Macromolecules 1991, 24, 460-463

Preparation of Poly(dimethylsiloxane) Macromonomers Having Ethynylene Functionality by the "Initiator Method"

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Received April 4, 1990; Revised Manuscript Received June 26, 1990

ABSTRACT: Novel poly(dimethylsiloxane) macromonomers with a (trimethylsilyl)ethynyl group at one end and a trimethylsilyl or (methacryloxypropyl)dimethylsilyl group at the other end have been obtained by nonequilibrium polymerization of hexamethylcyclotrisiloxane using lithium (trimethylsilyl)acetylide as initiator. The macromonomer with the methacrylic group was copolymerized with methyl methacrylate by a radical process with the (trimethylsilyl)ethynyl groups remaining unchanged.

Introduction

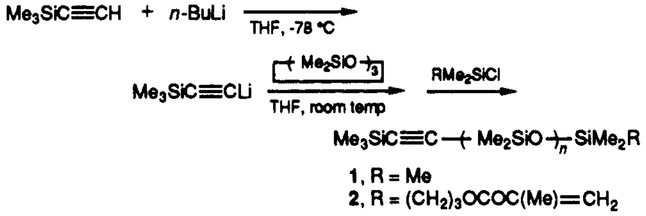
Poly(dimethylsiloxane) macromonomers (PDMS-M) have been gathering interest in both academic[1] and industrial[2] areas because of their peculiar physical and chemical properties such as high chain flexibility, high gas permeability, low surface energy, and hydrophobicity. Monofunctional PDMS-M containing a polymerizable functionality at one chain end are especially versatile for production of graft copolymers that incorporate surface properties of PDMS into organic copolymers.[3] General requirements for such monofunctional PDMS-M are well-defined structures (exactly one-end functionality) and narrow molecular weight distributions (usually $M_w/M_n < 1.3$) in order to facilitate characterization of the copolymers prepared from them.

We had previously reported a preparative method for PDMS-M in which totally or partially lithiated siloxanol compounds containing alkenyl groups are used as polymerization initiators.[4] The method was named the "initiator method". We had also demonstrated the advantages of this method with the synthesis of heterodifunctional macromonomers and utilized them in the preparation of cross-linkable copolymers.[5]

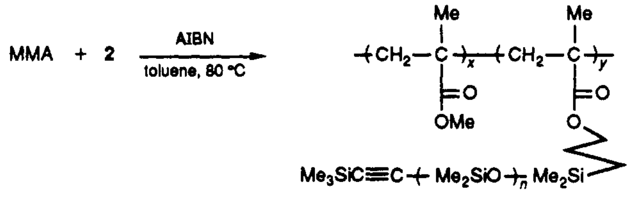
In the course of investigations carried out on functional initiators for anionic polymerization of hexamethylcyclotrisiloxane (D_3), we have found that the lithium salt of (trimethylsilyl)acetylene (Li-TMSA) can initiate polymerization to give well-defined PDMS-M with a (trimethylsilyl)ethynyl group at the initiation end (Scheme I). In this paper we will report the preparation of PDMS-M using Li-TMSA as the initiator. Like other PDMS-M prepared by initiator methods, polymers prepared by the present method can possess any functionality at termination ends as long as the corresponding monochlorosilanes are available. PDMS-M having a (trimethylsilyl)ethynyl group at the initiation end and a trimethylsilyl group or (methacryloxypropyl)dimethylsilyl group at the termination end were prepared (1 and 2 in Scheme I). Macromonomer 2 and methyl methacrylate were then copolymerized to give polymethacrylate 3 by AIBN at 80 °C. The (trimethylsilyl)ethynyl group remained unchanged after the radical copolymerization (Scheme II).

Experimental Section

Scheme I



Scheme II



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Materials. D_3 was distilled under reduced pressure, dissolved in dry tetrahydrofuran (THF, 50% w/w), and kept over molecular sieves that had been activated at 180 °C/0.1 mbar for 5 h. (Trimethylsilyl)acetylene (TMSA) was distilled over calcium hydride and kept under dry nitrogen. MMA, chlorotrimethylsilane (TMSCl), and (3-methacryloxypropyl)dimethylchlorosilane[6] (MA-SiCl) were freshly distilled before use. Azobisisobutyronitrile (AIBN) and butyllithium (BuLi, in hexane) were used as purchased. THF was dried over sodium and distilled from potassium-benzophenone. Other solvents were dried in conventional ways.

