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Full Paper

Anionic Ring Opening Polymerization of ε-Caprolactone Initiated by Lithium Silanolates

Angel J. Satti,[A,B,D] *Augusto G. O. de Freitas,*[C] *M. Loreta Sena Marani,*[B] *Marcelo A. Villar,*[B] *Enrique M. Vallés,*[B] *Cristiano Giacomelli,*[C] *and Andrés E. Ciolino*[B]

[A]Instituto de Química del Sur (INQUISUR), Departamento de Química, Universidad Nacional del Sur (UNS), Avenida Alem 1253, (8000) Bahía Blanca, Argentina.
[B]Planta Piloto de Ingeniería Química (PLAPIQUI), Departamento de Ingeniería Química, Universidad Nacional del Sur (UNS), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Camino 'La Carrindanga' Km. 7, (8000) Bahía Blanca, Argentina.
[C]Departamento de Química, Universidade Federal de Santa Maria (UFSM), 97105-900 Santa Maria-RS, Brazil.
[D]Corresponding author. Email: angel.satti@uns.edu.ar

Ring-opening homo- and co-polymerization reactions of ε-caprolactone were performed by employing anionic polymerization (high vacuum techniques) and lithium silanolates (LS) as initiators. LS were obtained by reaction between hexamethyl(cyclotrisiloxane) and *sec*-Bu^-Li^+, or from living poly(dimethylsiloxanyl)lithium chains. The results indicated that LS are efficient initiators for the ring-opening polymerization of ε-caprolactone, providing the respective homogeneous polymers in good yields.

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Introduction

Anionic polymerization, along with the newest controlled radical polymerization techniques (CRP), is one of the most powerful synthetic tools for the preparation of well defined polymers and copolymers. The former technique was developed in 1956 by Szwarc, Levy, and Milkovich,[1–4] who also coined the term 'living polymers' for the polymers obtained by this method, demonstrating the feasibility to obtain linear block copolymers. In classical anionic polymerization, high-vacuum techniques and whole-sealed glass reactors are employed to guarantee a reaction environment free of the reactive contaminants that can destroy the anionic centres.[5,6] Although it is a demanding and time-consuming technique, its potential to generate homogeneous and complex macromolecular structures is fully recognised.

The anionic polymerization of cyclic monomers is known as anionic ring-opening polymerization (AROP), and its mechanism was developed by Paul Flory in the mid-forties by testing the AROP of ethylene oxide (EO) mediated by potassium alkoxides.[7,8] After EO, many other cyclic monomers have been successfully polymerized, such as cyclic sulfides, lactones, and siloxanes, among others.[9]

Poly(ε-caprolactone) (PCL) is one of the most used biodegradable polyesters. It is an FDA-approved material for biomedical applications that has been extensively employed as a drug carrier and in tissue engineering.[10–13] Its excellent drug permeability, high crystallinity, and low degradation rate make PCL particularly suitable for long-term drug delivery systems.[10–12]

The conventional synthesis of PCL starts from the ring opening polymerization (ROP) of the cyclic monomer, ε-caprolactone (ε-CL), according to different mechanisms. The most common strategy involves the use of a suitable compound containing a hydroxy group as co-initiator, and tin alkoxides and carboxylates as catalysts.[14–16] Besides this conventional procedure, ε-CL monomer can also be polymerized by AROP using the carbanions formed by the reaction between alkyl lithium compounds and 1,1′-diphenylethylene, which yield a bulky anionic initiator.[17] More recently, PCL was also obtained by employing lithium aggregates with 2,2′-ethylidenebis(4,6-di*tert*-butyl-phenol) (EDBP-H_2) and enolate mixed ligands, with the formula $[(\mu^2\text{-}/\mu^3\text{-EDBP})_2(OCHCH_2)Li_5(THF)_4]$.[18]

Poly(dimethylsiloxane) (PDMS) is another polymer with high biocompatibility that can be synthesized by employing anionic polymerization. PDMS is hydrophobic, and is commonly used as a surface modifier, making PDMS-based copolymers excellent candidates for different biomedical applications.[19,20] The kinetically controlled AROP of PDMS is exclusively based on anionic polymerization of the hexamethyl(cyclotrisiloxane) monomer (D_3). In particular, high-vacuum anionic polymerization offers a powerful method for the controlled manipulation of the macromolecular architecture,[21] allowing the preparation of nearly monodisperse

