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### Synthesis and Characterization of Monodisperse $\alpha,\omega$ -Divinylpolydimethylsiloxane and $\omega$ -Vinylpolydimethylsiloxane

Marcelo A. Villar<sup>a</sup>; Miguel A. Bibbó<sup>ab</sup>; Enrique M. Vallés<sup>a</sup>

<sup>a</sup> Planta Piloto de Ingenieria Quimica UNS-CONICET Bahia, Blanca, Argentina <sup>b</sup> Petroquimica Cuyo, Mendoza, Argentina

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## **SYNTHESIS AND CHARACTERIZATION OF MONODISPERSE $\alpha,\omega$ -DIVINYLPOLYDIMETHYLSILOXANE AND $\omega$ -VINYPOLYDIMETHYLSILOXANE**

MARCELO A. VILLAR, MIGUEL A. BIBBÓ†, and ENRIQUE M. VALLÉS\*

Planta Piloto de Ingenieria Quimica  
UNS-CONICET  
Bahía Blanca, Argentina

### **ABSTRACT**

$\omega$ -Vinylpolydimethylsiloxanes ( $\omega$ -PDMS) and  $\alpha,\omega$ -divinylpolydimethylsiloxanes ( $\alpha,\omega$ -PDMS) have been synthesized by anionic polymerization of hexamethylcyclotrisiloxane (D3). The reactions were carried out in *n*-hexane and tetrahydrofuran (THF), respectively. The initiator was *n*-butyl-lithium (*n*-BuLi); tetrahydrofuran was used as an electron donor compound to promote the polymerization of D3. The synthesized polymers have been characterized by infrared (FTIR), proton nuclear magnetic resonance spectroscopy (NMR), light scattering (LALLS), and gel permeation chromatography (GPC). Molecular weights ranging from 20,000 to 100,000 were obtained with relatively narrow molecular weight distributions;  $M_w/M_n < 1.25$ .

### **INTRODUCTION**

Despite the large number of studies carried out in the past 40 years on rubber networks to study the relationship between their macroscopic physical properties and the molecular structure, many controversial points still remain to be solved. It is now clear that the use of well-defined networks is necessary to make significant advances toward a better understanding of the thermodynamic and dynamic proper-

†Present address: Petroquímica Cuyo, C.C. 73, (5507) Mendoza, Argentina.

ties of gels. Ideal networks for these purposes are those that consist of ensembles of identical chains with a controlled amount of network defects. The chains that compose these networks should be monodisperse in size and connected at their ends to the rest of the chains of the gel structure by chemical links of known functionality.

To fulfill these requirements, new synthetic methods based on endlinking procedures have been developed in several laboratories [1–3]. The general procedure is to synthesize, by anionic polymerization, a precursor telechelic polymer or macromonomer with reactive functional groups at both ends of the chain. In a subsequent step, the macromonomer is reacted with a multifunctional crosslinker to obtain a model network.

One aspect that has been poorly explored concerning the dynamic properties of networks is the role of dangling chains. These may be present in model networks owing to incomplete reaction of the polyfunctional crosslinker, and they are always present in significant amounts in networks obtained by more conventional methods such as vulcanization.

One simple way to study the influence of these chains on the dynamic and thermodynamic properties is to introduce a controlled amount of pendant chains in the structure of the networks. This can be accomplished performing the synthesis of a monodisperse linear polymer with a single functional group at one of the chain ends and mixing this reactant in appropriate amounts with regular difunctional prepolymer and crosslinker to obtain a network. This procedure allows one to change independently the concentration and size of the pendant chains in a model network.

In this work we report the synthesis and characterization of monofunctional  $\omega$ -vinylpolydimethylsiloxane ( $\omega$ -PDMS) and  $\alpha,\omega$ -divinylpolydimethylsiloxane ( $\alpha,\omega$ -PDMS) chains with narrow molecular weight distribution that can be used to prepare model networks with pendant chains.

## EXPERIMENTAL

### Reactive Preparation

The solvents utilized for the synthesis were *n*-hexane and  $H_4$ -furane (THF). *n*-Hexane was distilled and stored in the presence of a sodium dispersion, while THF was first refluxed for 2 h on KOH and then distilled and stored over a sodium dispersion. In both cases, solvents were redistilled several times under vacuum into flasks internally covered by Na mirrors until the inalterability of the mirrors assured that all the traces of water and another impurities in the solvents were removed. When this procedure was finished, part of the THF was fractionated in several vials and stored. These vials were then connected to the reactor, as shown in Fig. 1. The dried *n*-hexane or the remaining THF was stored and subsequently distilled into the reactors for each polymerization.