Measurements. GC analyses were carried out with a Hewlett-Packard 5890 gas chromatograph equipped with an FID and an HP-1 glass capillary column. A Kratos MS 25 mass spectrometer (ammonium ion emission) was used for confirming the molecular structure of the model compound. Molecular weight distributions of polymers were determined by gel permeation chromatography (GPC) using a Tosoh HLC-8020 chromatograph (columns: TSK 3000HXL, 4000HXL, 5000HXL, 6000HXL in series; refractive index detector; eluent: toluene; standard PDMS samples for calibration). The M_n values of the polymers were determined by vapor pressure osmometry (VPO) using a Knauer vapor pressure osmometer (solvent: toluene, 40 °C).

UV spectra were recorded on a Philips PU8720 scanning spectrophotometer using hexane as solvent. IR spectra were recorded on a Perkin-Elmer 783 infrared spectrophotometer.

Quantitative ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were taken with a Bruker AC-P 250 spectrometer [250.13 MHz for ^{1}H; room temperature; solvent: $CDCl_3$; reference: $CHCl_3$ (^{1}H), $CDCl_3$ (^{13}C), and Me_4Si (^{29}Si); NOE suppressor: $Cr(acac)_3$].

Synthesis of Model Compound 4. A solution containing TMSA (6.0 g, 61 mmol) in THF (10 mL) was placed under dry nitrogen and cooled to -78 °C. To this was added BuLi in hexane (22.5 mL, 61 mmol) with magnetic stirring. The resulting mixture was allowed to warm to room temperature. D_3 (28 g, 63 mmol) in THF (32 mL) was added to the mixture, and stirring was maintained for 40 min at 20 °C prior to termination by addition of TMSCl (8.0 g, 74 mmol). The solvents and unreacted reagents were removed under vacuum, and the residue was

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Table I
Preparation of Poly(dimethylsiloxane) Macromonomers Using Lithium (Trimethylsilyl)acetylide

run	product	Li-TMSA,[a] mol·L^{-1}	D_3, mol·L^{-1}	% conv	TMSCl,[b] mol·L^{-1}	MASiCl,[c] mol·L^{-1}
1	1	0.13	1.28	90	0.22	
2	1	0.27	3.66	80	0.34	
3	1	0.13	3.13	87	0.19	
4	2	0.20	1.80	81		0.26

[a] Lithium (trimethylsilyl)acetylide. [b] Chlorotrimethylsilane. [c] (Methacryloxypropyl)dimethylchlorosilane.

