

A Straightforward Methodology for the Synthesis of α,ω -Telechelic Poly(dimethylsiloxane)s

María M. Soledad Lencina,^A Franco L. Redondo,^B Camila Müller,^B
Viviana Hanazumi,^B Cristian Vitale,^C Mario D. Ninago,^{B,D}
Daniel A. Vega,^A Marcelo A. Villar,^B and Andrés E. Ciolino^{B,E}

^AInstituto de Física del Sur (IFISUR), Departamento de Física, Universidad Nacional del Sur (UNS), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Avenida Alem 1253, Bahía Blanca 8000, Argentina.

^BPlanta Piloto de Ingeniería Química (PLAPIQUI), Departamento de Ingeniería Química, Universidad Nacional del Sur (DIQ-UNS), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Camino 'La Carrindanga' Km. 7, Bahía Blanca 8000, Argentina.

^CInstituto de Química del Sur (INQUISUR), Departamento de Química, Universidad Nacional del Sur (UNS), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Avenida Alem 1253, Bahía Blanca 8000, Argentina.

^DFacultad de Ciencias Aplicadas a la Industria (FCAI), Departamento de Ingeniería Química, Universidad Nacional de Cuyo, Bernardo de Irigoyen 375, San Rafael 5600, Mendoza, Argentina.

^ECorresponding author. Email: aciolino@plapiqui.edu.ar

In this work we report the synthesis of α,ω -telechelic poly(dimethylsiloxane)s (α,ω -PDMS) by employing a novel bifunctional initiator obtained from a commercially available siloxane precursor, diglycidylether-terminated poly(dimethylsiloxane) (PDMS-DGE). The synthetic strategy was easily followed by different colour changes, and involved the high-vacuum reaction of $sec\text{-Bu}^-\text{Li}^+$ with 1,1'-diphenylethylene (DPE) to afford the addition adduct (bright red) that was subsequently reacted with PDMS-DGE, promoting the nucleophilic ring-opening from epoxide-end chains. The resulting bifunctional initiator (light green) was then employed to polymerize hexamethyl(cyclotrisiloxane) monomer (D_3) by using conventional anionic polymerization (from light green to pale yellow). From suitable terminating agents, silane ($-\text{SiH}$), vinyl ($-\text{CH}=\text{CH}_2$), hydroxy ($-\text{OH}$), and even methacryloyl α,ω -PDMS were obtained. ^1H NMR and FT-IR analyses confirmed the presence of the targeted functional groups in the resulting polymers. However, a careful siliconization procedure should be performed over glass surfaces during the fractionation of chlorosilane ampoules in order to avoid the presence of silanol moieties that decrease end-capping efficiency. This fact was observed not only from NMR but also from size exclusion chromatography (SEC) analyses, since narrow molar masses distributions ($1.15 \leq M_w/M_n \leq 1.3$) and a good control over the resulting molar masses were observed.

Manuscript received: 16 September 2017.

Manuscript accepted: 30 December 2017.

Published online: 30 January 2018.

Introduction

The synthesis of polymers with predictable, well defined structures is one of the most important research areas in polymer chemistry.^[1] Living anionic polymerization provides one of the best approaches for synthesizing complex macromolecular structures such as α,ω -telechelic polymers. These polymers are the initial step to explore versatile reaction pathways that involve well known synthetic strategies (such as click-chemistry reactions or macromonomer polymerization) to produce polymers with sophisticated architectures, like H-, pom-pom-, or comb-shaped homo- and block-copolymer structures or controlled networks, among other complex macromolecular structures.^[2–6]

α,ω -Telechelic polymers are obtained by different synthetic methods, which usually involve the use of bifunctional initiators.^[7] The synthesis of bi- or multifunctional initiators for anionic polymerization is one of the most outstanding challenges in the field. From the first sodium or potassium naphthalenides reported by Szwarc et al. in the 1950s^[8–10] up to the industrial production of lithium alkyls,^[11] anionic polymerization techniques take advantage of the versatility of functional initiators to synthesize complex macromolecular structures with predictable molar masses and narrow molar mass distributions.

One of the first employed methodologies to produce multifunctional anionic initiators was known as the 'titration method', in which di-isopropenyl benzene derivatives are reacted

with *n*-butyl or *sec*-butyl lithium in a direct Michael addition to afford the corresponding bifunctional initiators.^[12] However, the use of di-isopropenyl benzene derivatives presented several drawbacks, including the accurate control of the stoichiometry required to avoid the undesired presence of by-products.^[13] Since the Michael addition proved to be a good choice, other suitable alternatives were developed.

As it is well established by the literature, by steric restrictions, 1,1'-diphenylethylene (DPE) is not able to polymerize by an anionic mechanism.^[14] However, the bright red adduct obtained from the reaction with lithium alkyls is an excellent initiator for specific monomers, such as methyl methacrylates.^[15] By using a similar approach, the development of DPE derivatives gave rise to the next generation of bifunctional anionic initiators.^[1]

Double diphenylethylene derivatives (DDPE) were successfully employed to synthesize tri-block copolymers, as well as other complex macromolecular structures such as dendrimers, macromonomers, and star copolymers.^[16] This methodology provides an effective method to produce bi- or multifunctional initiators, an alternative to the conventional lithium/halide exchange (in which bromine is often the chosen halide).^[1,17] Its versatility as a synthetic tool in anionic polymerization was fully explained by Quirk et al. in a review published in 2000.^[1,18]

Although the above-mentioned methodologies do really provide the desired bifunctional initiators, the non-commercial availability of DDPE, modified DPE derivatives, or polyhalogenated compounds is a drawback. Frequently, these compounds should be obtained before the polymerization reaction, and many synthetic and purification steps are usually required.^[13,17] Consequently, besides the complexity of anionic polymerization techniques, the synthesis of these compounds involves additional synthetic steps to afford the targeted initiators.

In this work, we present a straightforward methodology to synthesize a bifunctional initiator that allows the synthesis of tailor-made α,ω -telechelic poly(dimethylsiloxane) (α,ω -PDMS) homopolymers. This initiator is obtained from a commercially available diglycidylether-terminated poly(dimethylsiloxane) (PDMS-DGE). The synthetic strategy involves the high-vacuum reaction of *sec*-Bu⁻Li⁺ with DPE, and subsequently with PDMS-DGE in order to promote the nucleophilic ring-opening of the epoxide ends. The resulting bifunctional initiator was then employed to polymerize hexamethyl(cyclotrisiloxane) (D₃) through conventional anionic polymerization methods. By using suitable terminating agents, silane (-SiH), vinyl (-CH=CH₂), hydroxy (-OH), and even methacryloyl α,ω -PDMS were obtained. The commercial availabilities of DPE, *sec*-Bu⁻Li⁺, and PDMS-DGE avoids prior synthetic steps and allows a straightforward methodology to obtain α,ω -PDMS. As added value, colour changes observed from the different carbanions produced throughout the reactions provide an easy way to follow qualitatively the synthetic pathway proposed.