The initiator utilized in the reaction was commercial *n*-butyl-lithium (Alfa Ventron, 2.1 M in hexane). It was first placed in a flask under a nitrogen atmosphere and then diluted in *n*-hexane or THF. For the  $\omega$ -PDMS synthesis it was diluted to approximately 0.5 M with purified *n*-hexane and fractionated in several sealed vials. For the  $\alpha,\omega$ -PDMS synthesis it was diluted approximately to 0.05 M with purified THF and fractionated in the same way. The vials containing the initiator were connected to the polymerization reactors, as shown in Fig. 1.

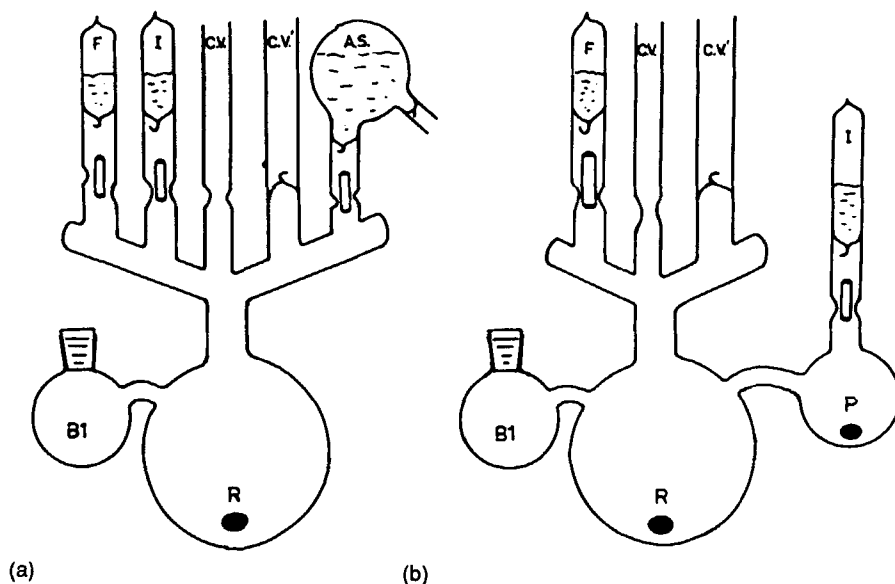


FIG. 1. Scheme of the reactors used for the synthesis of (a)  $\omega$ -PDMS and (b)  $\alpha,\omega$ -PDMS. B1, Monomer recipient; R, Reactor; P, initiation recipient; I, initiator vial; F, terminator vial; AS, solvation agent recipient; CV', vacuum line connection; CV, auxiliary vacuum line connection.

The monomer for both syntheses was hexamethylcyclotrisiloxane (D3) (Petrarch System). It was purified by sublimation as described below. Vinyltrimethylchlorosilane (ViDMCISi) (Petrarch System) was used for termination. It was distilled under vacuum into a flask, diluted with dried *n*-hexane, and fractionated in several vials that were also connected to the reactor, as shown in Fig. 1.

### $\omega$ -PDMS Synthesis

When the vials containing the initiator (I), termination (F), and solvating agents (AS) were connected to the system, the whole reactor was then joined to the vacuum line (CV) and evacuated for approximately 8 h. The system was then filled with dried nitrogen and, under a continuous  $N_2$  flow, approximately 300 g of the monomer (D3) was placed in recipient flask B1. After the monomer was added, the apparatus was closed and evacuated again.

By heating recipient B1 and cooling flask R with liquid air, the monomer was sublimated into the reactor. Subsequently, approximately 1000 mL of dried *n*-hexane was distilled onto the monomer. When the monomer was completely dissolved, the solution was frozen with liquid air and the reactor was separated from the vacuum line.

The seal of the vial containing the initiator was then broken, and the initiation took place at room temperature (approximately 20°C) under mild continuous agitation for 2 days. Since polymerization is not possible without the solvation of the  $Li^+$  cation, once the initiation was completed, a polar agent like THF was added to

react the living species with the rest of the monomer. The polymerization was kept under continuous agitation for 1 day, and finally, the living polymer was terminated with  $\text{ViDMClSi}$  to obtain the desired product. In order to avoid further reaction of the living ends, an excess of terminating agent was used.