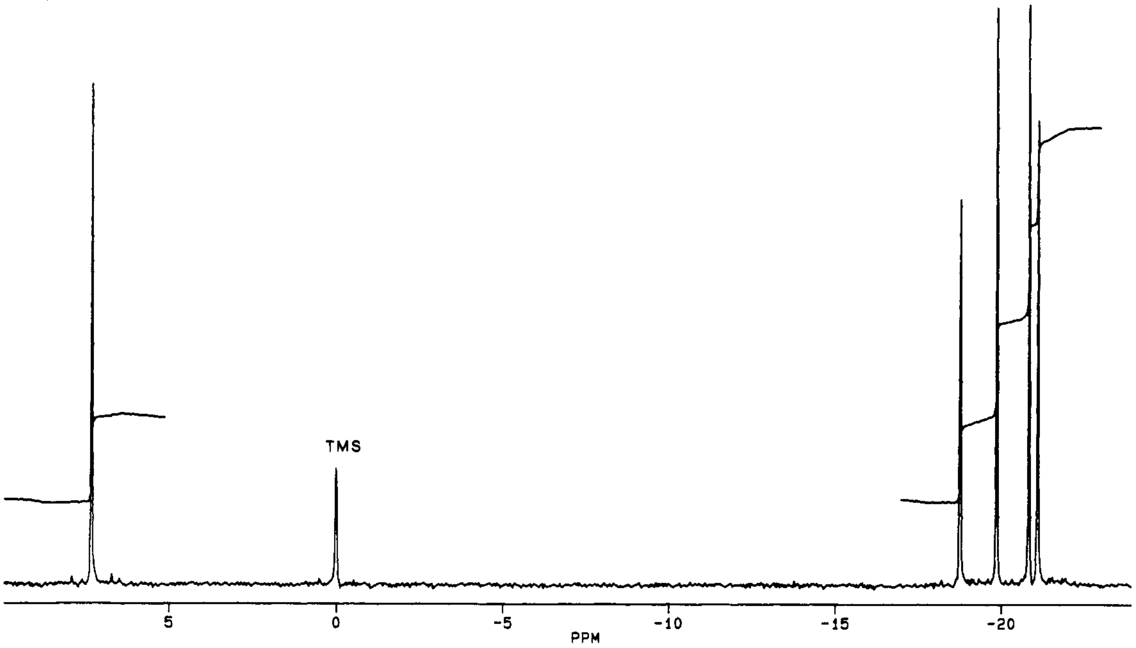


Figure 1. $^{29}Si\{^1H\}$ NMR (50 MHz) of model compound 4.

filtered. Oligomer 4 was obtained by fractional distillation [bp 68.5–70 °C at 3.3 mbar; purity: 98.5% by gas–liquid chromatography (GC), yield 76%].

MS m/e (relative abundance): 410 (93, M + NH_4^+), 377 (80, M^+ - Me), 295 (82, M^+ - Me_3Si), 90 (100, Me_3Si + NH_4^+ - H), 73 (Me_3Si^+, 100).

Preparation of PDMS-M. Table I lists the details of polymerization. The following is a typical procedure (run 1): TMSA (0.88 g, 8.9 mmol) in THF (42 mL), BuLi in hexane (2.88 M, 3.1 mL, 8.9 mmol), and D_3 (19.8 g, 89 mmol) in THF (28 mL) were allowed to react in the same manner as in the synthesis of compound 4. The mixture was stirred at 18–20 °C, and the conversion of D_3 was monitored by GC until it reached 90%. The reaction was terminated by addition of TMSCl (1.6 g, 15 mmol). Polymer 1 was obtained by removal of solvents and unreacted reagents under vacuum followed by filtration.

^{1}H NMR: 1, δ 0.3–0.0 (m); 2, δ 6.1 (s), 5.5 (m), 4.1 (t), 1.9 (s), 1.7 (m), 0.6 (m), 0.3–0.0 (m). IR (liquid film, cm^{-1}): 1, 2960, 2900, 1480, 1420, 1320, 1100, 1040, 800; 2, 2960, 2900, 1720, 1420, 1265, 1100, 1060, 800.

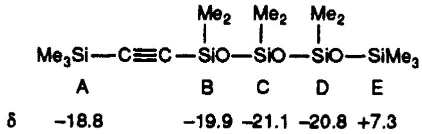
Redistribution of PDMS by Li-TMSA. The lithium salt of TMSA (Li-TMSA) was prepared as described above (2.9 mmol in 10 mL of THF). $Bu(Me_2SiO)_nSiMe_3$ (M_n = 3630, 5.4 g, 1.5 mmol) in THF (10 mL) was added to the solution at room temperature. The resulting mixture was stirred for 2 h at room temperature and was neutralized by addition of dry ice and water. Evaporation under vacuum followed by filtration gave the final product.

Copolymerization of 2 and MMA. A mixture containing 2 (M_n = 1900, 3.8 g, 2 mmol), toluene (20 mL), and MMA (4.5 g, 45 mmol) was magnetically stirred and heated to 60 °C prior to addition of AIBN (0.2 g, 1.2 mmol). The reaction temperature was raised to 80 °C and maintained for 1.5 h. When the conversion of MMA as shown by GC reached 60%, the reaction was terminated by pouring the mixture into 300 mL of methanol. The precipitated copolymer was washed with methanol, and any unreacted 2 was removed by extraction with hexane. Drying under vacuum gave 3.0 g of white powder.