Experimental

Materials

All materials were purified by standard anionic polymerization procedures, in whole-sealed glass apparatuses specially designed for each reagent.^[2,19,20] *sec*-Bu⁻Li⁺ was freshly prepared under vacuum from *sec*-butyl chloride (Fluka) and lithium metal (Fluka) as previously reported.^[2] Hexamethyl (cyclotrisiloxane) monomer (D₃, Aldrich) was purified

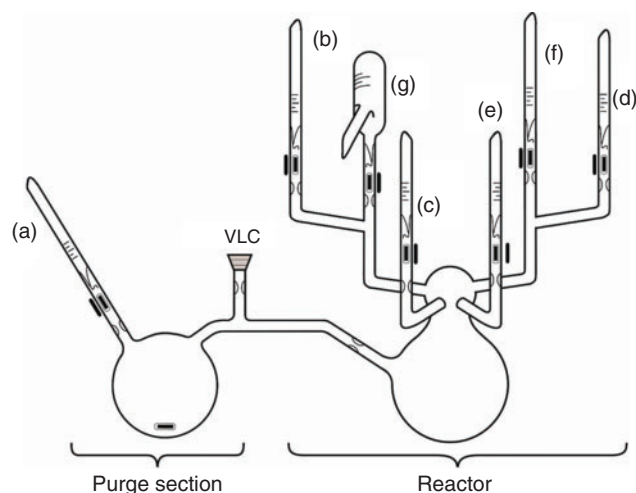


Fig. 1. Apparatus for the synthesis of α,ω -PDMS (high-vacuum techniques). (a, b) *sec*-Bu⁻Li⁺ (purge and initiator ampoules, respectively), (c) PDMS-DGE, (d) DPE, (e) terminating agent (specific for each polymerization), (f) THF, and (g) D₃ monomer.

according to standard procedures for anionic polymerizations (high-vacuum techniques).^[2,20,21] DPE (Aldrich) was purified by distillation in vacuum from calcium hydride. PDMS-DGE (Aldrich, $M_n \sim 800 \text{ g mol}^{-1}$) was used as received, and sealed in glass ampoules after pumping ($\sim 2 \text{ h}$) and many freezing–thawing cycles in a high-vacuum manifold. By vapour pressure osmometry measurements, the M_n value provided by the suppliers was checked ($M_n \sim 1080 \text{ g mol}^{-1}$, please refer to the Supplementary Material). Chlorodimethylsilane (Aldrich), chlorotrimethylsilane (Aldrich), chloro(dimethyl)vinylsilane (Aldrich), and glycidylmethacrylate (GMA, Aldrich) were purified by distillation under vacuum over calcium hydride by using well established methodologies^[2] (as it will be discussed later, a careful siliconization procedure by employing chlorotrimethylsilane must be performed over the glass surface in order to avoid the presence of silanol moieties in the resulting ampoules). Hexane (Cicarelli, solvent), tetrahydrofuran (THF, Cicarelli, promoter of D₃ polymerization), and methanol (Cicarelli, terminating agent) were also employed. These reagents were purified according to conventional anionic polymerization procedures, which involve freezing–thawing cycles and the use of suitable purifying reagents for each case.^[2,19]

Preliminary Procedures

All manipulations were performed under a high-vacuum manifold, in glass Pyrex reactors equipped with break-seals for the addition of the reagents and constrictions for removal of products.^[19] A scheme of the apparatus employed for the synthesis is shown in Fig. 1. The purge section and reactor were hand-made for each polymerization by employing specific glassware and glass-blowing techniques. Constrictions and heat-sealing procedures (with the aid of a flame torch) were employed to carry out the different polymerization stages.

The apparatus was attached to the vacuum line connection (VCL), checked for pinholes, and subsequently flame dried. After pumping for 5 min (in order to eliminate air and humidity traces inside), purified hexane ($\sim 30 \text{ mL}$) was distilled into the purge section by placing the purge balloon in a liquid nitrogen bath. Once the desired quantity was distilled, the solvent was

frozen and subsequently degassed in the vacuum line over 15 min. Afterwards, the apparatus was detached from the manifold by heat-sealing the corresponding constriction.

The *sec*-Bu⁻Li⁺ ampoule (2 mL, 0.28 M) from the purge section was then broken and the whole apparatus was washed with the diluted *sec*-Bu⁻Li⁺ solution formed inside in order to remove impurities on the glass surface. Every section of the apparatus was carefully washed with gentle manual movements and rinsed thoroughly by condensing solvent on the walls. Finally, hexane was distilled from the purge section to the reactor by placing the former in a hot water bath and the later in an ice/salt bath. After complete solvent distillation, the purge section was detached from the main reactor by heat-sealing the corresponding constriction. This last step left the reactor with pure solvent inside, ready for the synthesis.

Synthesis of α,ω -PDMS

A DPE ampoule (1 mL, 5.66 mmol) was broken and its contents poured inside the reactor. After mixing with the solvent, a *sec*-Bu⁻Li⁺ ampoule (8.8 mL, 2.46 mmol) was broken. A bright-red solution was immediately observed. After 3 h, the PDMS-DGE ampoule (1 mL, 1.23 mmol) was broken, and its contents were poured inside the reactor. A light-green solution was observed. The reaction between PDMS-DGE and the *sec*-Bu⁻Li⁺/DPE adduct was left to proceed for 24 h at room temperature. The D₃ ampoule (6.2 g, 27.8 mmol) was then broken, and a bright-yellow solution was immediately observed. This solution was left in equilibrium, at room temperature, for one day in order to obtain dimethylsiloxanyl lithium anions. Subsequently, the THF ampoule (15 mL, 185 mmol) was broken in order to promote monomer polymerization. After 24 h of reaction at room temperature, the break seal of the terminating agent ampoule (which was in a molar excess regarding the initial PDMS-DGE ampoule) was broken. The reaction was left to proceed for at least 3 h and the resulting product was precipitated in cold methanol, re-dissolved in THF, re-precipitated in cold methanol, filtered off, and finally vacuum dried. When chlorosilanes were employed as terminating agents, an initial organic/aqueous extraction step (three times, 20/80 v/v, hexane/10 wt.-% of sodium hydrogen carbonate solution) before the methanol precipitation was employed. This additional procedure was necessary in order to avoid the presence of hydrochloric acid residues in the resulting polymer.

Nomenclature

The resulting α,ω -PDMS were labelled as B2-X, in which X stands for the targeted end groups.

Characterization

Samples were characterized by size exclusion chromatography (SEC) on a system built with a Waters 515 HPLC pump and a Waters model 410 differential refractometer detector, equipped with three mixed bed Phenogel linear (2) columns and a pre-column with 5 μ m bead size (Phenomenex). The solvent employed was toluene with a flow rate of 1 mL min⁻¹. The injection volume was 200 μ L, and polystyrene (PS) standards were used for calibration. Mark-Houwink calibration constants used for each polymer were $K_{PS} = 0.012 \text{ mL g}^{-1}$, $\alpha_{PS} = 0.71$ for PS, and $K_{PDMS} = 0.0136 \text{ mL g}^{-1}$, $\alpha_{PDMS} = 0.69$ for PDMS.^[22]

NMR spectra of the copolymers were recorded on a Bruker 300 MHz instrument using deuterated chloroform (Aldrich) as solvent.

FT-IR spectra of the resulting polymers were recorded on a Nicolet FTIR 520 spectrometer. Cast films from polymer solutions were prepared (1 wt.-% in hexane or THF). FT-IR spectra were recorded at a 4 cm⁻¹ resolution over the 4000–400 cm⁻¹ range using an accumulation of 20 scans and air as the background.

Results and Discussion

The reaction between DPE and alkyllithiums is a versatile synthetic tool widely used in organic and polymer chemistry.^[1] The bright red adduct so obtained is a powerful carbanion that is able to react with many chemical species. In this work, we took advantage of this reaction to promote the ring-opening of epoxide rings from PDMS-DGE.^[23] The synthetic pathway employed is shown in Scheme 1.

