloxane in the presence of Pt, it was confirmed[4] that each polymer molecule had only one alkenyl group. The mechanism of the polymerization will be reported elsewhere.

The attachment of a polymerizable functionality to the chain end was confirmed by ^1H n.m.r. *Figure 1* shows the spectrum of $VD_{28}Ma$ as a typical example.

The wiped film evaporator proved to be very helpful in stripping off undesirable materials from PDMS-M. As the boiling point of methacryloxypropyldimethylmethoxysilane is very high, stripping with usual equipments sometimes causes gelation.

Table 1 Characterization of PDMS-M

Sample code	$VD_{18}Ma$[a]	$VD_{28}Ma$[b]	$HD_{30}Ma$[c]	$HD_{30}St$[d]
Vinyl content of precursor (wt%)				
Observed	1.85	1.24	1.20	1.15
Calculated	1.88	1.24	1.20	1.14
M_n(obs)	2150	2530	2430	2930
M_n(calc)	1620	2370	2760	2530
M_w(obs)	2730	3170	2760	3590
M_w/M_n	1.27	1.25	1.14	1.22

[a] $H_2C{=}CH(Me_2)Si{-}(OMe_2Si)_{18}{-}OSi(Me_2){-}(CH_2)_3OCOC(Me){=}CH_2$
[b] $H_2C{=}CH(Me_2)Si{-}(OMe_2Si)_{28}{-}OSi(Me_2){-}(CH_2)_3OCOC(Me){=}CH_2$
[c] $H_2C{=}CH{-}(CH_2)_4(Me_2)Si{-}(OMe_2Si)_{30}{-}OSi(Me_2){-}(CH_2)_3OCOC(Me){=}CH_2$
[d] $H_2C{=}CH{-}(CH_2)_4(Me_2)Si{-}(OMe_2Si)_{30}{-}OSi(Me_2){-}C_6H_4{-}CH{=}CH_2$

Table 2 Copolymerization

Sample code[a]	VM18/7.5	VM28/12.5	VM28/20	HM30/33	HS30/20
PDMS-M[b]	$VD_{18}Ma$	$VD_{28}Ma$	$VD_{28}Ma$	$HD_{30}Ma$	$HD_{30}St$
(mmol)	30	8.5	8.3	3.6	4.0
Comonomer	MMA	MMA	MMA	MMA	styrene
(mmol)	226	106	166	118	78.7
Comonomer/PDMS (molar ratio)	7.5	12.5	20	33	20
AIBN (mmol)	3.0	2.4	2.4	1.8	1.2
Temperature (°C)	72	85	90	90	90
Time (h)	3.5	2.0	2.0	3.0	12
Comonomer conversion (%)	79.4	76.9	84.7	78.8	74.6
Gel content[c] (wt%)	0.5	–	–	0.4	–
Extraction					
Solvent	EtOH	hexane	hexane	hexane	2-PrOH
Times	1	2	2	1	2
Residue[d] (wt%)	71	52	69	76	77

[a] See text

[b] See the footnotes of *Table 1* for the sample codes of PDMS-M

[c] (Gel weight)/(total loaded weight)

[d] (Extraction residue)/(before extraction)