^{1}H NMR: δ 3.6 (br s), 1.9–1.6 (m), 1.0 (br s), 0.8 (br s), 0.2–0.0 (m). $^{13}C\{^1H\}$ NMR: δ 177.6, 176.6, 112.9, 112.6, 54.4, 54.2, 51.7, 44.9, 44.5, 18.7, 16.5, 2.1–0.0 (6 peaks).

Results and Discussion

The Model Compound. Model compound 4 was obtained in relatively high yield. The $^{29}Si\{^1H\}$ NMR spectrum (Figure 1) shows five distinct peaks having identical integrals. The chemical shifts were assigned as follows:



$$\underset{A}{Me_3Si}-C\equiv C-\underset{B}{\overset{Me_2}{\overset{|}{Si}}O}-\underset{C}{\overset{Me_2}{\overset{|}{Si}}O}-\underset{D}{\overset{Me_2}{\overset{|}{Si}}O}-\underset{E}{SiMe_3}$$

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The chemical shifts of silicons E and C were assigned based on established data for PDMS.[7] The chemical shift of silicon A was assigned from the data of bis(trimethylsilyl)acetylene (δ = −19.2). The other two chemical shifts were assigned with the assumption that silicon B should resonate at lower field than silicon D because it is attached to the carbon–carbon triple bond.

The reaction between alkyllithium and D_3 has previously been reported to give, instead of the expected trimer [$R(Me_2SiO)_3Li$, R = alkyl], the monomer [RMe_2SiOLi] and dimer [$R(Me_2SiO)_2Li$] as the major products because of fast redistribution reactions.[8,9] However, in our case the trimer was the major product (90% by GC after reaction with TMSCl) in the reaction mixture. This discrepancy might be explained by the differences in polarities of solvents used in our study (THF) versus those used in previous studies (hexane or hexane/DME). Bis-

Table II
Characterization of Macromonomers

run	calc[a] M	GPC anal. M_w	M_n	M_w/M_n	UV M_n	^{29}Si NMR M_n	VPO M_n
1	2180	3370	2790	1.21	2200	2540	2100
2	2580	4320	3460	1.25	2870	3360	2760
3	4830	6800	5800	1.17	5610	5430	5480
4	1900	3170	2590	1.22	*b*	2060	2000

[a] Based on the molar ratio of initiator and converted D_3. [b] Not available because of the absorption by the methacrylic group.