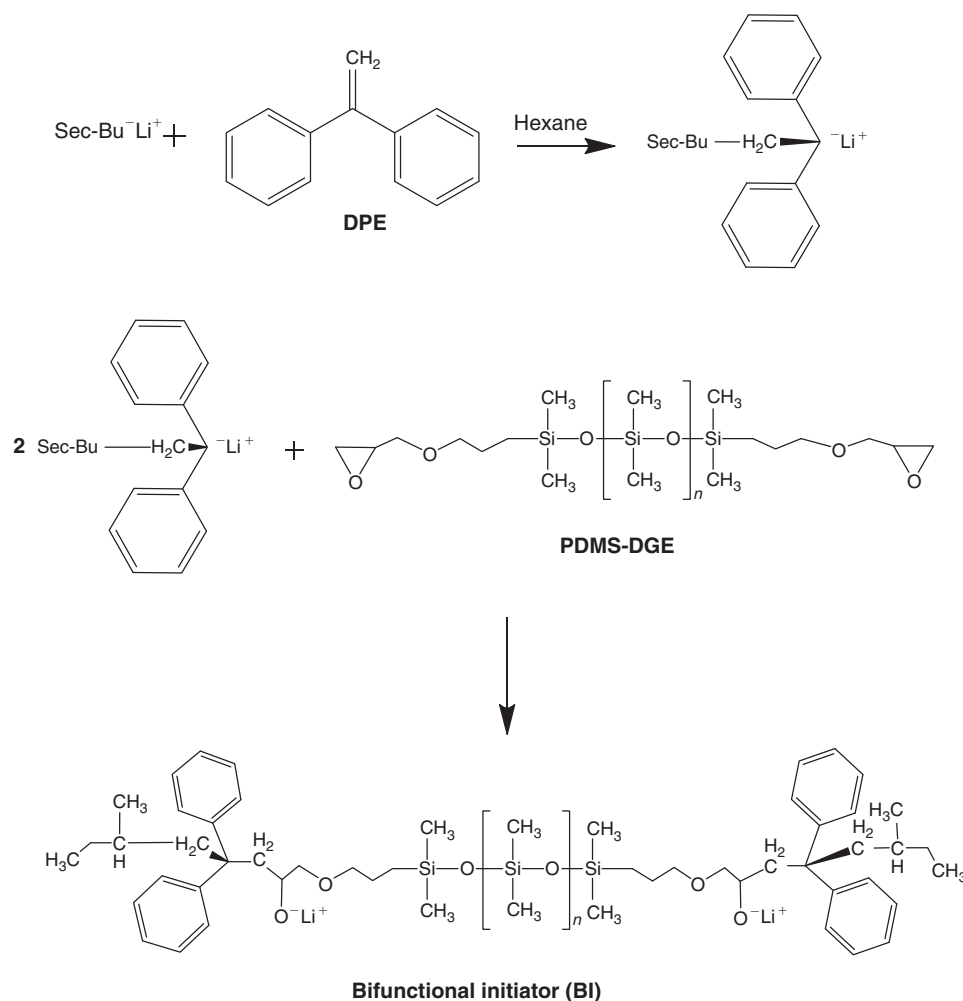
The literature reports that the direct use of *sec*-Bu⁻Li⁺ over PDMS-DGE would lead to the addition of the corresponding *sec*-Bu moieties and the formation of the corresponding substituted olefins without promotion of D₃ polymerization.^[24] Consequently, in order to favour ring-opening of both epoxide ends, a suitable base is needed. The selected carbanion should provide not only a good basicity to promote the ring-opening of the epoxide but also steric hindrance to avoid undesired by-products. As it was suggested by Zhang et al.^[23] the adduct obtained by the reaction between *sec*-Bu⁻Li⁺ and DPE is a good choice for such a purpose.

The reaction between *sec*-Bu⁻Li⁺ and DPE was evidenced by the formation of the bright red adduct,^[25] and it was left to proceed for 3 h in order to promote the total consumption of the alkyllithium compound. A little excess of DPE over *sec*-Bu⁻Li⁺ was employed to achieve this goal. After this period of time, PDMS-DGE was added to promote the ring-opening of the epoxide-ended chains. The evolution of the reaction was evidenced by the change in the colour of the resulting solution, which turned from bright red to light green. The reaction was left to proceed over 24 h in order to assure the complete conversion of epoxide rings. By employing this procedure, a bifunctional anionic initiator (BI) suitable for the polymerization of D₃ monomer is obtained.

The following step involves the addition of D₃ monomer in order to obtain the corresponding dimethylsiloxanyl lithium anions.^[26–29] For such a purpose, an excess of D₃ over the BI is used in order to promote the formation of these reactive species. The propagation reaction is avoided under these conditions because of the non-polar solvent employed.^[27] The reaction was left to proceed for 24 h, at room temperature, to ensure that all BI has reacted. The colour change of the solution from light green to pale yellow takes account of this fact. THF was then added to promote D₃ polymerization, since it is well established that the addition of a polar additive breaks dimethylsiloxanyl lithium aggregates^[21] and enhances the ring-opening of the remaining monomer, yielding the desired PDMS homopolymer. This reaction was left to proceed at room temperature for 24 h. Fig. 2 shows the photographs taken step by step during the reaction in order to record the above mentioned colourimetric changes.

Finally, after D₃ polymerization, the terminating agent ampoule was broken in order to obtain the α,ω -PDMS. These last steps can be visualized in Scheme 2.

Table 1 shows the data obtained from SEC analysis of α,ω -PDMS samples. Telechelic polymers with polydispersity indexes (M_w/M_n) less than 1.3 were obtained in almost all cases;



Scheme 1. Synthetic pathways for the synthesis of bi-functional initiator (BI).

the exception is methacryloyl-ended α,ω -PDMS (B2-GMA), and a potential explanation for this fact will be discussed in the following paragraphs. In addition, excellent agreement between expected and obtained M_n values is observed. Although there are specific applications that require polydispersity values below 1.1 (for example, self-assembling block copolymer templates for nanolithography), the simplicity of the technique proposed here combined with the relatively narrow molar mass distributions of the synthesized polymers make it useful for a diversity of applications. In the particular case of this work, three leading factors might be affecting polydispersity indexes (M_w/M_n) from optimum values (≤ 1.1):^[30] purification of the PDMS-DEG precursor, purification of silane agents, and backbiting or side reactions.

First, the purification of the PDMS-DEG precursor might involve many reaction steps that were avoided for the lack of simplicity. For example, since it is not possible to distill it under vacuum, a previous treatment with calcium hydride should be discarded unless a special sintered-glass filter is designed. Seeking simplicity, only degasification of PDMS-DGE by freezing–thawing steps was employed. Although these facts can be considered as plausible, the NMR analysis of the commercial product denotes a high degree of purity. On the other hand, D_3 polymerization was performed at room temperature, and it is well known that backbiting reactions are favoured under these circumstances.^[26] Finally, chlorosilanes are well known for their spontaneous and fast hydrolysis. An exhaustive

siliconization of the inner walls of laboratory glassware is required to avoid the reaction between chlorosilanes and silanol groups from glass surfaces.^[31–35] Consequently, traces of hydrochloric acid might be present in the reaction medium and this fact would promote breakage of polymeric chains. Indeed, this reaction has been explored in the literature to induce changes in PDMS substrates,^[36–40] and by considering the fast reactions produced in astringent, anionic polymerization conditions it is quite reasonable to consider it as an important factor. As it will be discussed later, this fact might explain not only M_w/M_n values but also end-capping efficiency.