After 4–6 h, the reactor was opened and distilled water was added to the system to dissolve the  $\text{LiCl}$ . The organic solution containing the polymer was washed several times and then it was slowly poured onto cold methanol to induce precipitation of the polymer. Finally, the polymer was dried at room temperature under vacuum to eliminate the remaining solvent.

### $\alpha,\omega$ -PDMS Synthesis

The reactor used for synthesis of the  $\alpha,\omega$ -PDMS is shown in Fig. 1b. When the vials containing the initiator (I) and termination (F) were connected to the system, the whole reactor was then joined to the vacuum line (CV) and evacuated as before. An entirely similar procedure was followed to charge D3 into the reactor, but this time THF instead of *n*-hexane was used to dilute the monomer.

The rate of initiation of this reaction at room temperature is considerably less than the rate of polymerization; this precludes the synthesis of a narrow distribution polymer. In order to circumvent this problem, the *n*-BuLi must be "preinitiated." To do this, approximately 200 mL of the monomer solution was passed to flask P before proceeding with the initiation reaction. The seal of the vial containing the initiator was then broken to allow the reaction with the monomer solution in flask P. The preinitiation took place at approximately 20°C under mild continuous agitation for 4 days. In these conditions complete D3 conversion and redistribution of the polymer occurred, yielding a low-molecular-weight living polymer ( $M_n$  3000 approximately) with a normal molecular weight distribution. The living polymer was then added to the remaining D3 solution in flask R to prepare the narrow distribution polymer with the desired molecular weight. The polymerization was kept under continuous agitation for 2 hr, and finally the living polymer was terminated with  $\text{ViDMClSi}$ . The reactor was opened and the polymer precipitated and dried as before.

### Polymer Characterization

The resulting polymers were characterized by end-group titration (FTIR and NMR), light scattering (LALLS), and gel permeation chromatography (GPC).

#### Infrared Spectroscopy (FTIR)

The concentration of terminal vinyl groups in the polymers was measured by infrared spectroscopy (FTIR). The absorption band at  $4650\text{ cm}^{-1}$  corresponding to the stretching of the vinyl group was used for this purpose. No interference of other groups was observed at this wavenumber. Measurements were made in a Nicolet FTIR 20 DXB at room temperature. A 1-cm cell with NaCl windows was used for the determination. Low-molecular-weight silicone oil with no vinyl terminal groups was used for reference. Spectrums to determine vinyl concentration were obtained as the difference between those corresponding to the polymer and the reference.

Divinyltetramethyldisiloxane (DVITMDS; Petrarch System) was used to obtain a calibration curve. Several solutions were made by using the reference silicone oil and adding known quantities of DVITMDS. Plotting absorbance versus concentration, Beer's law was verified. A value of  $1699.4 \text{ (mol/cm}^3\text{)}^{-1}$  was obtained for the slope of the resulting straight line. This is in good agreement with previous data from the literature [4].

### Nuclear Magnetic Resonance (NMR)

The polymer structure was confirmed by proton NMR in a Jeol-400 instrument. The samples were solubilized in  $\text{CDCl}_3$  and irradiated at 0.1 ppm. The temperature was  $50^\circ\text{C}$  and the speed 15 Hz. The ratios of the areas corresponding to  $\text{CH}_2=\text{CH}-$  (around 6 ppm) and  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  (around 1 ppm) of the  $\omega$ -PDMS were analyzed to confirm the proposed structure.

### Light Scattering (LALLS)

The weight-average molecular weight ( $M_w$ ) was determined by LALLS. Measurements were performed in a low-angle Chromatix KMX-6 photometer at room temperature. The polymers were dissolved in toluene at concentrations ranging from 0.02 to 0.30%. Toluene refractive index was taken as 1.4961, and the variation of this index with the concentration ( $dn/dc$ ) was taken as  $-0.0913$  [5].