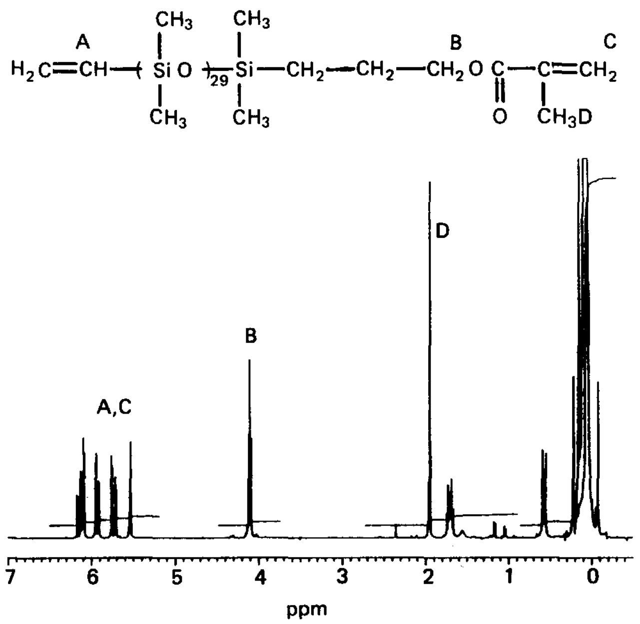


Figure 1 ^1H n.m.r. spectrum (400 MHz) of $VD_{28}Ma$

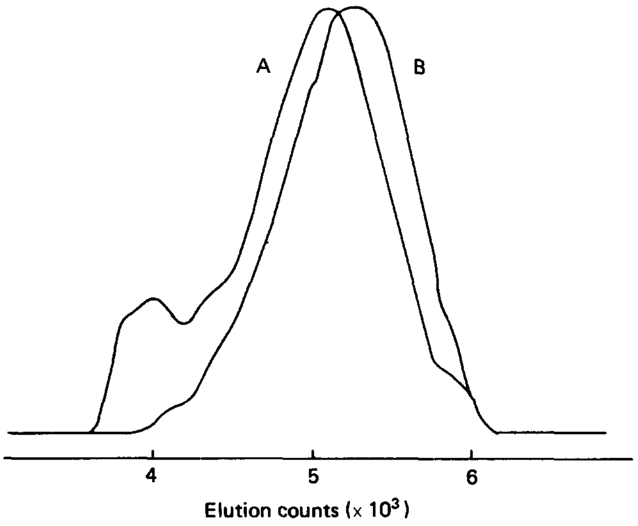


Figure 2 G.p.c. traces of (A) VM28/12.5 and (B) VM28/20 (see *Table 3*)

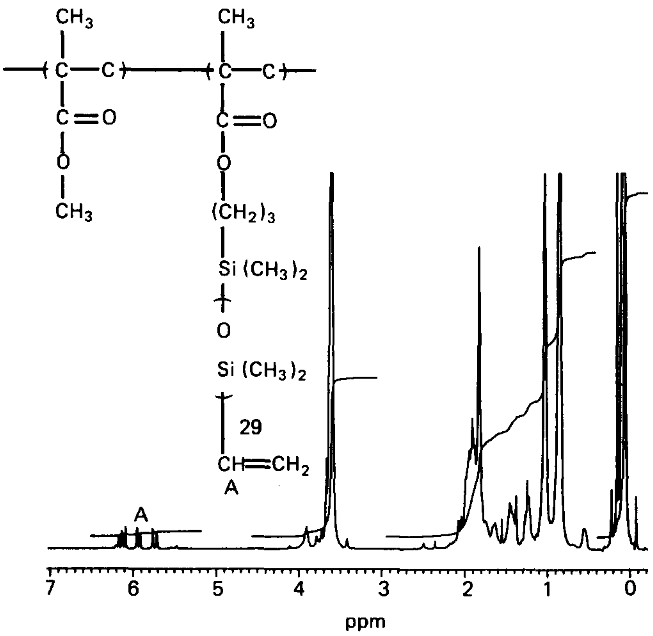


Figure 3 ^1H n.m.r. spectrum (400 MHz) of VM28/20

Copolymerization

The radical copolymerizations of PDMS-M with MMA or styrene were carried out under the conditions shown in *Table 2*. The properties of the copolymers thus obtained are shown in *Table 3*. The sample codes for the copolymers (e.g. VM18/7.5) mean, from left to right, 'vinyl (V) or hexenyl (H)' regarding residual functionality, 'MMA (M) or styrene (S)' regarding comonomer, 'degree of polymerization of PDMS-M' and 'comonomer/PDMS-M molar ratio'. Copolymerizations carried out at temperatures higher than 100°C often resulted in gelation (data not shown).

Solvent extractions were done until no PDMS-M peak was detected by g.p.c., except for VM18/7.5 which appeared impossible to separate from $VD_{18}Ma$ with any solvent. (In *Table 3*, the third peak of the g.p.c. eluogram for VM18/7.5 corresponds to $VD_{18}Ma$.) For other copolymers, the residual weight after the extraction is higher when less PDMS-M is employed.

Table 3 Properties of copolymers

Sample code[a]	VM18/7.5	VM28/12.5	VM28/20	HM30/33	HS30/20
G.p.c.					
Peak multiplicity	3	2	1	1	2
M_w($\times 10^3$)					
Peak 1	2180	212	66.6	26.8	757
(area %)	(12)	(8)	(100)	(100)	(17)
Peak 2	51.9	100			41
(area %)	(48)	(92)			(83)
Peak 3	4.5				
(area %)	(40)				
Si content (wt %)					
Observed	20.9	21.0	15.6	14.2	17.6
Loaded	23.2	23.3	19.4	16.2	19.5
Vinyl content (wt %)					
Observed	0.93	0.61	0.48	0.39	–
Calculated from Si content	1.01	0.67	0.50	0.43	0.53
Melting temperature (°C)	180	140	149	156	108
Solubility[b]					
2-propanol	s	i	i	i	i
Hexane	s	i	i	i	s
Acetone	s	s	s	s	s
Toluene	s	s	s	s	s