In the case of B2-GMA, the synthesis also departs from ideality due to the number of reactive sites in the terminating agent (glycidylmethacrylate monomer) employed to obtain this telechelic PDMS. The molecule has three reactive sites in its structure (the double bond, the carbonyl moiety, and the epoxide ring), and reaction conditions would favour one reaction against others^[41–43] (for example, low temperatures are required to promote its anionic polymerization^[44]). Consequently, the probability of having higher polydispersity indexes in the resulting polymers is much broader. This fact is a plausible explanation for the result obtained by SEC, and might explain the results presented in Table 1. NMR characterization will confirm this assumption.

SEC traces are shown in Fig. 3. As it was mentioned above, the broader molar mass distribution corresponds to B2-GMA,

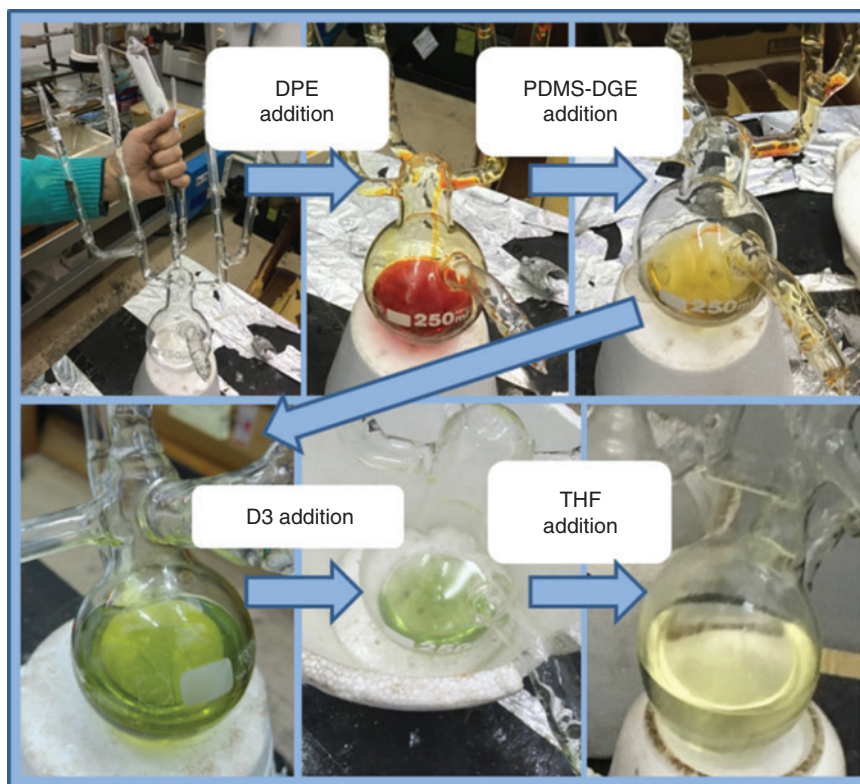
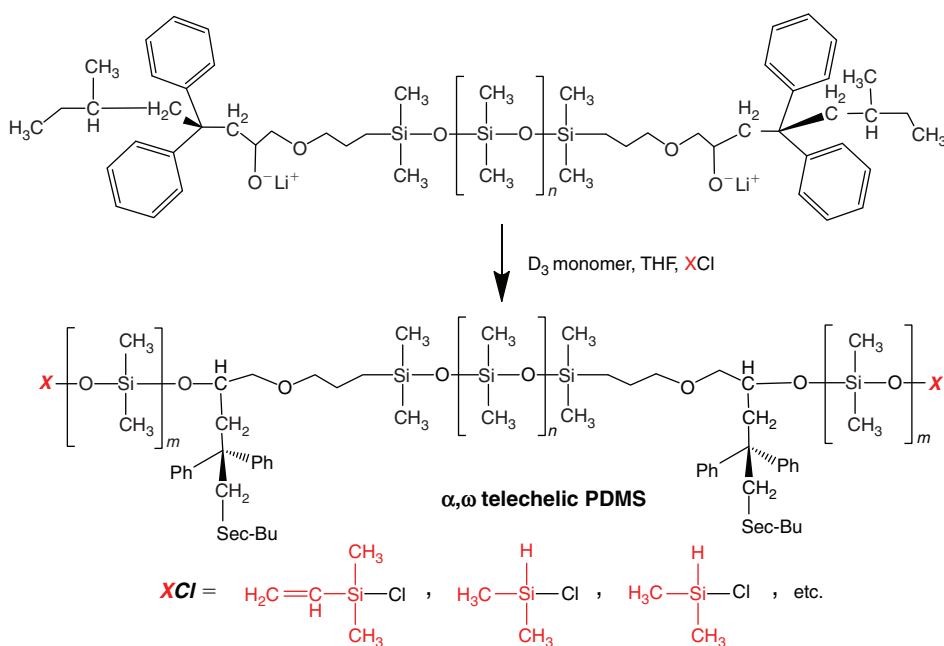


Fig. 2. Colour evolution during the different stages of reaction.



Scheme 2. D_3 polymerization and synthesis of α, ω -PDMS.

whereas B2-OH exhibits the narrower one. M_w/M_n values for B2-Vi and B2-SiH are equivalent, although their molar mass distributions seem to be quite different. In addition, both exhibit higher molar masses compared to other polymers. The explanation for this fact might be the employed reaction times and the specific particulars of each reaction. At this point it is worth

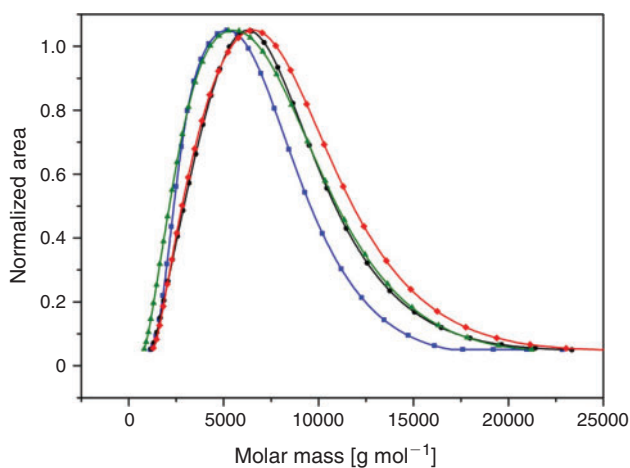
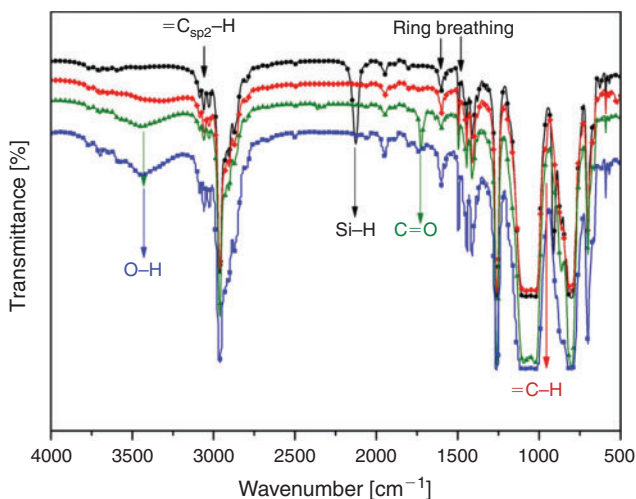
mentioning that although M_w/M_n for the PDMS-DGE precursor is unknown, it should be higher or at least equal when compared with the resulting M_w/M_n values for α, ω -PDMS polymers.^[45]

FT-IR characterization confirms the presence of the targeted functional groups in the resulting polymers. Fig. 4 shows the spectra recorded between $4000\text{--}400\text{ cm}^{-1}$ for α, ω -PDMS.