### Gel Permeation Chromatography (GPC)

Gel permeation chromatograms were obtained using a Waters 440 liquid chromatograph equipped with four  $\mu$ -bondagel columns (E-125, E-500, E-500, and E-1000). Toluene was utilized as the eluent solvent at a flow rate of 0.5 mL/min. The concentration of the samples was 1 mg/mL. A universal calibration curve was obtained using 11 polystyrene standards from Pressure Chemical Company, ranging in molecular weight from  $1.8 \times 10^6$  to  $2 \times 10^3$ . The following values were used for the Mark-Houwink relationship [6]  $[\eta] = K M^\alpha$  with

$$\begin{aligned} K_{\text{PS}} &= 3.45 \cdot 10^{-4} & \alpha_{\text{PS}} &= 0.62 \\ K_{\text{PDMS}} &= 2.0 \cdot 10^{-4} & \alpha_{\text{PDMS}} &= 0.66 \end{aligned}$$

The molecular weight retention time curve was fitted by least-square regression to the form

$$\log M = A + BT_R + CT_R^2 + DT_R^3$$

where  $T_R$  is the retention time and  $A$ ,  $B$ ,  $C$ , and  $D$  are constants with the following values:  $A = 41.4688$ ,  $B = -3.8266 \cdot 10^{-4}$ , and  $D = -2.4645 \cdot 10^{-7}$ . No correction was made for axial dispersion of the columns.

## RESULTS

Five monofunctional  $\omega$ -PDMS and three bifunctional  $\alpha,\omega$ -PDMS were synthesized and labeled M1-M5 and B1-B3, respectively. The weight- and number-average molecular weights and the polydispersity for each polymer are shown in Table 1.

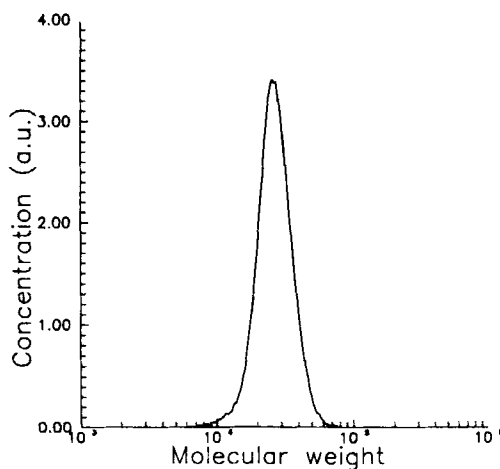
TABLE 1. Weight- and Number-Average Molecular Weights and Polydispersity of Eight Polymers

Polym.	Mn NMR	Mn FTIR	Mn GPC	Mw LALLS	Mw GPC	Mw/Mn GPC
M1	—	21,200	24,200	26,900	26,500	1.08
M2	—	46,300	47,800	52,400	51,300	1.07
M3	—	47,000	53,100	63,600	60,600	1.14
M4	—	61,500	67,600	101,100	83,500	1.20
M5	—	96,600	97,800	128,700	121,300	1.24
B1	34,900	32,400	30,000	44,000	34,100	1.14
B2	44,400	41,100	40,000	52,300	49,000	1.22
B3	45,800	42,800	40,000	50,400	49,500	1.24

There is a very good agreement between the weight-average molecular weight calculated by LALLS and GPC. All the synthesized polymers have narrow molecular weight distributions.

Figure 2 shows the GPC curve from sample M1. Low-molecular-weight polymers like M1 and M2 resulted with a polydispersity very close to 1; for higher molecular weights the polydispersity was slightly increased.

The number-average molecular weight of the bifunctional polymers was calculated by NMR comparing the peak area of the vinyl groups with that of the methyl groups and assuming complete bifunctional termination (Table 1). FTIR was used to obtain the vinyl concentration of terminal groups for each polymer. With these results the number-average molecular weight for all polymers was calculated assuming a functionality of 1 for polymers M1–M5 and 2 for B1–B3. These values were compared with those obtained from GPC and NMR (Table 1). The molecular

FIG. 2. GPC curve of  $\omega$ -PDMS (sample M1).

weights by NMR were in very good agreement with the determinations of molecular weight by GPC and FTIR since the results from all these techniques differ at most in 15%. This confirms that a good degree of vinyl termination was achieved in all cases.

To analyze further the quality of the vinyl termination step, proton NMR of the sample labeled M1 was performed. Figure 3 shows the spectrum corresponding to this sample. Integration of the spectrum demonstrates that the ratio of the chemical shift of the protons from the  $-\text{CH}=\text{CH}_2/-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is very close to  $1/3$ . This supports the structure of one long PDMS chain with a vinyl terminal group on one side and a butyl group on the other.

### DISCUSSION

Lee et al. showed that D3 can be polymerized anionically to give narrow-distribution PDMS [7]. The feasibility of this reaction was explained by the ring-strain of D3, which enhances the reactivity of the Si-O bonds with respect to those in higher-order rings. With this monomer it is then possible to use Li bases as initiators of the polymerization reaction. Later, siloxane-styrene and other copolymers were obtained by this method [8-10].