PDMS with tailored structures. The method is based on a chain extension reaction in which a particular initiator reacts with D_3 to yield short silanolate-ended chains that are able to attack other molecules to yield the desired PDMS polymer.[22–26]

Taking into account the above mentioned facts, in this report we explored the synthesis of poly(dimethylsiloxane)-*block*-poly (ε-caprolactone) copolymers (PDMS-*b*-PCL) by AROP mediated by anionic lithium silanolates (LS). We followed a strategy similar to that reported in several papers by the group of Jérôme in 1998, regarding the anionic polymerization of methyl methacrylate (MMA).[27–29] In our work, we explore the temperature-promoted nucleophilic attack of the LS on the carbonyl carbon of the ε-CL ring, leading to the AROP of the monomer through acyl-oxygen bond cleavage.

The polymers obtained were characterized by size exclusion chromatography (SEC), NMR spectroscopy, differential scanning calorimetry (DSC), FT-IR spectroscopy, and energy dispersive X-ray spectroscopy (EDX).

Experimental

Synthesis of PDMS-b-PCL Copolymers

Materials

All materials were purified by standard anionic polymerization procedures, in whole-sealed glass apparatuses specially designed for each reagent.[5,6,30] The anionic initiator, *sec*-Bu^-Li^+, was freshly prepared in vacuum from *sec*-butyl chloride (Fluka) and lithium metal (Fluka) as previously reported.[5] Hexamethyl(cyclotrisiloxane) monomer (D_3, Aldrich) was purified according to the standard procedures for anionic polymerizations (high-vacuum techniques).[5,30,31] ε-CL monomer (Aldrich) was purified by distillation under vacuum from calcium hydride. Freshly distilled ampoules of pure monomers, or diluted in benzene solution, were collected and stored at −20°C before use. Tetrahydrofuran (THF; Ciccarelli) was used as a promoter of D_3 polymerization, whereas benzene (Ciccarelli) and degassed methanol (Química Industrial) were used as solvent and terminating agent, respectively. All the solvents employed were purified according to conventional anionic polymerization procedures, which involve a pretreatment with calcium hydride, freeze–thawing steps, and a final purification with suitable reagents, according to every chemical employed (for more specific details, please see the papers from Hadjichristidis et al.[5] and Uhrig and Mays[6]).

Synthesis

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. A scheme of the synthesis apparatus employed in all polymerizations is shown in Fig. 1. The apparatus was handmade using glass-blowing techniques and following the specifications given by the group of Roovers and Bywater.[5] The broken ampoules that contained the original reagents were subsequently used to collect samples at different stages of the reaction. Constrictions and heat-sealing procedures (by using a flame torch) were employed to obtain these samples.

Anionic Synthesis of PCL by Using LS as Initiators

D_3 (3.15 mmol, 0.7 g) was left in equilibrium, at room temperature, for one day with 0.80 mmol (51 mg) of *sec*-Bu^-Li^+, in a molar ratio equal to 4 : 1 (D_3 moles respect to organolithium base) in order to obtain the single *sec*-butylsilanolate anion. The break-seal of a sealed ampoule containing 64 mmol (7.3 g) of ε-CL liquid monomer was then broken, and its contents were poured into the reaction media to promote its polymerization at 50°C over 24 h. After this, the break seal of a methanol ampoule was broken. The reaction product was precipitated in cold methanol, re-dissolved in pure THF, re-precipitated in cold methanol, filtered, and finally dried under vacuum.

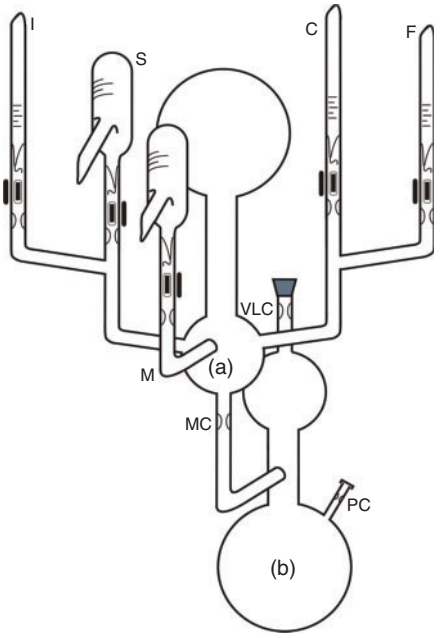


Fig. 1. Apparatus for anionic polymerization (high-vacuum techniques). (a) Reactor. (b) Purge section. I: *sec*-Bu^-Li^+ ampoule, S: THF ampoule, M: D_3 monomer ampoule, C: ε-CL monomer ampoule, F: methanol ampoule, VLC: vacuum line constriction, MC: middle constriction, PC: purge constriction.