Table 1. SEC characterization of α,ω -PDMS polymers

OH, hydroxy; SiH, silane; Vi, vinyl; GMA, methacryloyl. Average molecular masses are expressed in units of Da

| Sample | M_n^A | M_n^B | M_w | M_w/M_n^C |
|--------|---------|---------|-------|-------------|
| B2-OH | 4000 | 4500 | 5700 | 1.26 |
| B2-SiH | 5000 | 4900 | 6300 | 1.29 |
| B2-Vi | 5000 | 5100 | 6600 | 1.29 |
| B2-GMA | 4000 | 4100 | 5700 | 1.39 |

^AExpected M_n value according to stoichiometry.^BObtained M_n value according to SEC analysis.^C M_w/M_n .**Fig. 3.** SEC traces for α,ω -PDMS samples. (●) B2-SiH, (◆) B2-Vi, (▲) B2-GMA, and (■) B2-OH.**Fig. 4.** FTIR spectra from α,ω -PDMS samples. (●) B2-SiH, (◆) B2-Vi, (▲) B2-GMA, and (■) B2-OH.

Characteristic bands of C_{sp^2} -H stretching at 3100 – 3000 cm^{-1} , and those corresponding to the ring breathing at 1600 and 1493 cm^{-1} are observed in all samples. These bands are a clear evidence of the presence of DPE structure as an integral part of polymer chains. All spectra exhibit the typical strong absorption bands from PDMS polymers at 1260 (symmetric- CH_3

deformation in $Si-CH_3$ bonds), 1100 – 1000 (asymmetric $Si-O-Si$ stretching vibrations), and 800 cm^{-1} ($Si-C$ stretching vibration).^[46] Individually, the B2-OH spectrum displays a broad absorption band at 3900 – 3200 cm^{-1} ($-OH$ stretching region), while the B2-SiH spectrum exhibits an acute absorption band at 2360 – 2100 cm^{-1} ($-SiH$ stretching). In addition, the B2-GMA spectrum presents a characteristic absorption band at 1735 cm^{-1} ($>C=O$ stretching, ester group), although the intensity of this band was not as pronounced as expected. Moreover, the broad band above 3200 cm^{-1} exposes the presence of $Si-OH$ endings, probably due to the fact that GMA was not completely consumed during the last step, leading to unreacted polymer chains.

From 1H and ^{13}C NMR characterization the mechanism of the reaction proposed in Scheme 1 was successfully confirmed. At first, unsymmetrical epoxide groups from PDMS-DGE could be attacked by the following two alternatives: (a) at the most substituted carbon atom from the epoxide ring, as it is expected in acid-catalyzed ring opening or (b) at the least substituted carbon atom in the case of base-catalyzed ring opening, by following a S_N2 mechanism. The ring-opening process in epoxides depends on reaction conditions. Under basic conditions (as they can be considered when carbanions are present) ring-opening follows option (b). The main barrier to the S_N2 mechanism is steric hindrance; consequently, the nucleophile will attack the less substituted carbon atom from the epoxide.

Fig. 5 displays the ^{13}C NMR spectrum of PDMS-DGE. The signals from both epoxide rings appear at 50.85 ($-CH-$) and 44.32 ppm ($-CH_2-$). After the ring-opening reaction, these signals must be shifted, since a higher deshielding effect from the O atom in open chain ethers is observed when compared with epoxides. To prove this, Fig. 6 shows the spectrum of B2Vi. Most of the ^{13}C NMR signals remained unaffected by comparing to the PDMS-DGE skeleton. Nevertheless, signal b (that corresponds to the most substituted C atom in the epoxide) shifted from 50.85 to 69.34 ppm after the ring-opening reaction.

A new set of signals also appear in Fig. 6, and they could be assigned to the corresponding C atoms. Terminal vinyl C atoms are detected at 131.62 and 139.34 ppm , proving the success of the functionalization process. In the case of the B2-GMA spectrum, the weak signal for the carbonyl group and the poor peaks observed for vinyl carbons are in agreement with FT-IR results, by indicating the low effectivity of GMA as a terminating agent that might be explained by the lack of reaction time.

1H NMR analysis confirmed the reaction mechanism proposed. Figs 7 and 8 display commercial PDMS-DGE and B2-Vi 1H NMR spectra. In these figures, letters have been used to indicate H atoms from chemical structures. For PDMS-DGE, characteristic signals are observed at 2.81 (a, 1.94, 2H), 2.62 (a', 1.95, 2H), 3.15 (b, 1.93, 2H), 3.74 – 3.70 (c, 2.03, 2H), 3.49 – 3.44 (d and c', 6.04, 6H), 1.63 (e, 4.38, 4H), and 0.54 ppm (f, 4.00, 4H). After polymerization, the resulting 1H NMR spectrum presents slightly shifted signals to lower values due to the different mobility of molecules.^[47] However, the assignment of the observed signals and their integrated area values are in good agreement with the composition expected for the B2-Vi polymer: the presence of *sec*-butyl groups, vinyl end groups, phenyl rings, and PDMS-DGE precursor signals are observed at 1.07 – 0.44 (i, j, k, and f, 10, 10H), 5.82 (p, 0.76, 1H), 6.01 (q, 0.79, 1H), 6.13 (r, 0.75, 1H), 7.44 – 7.13 (m, 11, 10H), 3.26 – 2.77 (c' and d, 2.66, 3H), and 3.69 ppm (b, 0.94, 1H).

From the integration ratio between i, j, k and f, b, 1H NMR signals and those from vinyl groups (p, q, and r), a quantitative

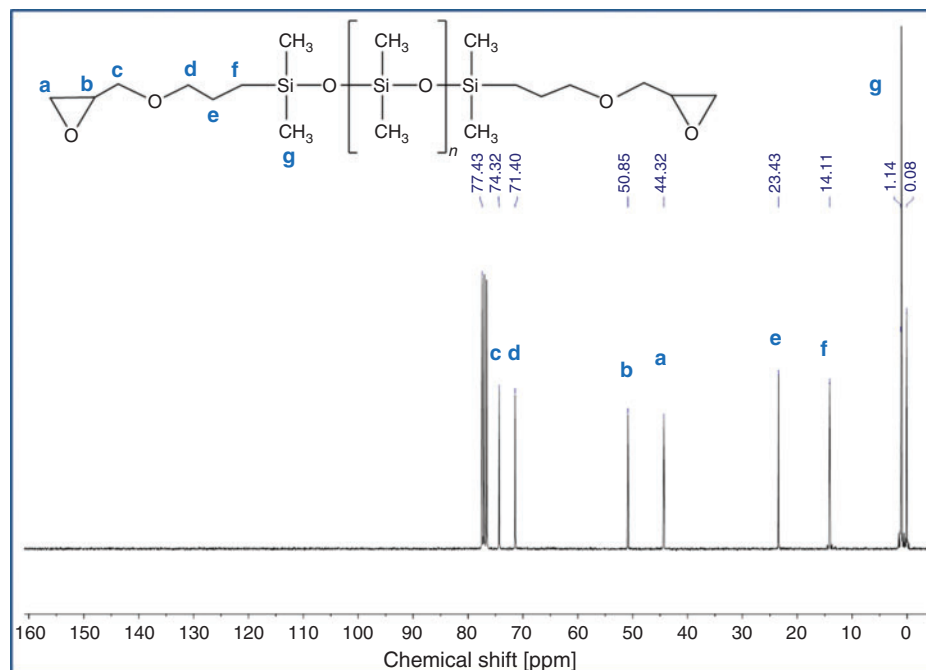


Fig. 5. ^{13}C NMR spectrum of PDMS-DGE.