In only a few cases *n*-BuLi was used as initiator in the synthesis of PDMS polymers. Hölle and Lehnen [11] used *n*-BuLi with a different design of polymeriza-

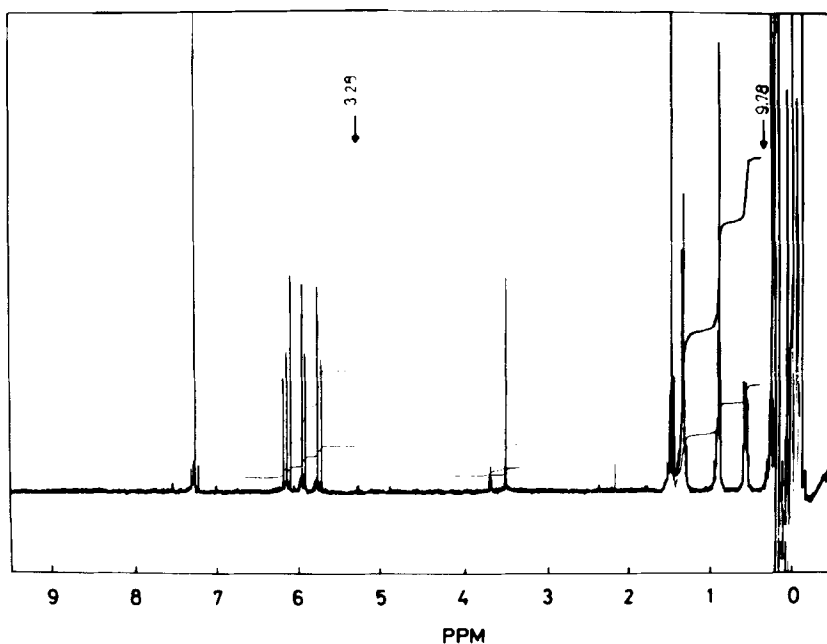


FIG. 3.  $^1\text{H}$  NMR of  $\omega$ -PDMS (sample M1). The sample was irradiated at 0.1 ppm. The numbers indicate the integration of the areas corresponding to  $\text{CH}_2=\text{CH}-$  (around 6 ppm) and  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  (around 1 ppm).



tion reactor. Their system was kept in an argon atmosphere. The high-molecular-weight polymers produced by this procedure were of wide MWD, and a bimodal distribution was obtained, indicating the presence of water in the reaction system.

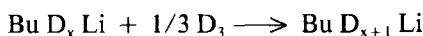
Our results show that *n*-BuLi, when used under vacuum in a closed reactor in adequate conditions, is a useful initiator to produce narrow MWD polymers.

The mechanism proposed for the synthesis of the  $\omega$ -PDMS is the following:

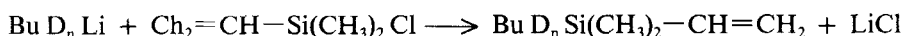
#### Initiation



#### Propagation



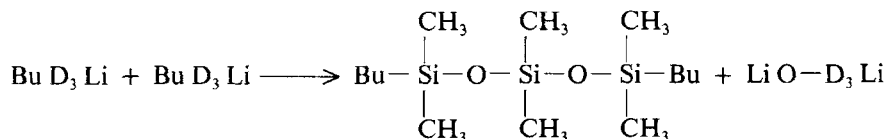
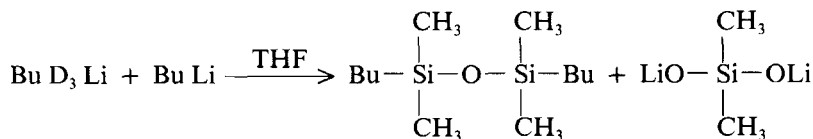
#### Termination



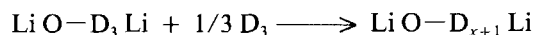
The initiation reaction between *n*-BuLi and D<sub>3</sub> was studied by Frye et al. [12]. In this work the reaction was carried out in a nonpolar solvent (hexane or toluene). These authors found that *n*-BuLi reacted with the cyclical monomer to give Bu D<sub>3</sub> Li. Subsequently, this compound decomposes in an equilibria mixture of Bu D<sub>1</sub> Li, Bu D<sub>2</sub> Li, and Bu D<sub>3</sub> Li. No polymerization takes place in this reaction medium; it is necessary to add a polar solvent to obtain the cation solvation that is able to give the propagation step [9]. In our case THF was used as polar solvent. The finalization step between the ViDMClSi and the cation also proceeds in a polar medium.