Anionic Synthesis of PCL by Using $PDMS^-Li^+$ as Macroinitiators

Two copolymers with different molecular weights were synthesized by using poly(dimethylsiloxanoyl) lithium anions ($PDMS^-Li^+$) as macroinitiators (for quantities, M_n of the PDMS block, and yields please refer to Table 1). The experimental procedure employed is described as follows.

The break-seal of the D_3 monomer solution was first broken, and the contents were poured into the reactor flask followed by the addition of the *sec*-Bu^-Li^+ ampoule. Both ampoules were rinsed with the solution of the initiator and the monomer in order to remove any traces inside the broken ampoules. The reaction between monomer and initiator was left to proceed for 20 h at room temperature. The reactor was then placed in a water bath, and the break-seal of the THF ampoule was broken in order to promote D_3 polymerization. A sample of the resulting product was taken after 36 h to perform SEC analysis of the PDMS block. After that, the temperature was raised to 50°C. When the system reached this temperature, the break-seal of the ε-CL monomer was broken and its contents were poured into the reaction media to promote its co-polymerization. Samples of the resulting product (around 1–2 mL) were taken at different times of the polymerization, and quenched with well degassed methanol. After 24 h of reaction, the break seal of the methanol ampoule was broken. The reaction product was precipitated in

Table 1. Molecular characterization of a-PCL and PDMS-*b*-PCL copolymers

Copolymer	I_0 [mmol]	$n_{\varepsilon CL}$ [mmol]	n_{D3} [mmol][A]	$M_{n,PCL,t}$ [g mol^{-1}][B]	$M_{n,PDMS}$ [g mol^{-1}][C]	$x_{\varepsilon CL,t}$	$x^{D}_{\varepsilon CL}$	PD[C]	$M_{n,PDC}$ [g mol^{-1}][E]
a-PCL	0.80	64	–	9100	–	1.00	1.00	1.14*	11000[F]
a-BC(130)	0.06	44	17	83700	29300	0.65	0.69	1.09	129 900
a-BC(50)	0.17	45	12	30200	13100	0.60	0.63	1.10	47500
c-BC	0.138	19	–	15700	3620	0.74	0.78	1.19	24900

[A] n_{D3} values correspond to comonomer incorporation.
[B] Theoretical PCL M_n of the homopolymer or block, due to 100 % conversion.
[C] According to SEC analysis. Polydispersity index of PDMS block (except for *).
[D] ε-CL molar fraction determined by ^{1}H NMR spectroscopy.
[E] M_n of the copolymer according to $M_{n,PDMS}$ obtained by SEC and then, relation of integrated areas of each copolymer block, from ^{1}H NMR analysis.
[F] For a-PCL, the molecular weight of a-PCL is obtained by SEC since there is not a PDMS block.

cold methanol, re-dissolved in pure THF, re-precipitated in cold methanol, filtered, and finally vacuum dried.

Conventional Synthesis of PCL by Using Hydroxy-Terminated Poly(dimethylsiloxane) (PDMS-OH) and Tin(II) 2-Ethylhexanoate as Catalyst

The reaction was performed in a Schlenk glass reactor, under nitrogen atmosphere. In a typical experiment, 0.5 g of PDMS-OH ($M_n = 3620$ g mol^{-1}, synthesized by conventional anionic polymerization),[31] and 17.5 mmol (2.0 g) of ε-CL monomer were put inside the reactor, along with 6.0 mL of well degassed toluene (reaction solvent). $Sn(Oct)_2$ was used as catalyst, in a [$Sn(Oct)_2$] to[PDMS-OH] molar ratio equal to 0.5. The reaction was left to proceed at 120°C for 24 h. The resulting copolymer was precipitated in cold methanol, re-dissolved in pure THF, re-precipitated in cold methanol, filtered, and finally vacuum dried.

Nomenclature

The obtained polymers were labelled as a-PCL, a-BC, and c-BC in which a-PCL stands for the anionic PCL homopolymer, a-BC stands for the anionic PDMS-*b*-PCL copolymer, and c-BC stands for the PDMS-*b*-PCL copolymer obtained by conventional ROP by using $Sn(Oct)_2$ as catalyst.