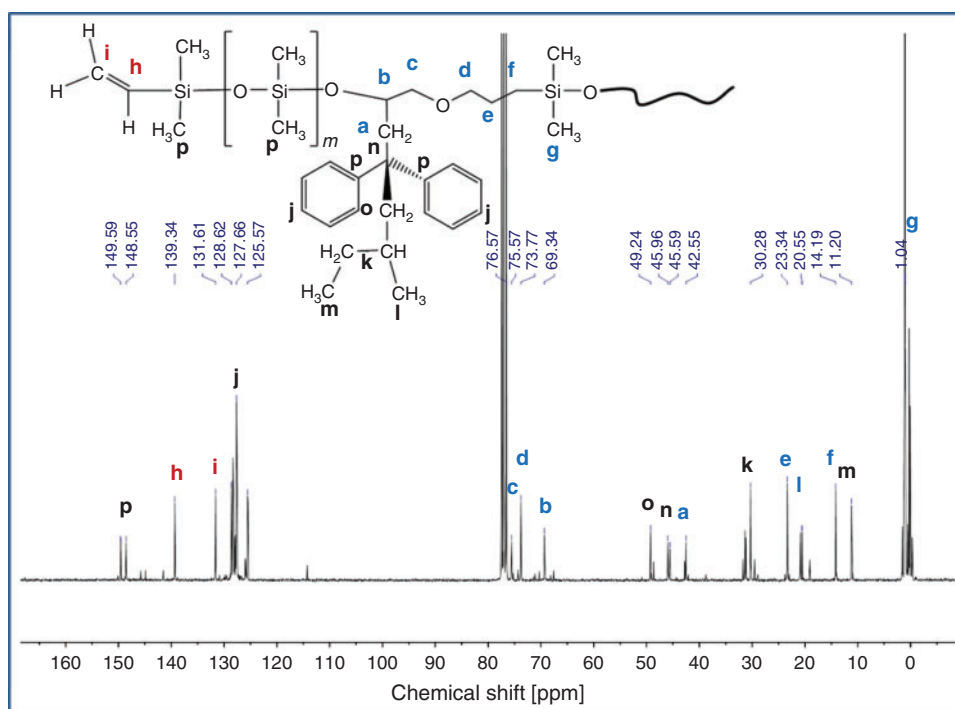


Fig. 6. ^{13}C NMR spectrum of B2-Vi.

relationship can be estimated for end-capping ($> 75\%$). However, it should be noted that at 5.52 ppm a new signal appears, that is also present in the B2-SiH and B2-GMA spectra (Figs S2 and S3, Supplementary Material). This signal is associated with the presence of Si-OH moieties (silanols) in the resulting polymer. Their appearance might be attributed to many factors (incomplete reaction with the corresponding terminating agent, reaction conditions), but it is highly probable that partial hydrolysis of chlorosilanes would favour the presence of Si-OH

derivatives in the medium. We suspect that during their fractionation, the previous siliconization step of the glass ampoules was not really achieved, and this might explain the appearance of Si-OH in a low content mixed with the targeted terminating agents.^[31–33,35] From the analysis of B2-OH, B2-SiH, and B2-GMA ^1H NMR spectra, 95, 85, and 25% of end capping was obtained, respectively. It is important to remark that end-capping values are estimated from the area ratio between functional group signals (–OH, Si–H, and $\text{CH}_2=\text{CH}-$) and i, j,

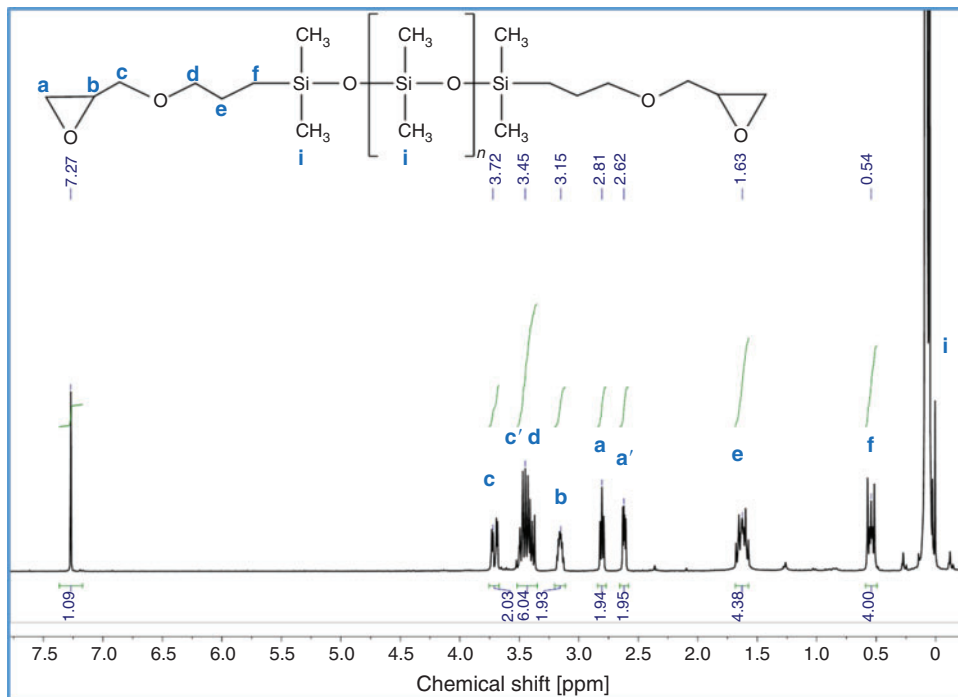


Fig. 7. ^1H NMR spectra of the PDMS-DGE precursor.