In a pure polar solvent like THF, the reaction between *n*-BuLi and D<sub>3</sub> gives bifunctional living species the ability to polymerize in two directions. This produces, on termination with ViDMClSi, a bifunctional telechelic PDMS. A possible mechanism for the reaction is the following:

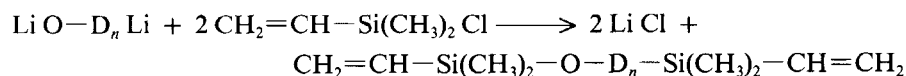
#### Initiation



#### Propagation



#### Termination



This mechanism is based on the observation that no H belonging to methylene

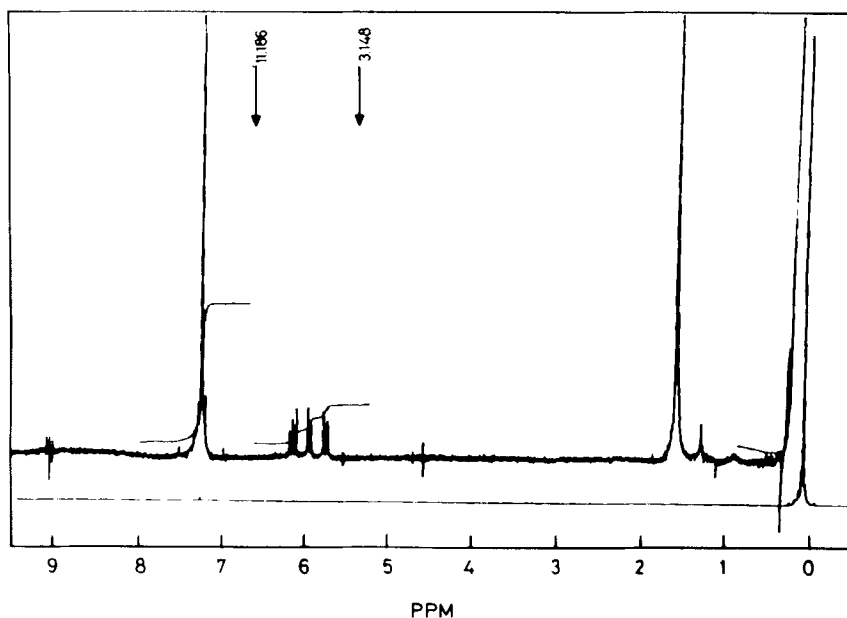


FIG. 4.  $^1\text{H}$  NMR of  $\alpha,\omega$ -PDMS (sample B1). The sample was irradiated at 0.1 ppm. The number indicates the integration of the area corresponding to  $\text{CH}_2=\text{CH}-$  (around 6 ppm).

structures was detected in the NMR measurements (Fig. 4) whereas these protons were easily detected in the  $\omega$ -PDMS obtained during polymerization in *n*-hexane. The good degree of bifunctional termination determined by NMR and FTIR is also in agreement with the sequence of reactions proposed for polymerization in THF. According to this, two different species are generated in the initiation step: active bifunctional species containing one or more repeated units with the structure— $(\text{Si}(\text{CH}_3)_2\text{O}-$  and unreactive species containing the butyl part of the original initiator. This reaction may be favored by the polar medium and the high concentration of *n*-BuLi used to initiate the prepolymerization.

## CONCLUSIONS

Narrow monofunctional and bifunctional molecular weight polymers ( $\omega$ -PDMS and  $\alpha,\omega$ -PDMS) have been synthesized by anionic polymerization utilizing commercial *n*-BuLi as initiator. The weight-average molecular weight of these polymers ranged from 20,000 to 125,000. Polymers were synthesized to prepare networks with controlled amounts of pendant chains, but they may also be very useful as precursors for the synthesis of branched stars of different functionalities and block and grafted copolymers.

The results of this work showed that the reaction between *n*-BuLi and the D3 monomer leads to different products according to the polarity of the solvent. Monofunctional initiation leading to  $\omega$ -PDMS is obtained with nonpolar solvents like *n*-hexane and toluene. Bifunctional initiation takes place in THF.

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