Characterization

Size Exclusion Chromatography (SEC)

The samples were characterized by 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 µm bead size (Phenomenex). The solvent employed was toluene with a flow rate of 1 mL min^{-1}. The injection volume was 200 µL, and polystyrene (PS) standards were used for calibration. The Mark–Houwink calibration constants used for each polymer were $K_{PS} = 0.012$ mL g^{-1} and $\alpha_{PS} = 0.71$ for PS, and $K_{PDMS} = 0.0136$ mL g^{-1} and $\alpha_{PDMS} = 0.69$ for PDMS.[32] PCL samples were characterized in $CHCl_3$ at 1 mL min^{-1}, also using a PS calibration method, with the following constants: $K_{PS} = 0.0049$ mL g^{-1} and $\alpha_{PS} = 0.794$ for PS, and $K_{PCL} = 0.01298$ mL g^{-1} and $\alpha_{PCL} = 0.828$ for PCL.[32] The data was processed via *Empower* software.

^{1}H and ^{13}C NMR Spectroscopy

The NMR spectra of the copolymers were recorded on a Bruker 300 MHz instrument using deuterated chloroform (Aldrich) as solvent. The compositions of PDMS-*b*-PCL copolymers were determined from the integrated areas of characteristic ^{1}H signals of each monomer.

FT-IR Spectroscopy

The FT-IR spectra of the resulting polymers were recorded on a Nicolet FTIR 520 spectrometer. Cast films from the copolymer solutions were prepared (1 wt-% in chloroform). The FT-IR spectra were recorded at 4 cm^{-1} resolution over the 4000–600 cm^{-1} range using an accumulation of 20 scans and air as the background.

EDX Analysis

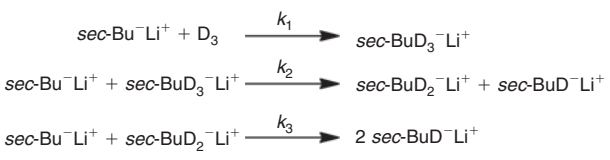
A JEOL 35 CF scanning electron microscope equipped with an EDX microanalyzer (EDAX DX-4) was used in order to observe the local distribution of chemical elements in the samples.

Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained using a DSC 8500 annexed to a 2P intracooler (Perkin Elmer). Samples were run under nitrogen atmosphere from −70 to 70°C with a heating rate of 10°C min^{-1}. Transition temperatures were taken from the second heating run. The degree of crystallinity was obtained by dividing the enthalpy of fusion by the reference enthalpy of a totally crystalline PCL ($\Delta H^0_f = 142$ J g^{-1}).[33]

Results and Discussion

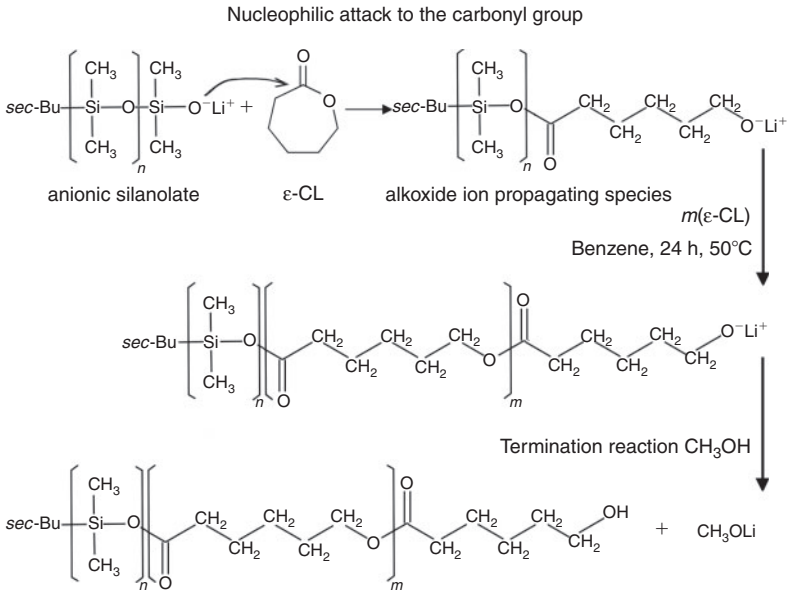
As it is reported in the literature, when D_3 monomer and a suitable organic lithium compound (e.g. *sec*-Bu$^-$Li$^+$) are left to react in a non-polar solvent, the set of alkylation reactions of Scheme 1 takes place:[34]



Scheme 1. Alkylation reactions between D_3 and *sec*-Bu$^-$Li$^+$.

where k_1, k_2, and k_3 are the corresponding rate constants, with $k_1 << k_2, k_3$.