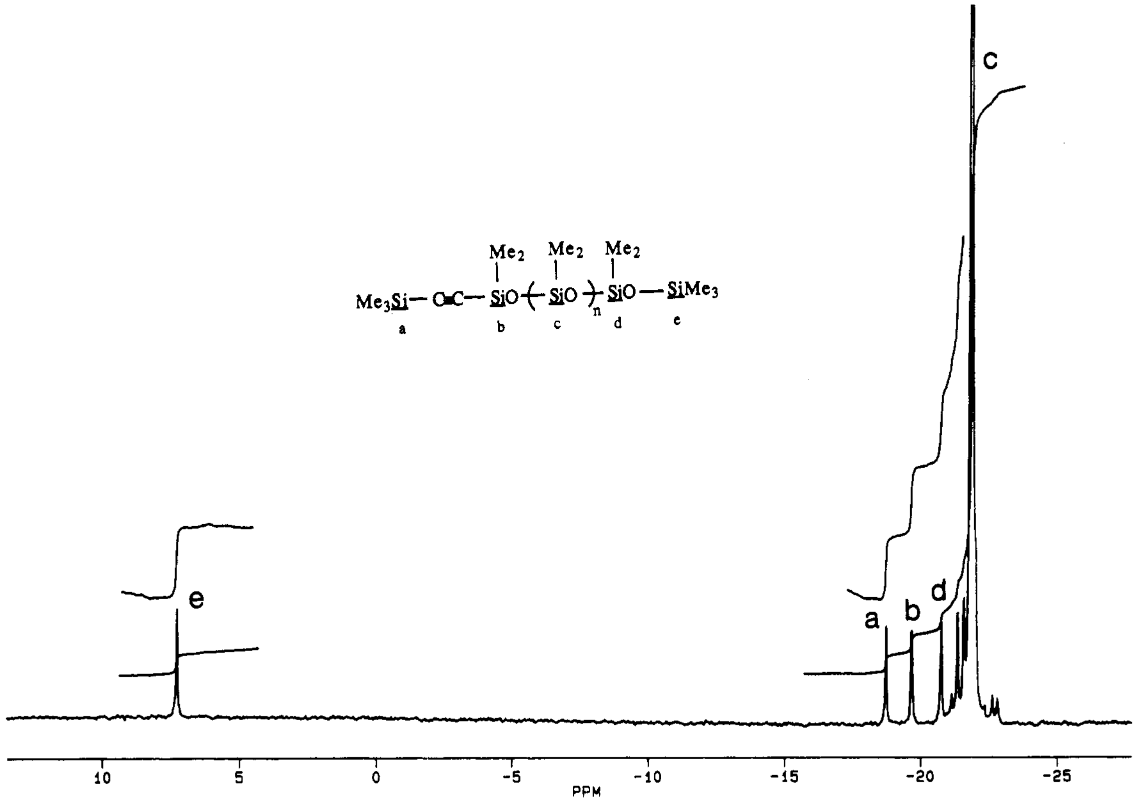

Figure 2. ^{29}Si{^{1}H} NMR (50 MHz) of macromonomer 1 (run 1 in Table I).

(trimethylsilyl)acetylene was not detected, indicating that all Li-TMSA had reacted with D_3 to form lithium silanolate.

Model compound 4 was used for calibration of M_n determination by UV spectroscopy. Although the peak at 215 nm is not the maximum, it is practical to measure at this wavelength for the present purpose because absorptions at lower wavelengths are affected by solvent and small particles. The absorption coefficient (ϵ) of this compound in hexane was 395 L·mol^{-1}·cm^{-1} at 215 nm, which is lower than that of bis(trimethylsilyl)acetylene ($\epsilon \approx 800$ L·mol^{-1}·cm^{-1} at 215 nm), though both compounds have a C≡C group bonded to two silicon atoms.

Preparation of PDMS-M. Table II contains characterization data of the obtained PDMS-M. The GPC traces obtained were symmetric curves, similar to those obtained by usual nonequilibrium polymerization. Molecular weight distributions (M_w/M_n = 1.21–1.25) are not as narrow as expected. However, this should not be taken as an indication that redistribution reactions due to cleavage of main chains had taken place. It is more likely that, with the relatively low molecular weight of the macromonomers, redistribution reactions at the terminal silanolate silicon atoms during the course of polymerization led to the observed M_w/M_n.[10]

$$\mathrm{R(SiO)_pSiOSiO^-Li^+ + R(SiO)_qSiOSiO^-Li^+ \rightarrow R(SiO)_pSiOSiOSiO^-Li^+ + R(SiO)_qSiO^-Li^+}$$

Gnanou and Rempp reported that they obtained PDMSs with very wide molecular weight distributions (presumably $M_w/M_n > 3$ though only GPC traces were reported) when dilithiostilbene or lithium dihydronaphthylide was used as initiator.[11] They attributed the wide distributions to slow initiation and showed evidence of unreacted initiator remaining in the reaction mixture. The results in our study do not indicate such slow initiation. Li-TMSA reacted very quickly with D_3 in the model compound synthesis, and GPC traces are quite different from those in Gnanou and Rempp's report.