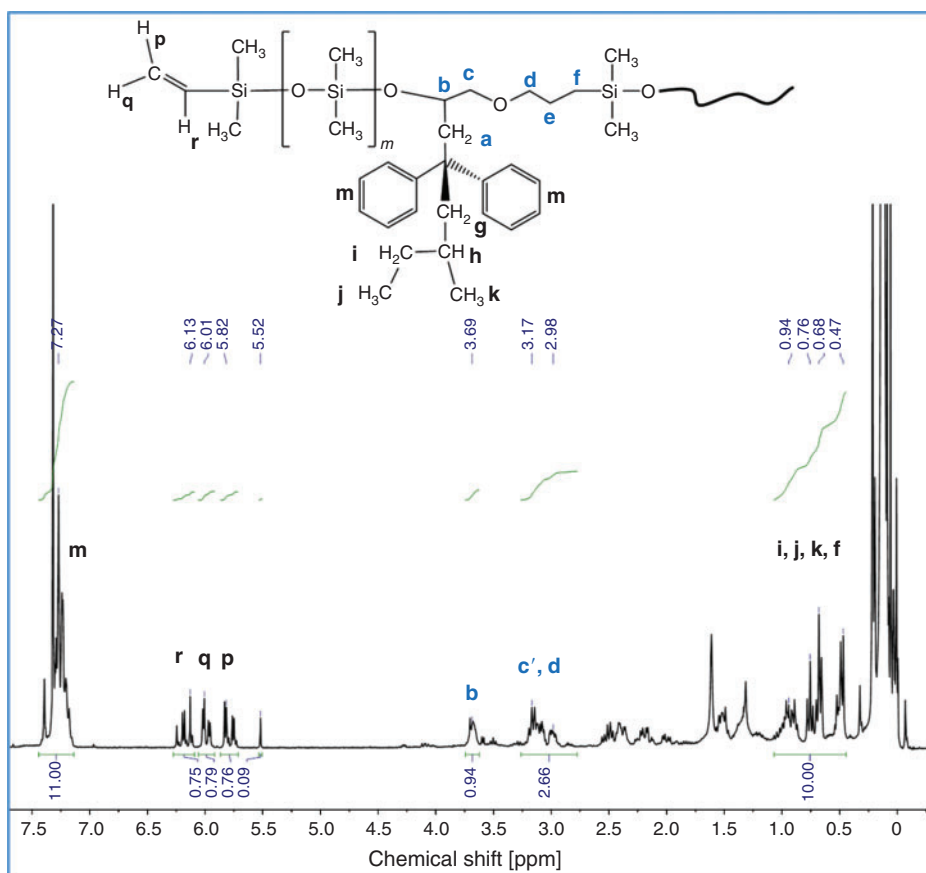


Fig. 8. B2-Vi ^1H NMR spectrum.

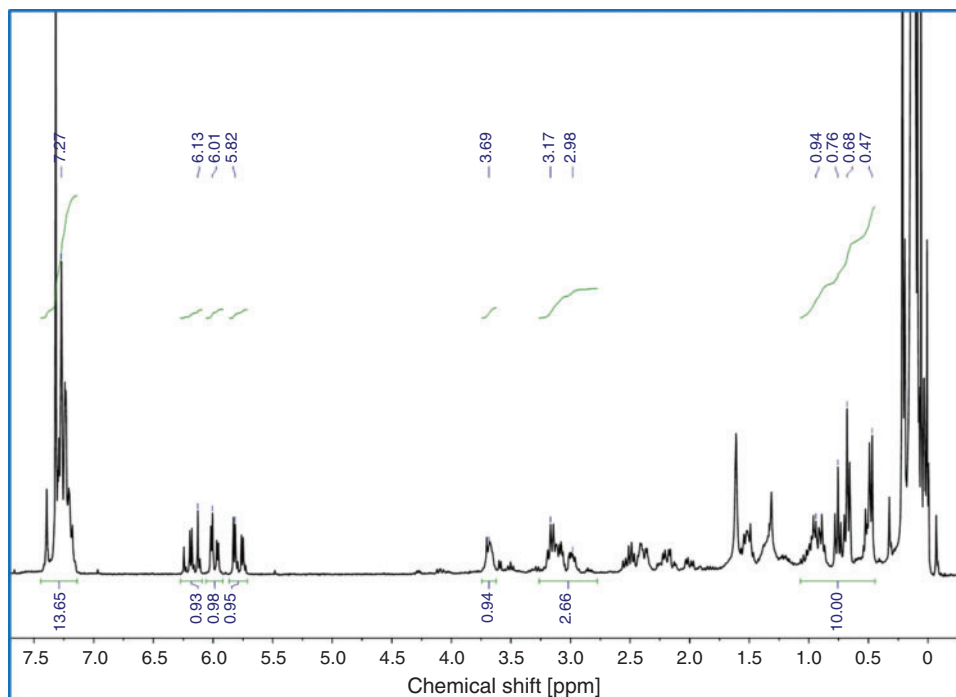


Fig. 9. B2-Vi ^1H NMR spectrum obtained after a careful siliconization process of the glass surface of the terminating agent ampoule.

k, and f signals. At this point it is worth mentioning that integration area values from phenyl rings should consider solvent (deuterated chloroform), which might also contribute to their final values.

To verify if the siliconization process was contributing to the Si–OH signal appearance, a synthesis was performed employing a fresh chloro(dimethyl)vinylsilane ampoule obtained after a careful siliconization of the fractionation apparatus (please refer to Supplementary Material, p. S7). The ^1H NMR spectrum obtained is shown in Fig. 9. The signal at 5.22 ppm disappeared and those corresponding to the targeted functional group illustrates a full functionalization of the chain-ends. In addition, molecular parameters of the resulting polymer ($M_n = 19621 \text{ g mol}^{-1}$; $M_w/M_n = 1.15$) were in accordance to those expected for a model polymer.

Conclusions

α,ω -Telechelic poly(dimethylsiloxane)s (α,ω -PDMS) were obtained by anionic polymerization employing a novel and successful bifunctional initiator prepared from a commercially available siloxane precursor, diglycidylether-terminated poly(dimethylsiloxane) (PDMS-DGE). From suitable terminating agents, silane ($-\text{SiH}$), vinyl ($-\text{CH}=\text{CH}_2$), hydroxy ($-\text{OH}$), and even methacryloyl ended PDMS were obtained. Synthesized polymers were fully characterized by using SEC, FT-IR, and ^1H and ^{13}C NMR techniques. From SEC analysis, narrow molar mass distributions ($M_w/M_n < 1.3$) and a good control over the resulting molar masses were observed. In addition, ^{13}C and ^1H NMR analyses confirmed the mechanism proposed for the reaction. Targeted functional groups in the resulting polymers were confirmed qualitatively and quantitatively by FT-IR and ^1H NMR spectroscopy. The reaction pathway discussed in this paper is proposed as a true strategy for the synthesis of α,ω -PDMS. Nevertheless, a careful siliconization of the glass

surface of fractionation ampoules should be achieved when chlorosilanes are employed as terminating agent. Partial hydrolysis of these compounds would lead to the presence of silanol moieties in the resulting polymer, decreasing the end-capping efficiency. By taking into account this fact, silanol moieties disappear according to ^1H NMR analysis. In addition, the polydispersity index of the resulting α,ω -PDMS decreases ($M_w/M_n \leq 1.15$).

Supplementary Material

Vapour pressure osmometry measurements from commercial PDMS-DGE, NMR spectra from α,ω -PDMS, and a detailed description of the siliconization procedure are available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgements

The authors acknowledge the Universidad Nacional del Sur (UNS), Ministerio de Ciencia, Tecnología e Innovación Productiva (MinCyT), and Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET) for their financial support.