[a] See text

[b] s = soluble, i = insoluble

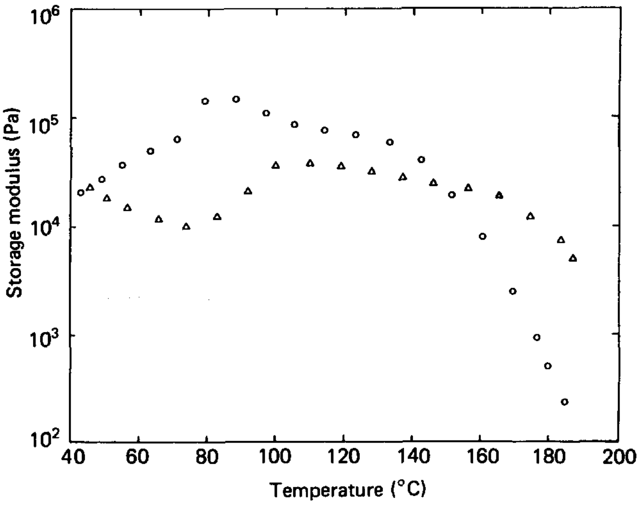


Figure 4 Storage modulus of VM28/20 in *Table 3* as a function of temperature (heating rate: 10°C min^{-1}). ○, Uncrosslinked; △, crosslinked

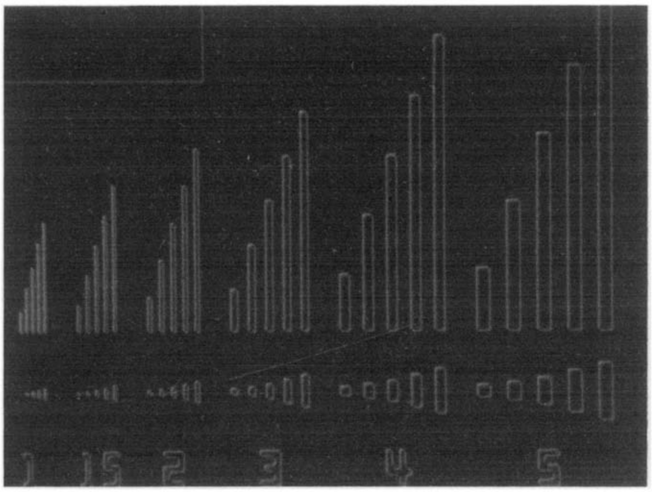


Figure 5 Microscopic photograph of a photodelineated pattern obtained from VM28/20. Each number denotes the width of line and space (in μm). Coating thickness: 0.5 μm; irradiation: wavelength = 405 nm; dose = 300 mJ cm^{-2}

All copolymers were colourless clear solids with varying physical properties depending on the molar ratio of MMA (or styrene)/PDMS segments. For example, VM18/7.5 is elastic and flexible like soft poly(vinyl chloride), whereas HM33/33 is brittle but slightly flexible like dry resins (more flexible than glass).

G.p.c. analysis (*Table 3*) showed the copolymers to fall into two groups, one with a unimodal distribution and another with a bimodal distribution where an extremely high molecular weight portion is a minor component. There seems to be no clear relationship between polymerization conditions and the generation of the high molecular weight portion. Results might be different if the polymerization had been done under milder conditions. *Figure 2* shows g.p.c. traces for VM28/12.5 (bimodal) and VM28/20 (unimodal).

Almost all alkenyl groups in PDMS-M were kept unreacted in copolymers. The ^{1}H n.m.r. spectrum of VM28/20 is shown in *Figure 3*. The vinyl contents are in good agreement with those calculated from the silicon contents, although they are slightly smaller than the calculated values probably due to a loss of the vinyl terminal groups via polymerization. The vinyl content of HS33/20 could not be measured by iodometry because the Si–phenyl bond is vulnerable to the attack of Wijs reagent.

Crosslinking (hydrosilylation)

VM28/20 was crosslinked by hydrosilylation (*Scheme 3*). The cured material neither dissolved in toluene or acetone nor melted even when heated to 200°C. *Figure 4* shows the dynamic viscoelasticity analysis data for the crosslinked and uncrosslinked samples of VM28/20. The storage modulus (G') of the uncrosslinked specimen decreased steeply at temperatures above 150°C.

Crosslinking (photocure)

Because of the good surface property, VM28/20 gave a dry, even and flat film upon spin-coating. The film was then crosslinked via a mask-aligning process (*Scheme 3*) to give fine patterns. *Figure 5* shows a microscopic photograph of the patterns obtained. It can be seen that the 1 μm line and space could be delineated using such a relatively long wavelength as 405 nm.

CONCLUSIONS

By copolymerizing the hetero-difunctional PDMS-M with MMA or styrene, crosslinkable copolymers were obtained. They are soluble in organic solvents and thermoplastic before crosslinking. They can be crosslinked via both hydrosilylation and the photoactivated thio-ene reaction to make insoluble and non-melting materials. Fine patterns can be obtained by a photodelineation process, which would give an opportunity that the copolymers be used as photoresists for semiconductors.

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