In Table II, M_n values determined by UV and VPO are in good agreement, and M_n values determined by NMR are quite similar to those. However, they are not consistent with M_n values obtained by GPC. The reason for this discrepancy is not yet clear. The terminal (trimethylsilyl)ethynyl group might have affected the GPC results because standard PDMS samples used for calibration do not contain such groups. ^{29}Si{^{1}H} NMR spectra of the PDMS-M showed clear distinct peaks as in the case of model compound 4 (Figure 2). The integrals for both terminal silicon atoms were identical, showing end-capping

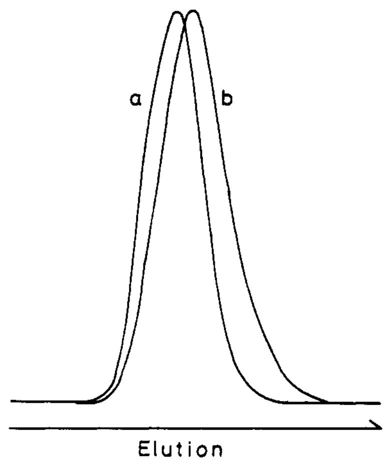

Figure 3. GPC traces of poly(dimethylsiloxane) reacted with lithium (trimethylsilyl)acetylide: (a) before reaction, $M_n = 3630$, $M_w/M_n = 1.16$; (b) after reaction, $M_n = 2220$, $M_w/M_n = 1.50$.

was achieved almost quantitatively.

An attempt to use lithium acetylide–ethylenediamine complex (the only commercially available form of lithium acetylide) instead of Li-TMSA to initiate polymerization was not successful due to the insolubility of the complex in solvents suitable for PDMS polymerization.

Redistribution Reaction of PDMS by TMSA. It has not been reported that Li-TMSA (supposed to be a weak base) cleaves linear PDMS chains. Lithium silanolate, also known to be a weak base, was reported not to cleave linear PDMS chains at room temperature.[12] Thus Li-TMSA and PDMS were allowed to react in THF, and the results are shown in Figure 3. As indicated, the molecular weight of the PDMS decreased and the molecular weight distribution widened after the reaction. ^{29}Si NMR showed the appearance of $\text{Me}_3\text{SiC}\equiv\text{C}$ (ca. −19 ppm) and SiOH groups (ca. −11 ppm). These results suggest that Li-TMSA cleaved the PDMS chain randomly to give shorter molecules having a $\text{Me}_3\text{SiC}\equiv\text{C}$ group or a SiOH group:

$$\sim\sim\sim\text{SiOSi}\sim\sim\sim + \text{Me}_3\text{SiC}\equiv\text{CLi} \rightarrow \sim\sim\sim\text{SiOLi} + \text{Me}_3\text{SiC}\equiv\text{CSi}\sim\sim\sim \xrightarrow{\text{H}^+} \sim\sim\sim\text{SiOH} + \text{Me}_3\text{SiC}\equiv\text{CSi}\sim\sim\sim$$

This gives further evidence that Li-TMSA reacted with D_3 instantaneously to initiate nonequilibrium polymerization.

Copolymerization of 2 and MMA. The obtained copolymer was a white powder soluble in toluene, acetone, and chloroform. Similar to other graft copolymers of PDMS and MMA, it was insoluble in methanol and hexane.[3] M_n and M_w, obtained by GPC (polystyrene standard), were 26 200 and 44 800, respectively. No gelation occurred during copolymerization. The ^{13}C NMR spectrum of the obtained copolymer showed the presence of the C≡C group ($\delta = 113$), and the ratio of its integral to that of the Si–Me carbon was identical (ca. 1:24) with the ratio in the original PDMS-M. These observations provided further evidence that each PDMS-M had only one methacrylic group (no gelation) and one C≡C group (retention of the C≡C group).

The ratio of the methoxy group of the MMA moiety to Si–Me obtained by ^{1}H NMR was 1:1.7, from which the molar ratio of the MMA moiety to the PDMS moiety in the copolymer (x:y in Scheme II) was determined to be 28:1. The ratio is a little larger than the loaded value of 22.5:1 and confirmed the previous finding that methacrylic groups attached to PDMS-M are less reactive than MMA.[5]

Acknowledgment. We are grateful to Mr. R. Mikami and Mr. T. Okawa for their assistance in the GPC analyses.

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Registry No. 4, 130281-29-7; lithium trimethylsilylacetylide, 54655-07-1; hexamethylcyclotrisiloxane, 541-05-9.