References

- [1] R. P. Quirk, T. Yoo, Y. Lee, J. Kim, B. Lee, *Adv. Polym. Sci.* **2000**, *153*, 67. doi:10.1007/3-540-46414-X_3
- [2] N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211. doi:10.1002/1099-0518(20000915)38:18<3211::AID-POLA10>3.0.CO;2-L
- [3] S. Houli, H. Iatrou, N. Hadjichristidis, D. Vlassopoulos, *Macromolecules* **2002**, *35*, 6592. doi:10.1021/MA0204709
- [4] F. S. Bates, M. A. Hillmyer, T. P. Lodge, C. M. Bates, K. T. Delaney, G. H. Fredrickson, *Science* **2012**, *336*, 434. doi:10.1126/SCIENCE.1215368

- [5] H. Lentzakis, D. Vlassopoulos, D. J. Read, H. Lee, T. Chang, P. Driva, N. Hadjichristidis, *J. Rheol.* **2013**, *57*, 605. doi:10.1122/1.4789443
- [6] F. Campise, L. E. Roth, R. H. Acosta, M. A. Villar, E. M. Vallés, G. A. Monti, D. A. Vega, *Macromolecules* **2016**, *49*, 387. doi:10.1021/ACS.MACROMOL.5B01806
- [7] R. P. Quirk, S. H. Jang, H. Yang, Y. Lee, *Macromol. Symp.* **1998**, *132*, 281. doi:10.1002/MASY.19981320127
- [8] M. Szwarc, A. Rembaum, *J. Polym. Sci., Polym. Phys. Ed.* **1956**, *22*, 189.
- [9] M. Szwarc, M. Leavy, R. Milkovich, *J. Am. Chem. Soc.* **1956**, *78*, 2656. doi:10.1021/JA01592A101
- [10] M. Szwarc, *Nature* **1956**, *178*, 1168. doi:10.1038/1781168A0
- [11] T. T. Tidwell, *Angew. Chem.* **2001**, *113*, 343. doi:10.1002/1521-3757(20010119)113:2<343::AID-ANGE343>3.0.CO;2-R
- [12] G. G. Cameron, G. M. Buchan, *Polymer* **1979**, *20*, 1129. doi:10.1016/0032-3861(79)90305-7
- [13] F. Bandermann, H.-D. Speikamp, L. Weigel, *Makromol. Chem.* **1985**, *186*, 2017. doi:10.1002/MACP.1985.021861005
- [14] N. Hadjichristidis, S. Pispas, G. Floudas, *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications* **2003** (John Wiley & Sons, Inc.: Hoboken, NJ).
- [15] K. Matyjaszewski, A. H. E. Müller, *Controlled and Living Polymerizations: From Mechanisms to Applications* **2009** (Wiley-VCH: Weinheim).
- [16] L. H. Tung, G. Y.-S. Lo, D. E. Beyer, *Macromolecules* **1978**, *11*, 616. doi:10.1021/MA60063A036
- [17] R. Matmour, A. Lebreton, C. Tsitsilianis, I. Kallitsis, V. Héroguez, Y. Gnanou, *Angew. Chem. Int. Ed.* **2005**, *44*, 284. doi:10.1002/ANIE.200461056
- [18] H. Ma, L. Han, Y. Li, *Macromol. Chem. Phys.* **2017**, *218*, 1.
- [19] D. Uhrig, J. W. Mays, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6179. doi:10.1002/POLA.21016
- [20] M. Morton, L. J. Fetters, *Rubber Chem. Technol.* **1975**, *48*, 359. doi:10.5254/1.3547458
- [21] M. D. Ninago, Á. J. Satti, J. A. Ressia, A. E. Ciolino, M. A. Villar, E. M. Vallés, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4774. doi:10.1002/POLA.23530
- [22] J. Kurata, Y. Tsunashima, *Polymer Handbook* **1999** (Wiley: New York, NY).
- [23] W.-B. Zhang, B. Sun, H. Li, X. Ren, J. Janoski, S. Sahoo, D. E. Dabney, C. Wesdemiotis, R. P. Quirk, S. Z. D. Cheng, *Macromolecules* **2009**, *42*, 7258. doi:10.1021/MA901506D
- [24] E. Doris, L. Dechoux, C. Mioskowski, *Tetrahedron Lett.* **1994**, *35*, 7943. doi:10.1016/0040-4039(94)80017-0
- [25] A. G. Evans, D. B. George, *J. Am. Chem. Soc.* **1961**, 4653. doi:10.1039/JR9610004653
- [26] C. L. Frye, R. M. Salinger, F. W. G. Fearon, J. M. Klosowski, T. DeYoung, *J. Org. Chem.* **1970**, *35*, 1308. doi:10.1021/JO00830A012
- [27] T. Zundel, P. Teyssie, R. Jerome, *Macromolecules* **1998**, *31*, 2433. doi:10.1021/MA9711001
- [28] V. Bellas, H. Iatrou, N. Hadjichristidis, *Macromolecules* **2000**, *33*, 6993. doi:10.1021/MA000635I
- [29] A. E. Ciolino, M. A. Villar, E. M. Vallés, N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2726. doi:10.1002/POLA.22028
- [30] D. W. Van Krevelen, *Properties of Polymers* **1997** (Elsevier Science B.V.: Amsterdam).
- [31] B. Seed, *Curr. Protoc. Protein Sci.* **2001**, *13*, A.3E.1. doi:10.1002/0471140864.PSA03ES13
- [32] C. P. Tripp, M. L. Hair, *Langmuir* **1992**, *8*, 1961. doi:10.1021/LA00044A014
- [33] C. P. Tripp, M. L. Hair, *J. Phys. Chem.* **1993**, *97*, 5693. doi:10.1021/J100123A038
- [34] B. Reuter, C. Petersen, *TechnoPharm* **2012**, *244*, 238.
- [35] C. P. Tripp, M. L. Hair, *Langmuir* **1992**, *8*, 1120. doi:10.1021/LA00040A018
- [36] A. Y. N. Sofla, C. Martin, *J. Micromech. Microeng.* **2010**, *20*, 125024. doi:10.1088/0960-1317/20/12/125024
- [37] P. Kaali, D. Momcilovic, A. Markström, R. Aune, G. Czel, S. Karlsson, *J. Appl. Polym. Sci.* **2010**, *115*, 802. doi:10.1002/APP.31119
- [38] M. K. Chaudhury, T. Weaver, C. Y. Hui, E. J. Kramer, *J. Appl. Phys.* **1996**, *80*, 30. doi:10.1063/1.362819
- [39] G. Ducom, B. Laubie, A. Ohannessian, C. Chottier, P. Germain, V. Chatain, *Water Sci. Technol.* **2013**, *68*, 813. doi:10.2166/WST.2013.308
- [40] S. Perutz, E. J. Kramer, J. Baney, C.-Y. Hui, *Macromolecules* **1997**, *30*, 7964. doi:10.1021/MA970063A
- [41] A. Labbé, A. L. Brocas, E. Ibarboure, T. Ishizone, A. Hirao, A. Deffieux, S. Carlotti, *Macromolecules* **2011**, *44*, 6356. doi:10.1021/MA201075N
- [42] M. Benaglia, A. Alberti, L. Giorgini, F. Magnoni, S. Tozzi, *Polym. Chem.* **2013**, *4*, 124. doi:10.1039/C2PY20646C
- [43] H. Huang, J. Zhang, D. Wei, F. Hu, A. Zheng, H. Xiao, *Polym. Bull.* **2008**, *60*, 477. doi:10.1007/S00289-007-0880-8
- [44] L. Leemans, R. Fayt, Ph. Teyssie, H. Uytterhoeven, W. De Winter, *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 2187. doi:10.1002/POLA.1990.080280814
- [45] M. Rogosic, H. J. Mencer, Z. Gomzi, *Eur. Polym. J.* **1996**, *32*, 1337. doi:10.1016/S0014-3057(96)00091-2
- [46] M. D. Ninago, A. J. Satti, A. E. Ciolino, E. M. Vallés, M. A. Villar, D. A. Vega, A. Sanz, A. Nogales, D. R. Rueda, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3119. doi:10.1002/POLA.24093
- [47] A. J. Brandolini, D. D. Hills, *NMR Spectra of Polymers and Polymer Additives* **2000** (Marcel Dekker, Inc.: New York, NY).