We used an excess of D_3 in order to assure the formation of the *sec*-BuD$^-$Li$^+$ species. By this strategy, the presence of an excess of free *sec*-Bu$^-$Li$^+$ is prevented. Otherwise, the excess of *sec*-Bu$^-$Li$^+$ would lead to the presence of mixed associated



Scheme 2. Nucleophilic attack on the carbonyl group and subsequent propagation reaction of ε-CL from alkoxide species. Polymerization is initiated by silanolate ($n = 0$) or macrosilanolate ($n > 0$) species.

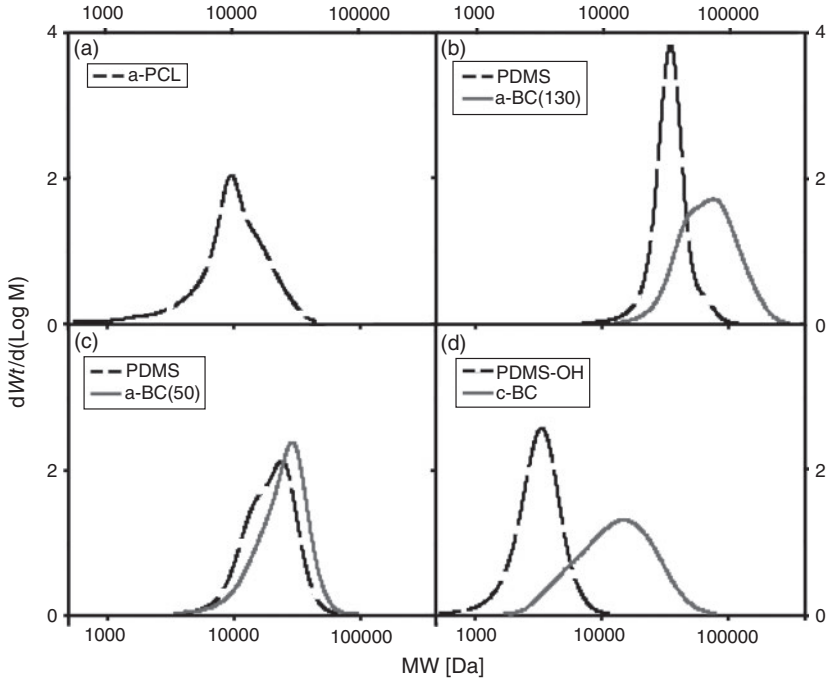


Fig. 2. SEC chromatograms for (a) a-PCL, (b) PDMS block and subsequent a-BC(130), (c) PDMS block and subsequent a-BC(50), and (d) PDMS-OH and subsequent c-BC. In all SEC traces, the dashed line refers to homopolymers, and the continuous to the block copolymers.

species as *sec*-Bu$^-$Li$^+$, (y – 1) *sec*-BuD$^-$Li$^+$.[27–29] Once the *sec*-BuD$^-$Li$^+$ species were formed, the ε-CL monomer was added to the reaction medium in order to promote its homopolymerization.

A nucleophilic attack of *sec*-BuD$^-$Li$^+$ to the carbonyl group of the ε-CL monomer is proposed in order to explain the polymerization. According to Albertson and Varma,[35] the AROP of lactones occurs in two ways, depending on which carbon of the lactone ring the base attacks: the carbonyl carbon or the alkyl-oxygen carbon. However, they indicate that in the case of larger lactones (as in the case of ε-CL), the reaction proceeds by the nucleophilic attack of the base to the carbon of the carbonyl group of the monomer ring. This pathway is favoured by the particular spatial position of the carbonyl group in the ε-CL ring (planar, C–O π-bond), which would allow the nucleophilic attack of bulky bases as in the case of *sec*-BuD$^-$Li$^+$ on either side of the planar C–O bond. This would lead to the formation of an alkoxide ion as propagating species.

Under the conditions studied in this work, we assumed that the attack on the alkyl-oxygen carbon is not stereospecifically

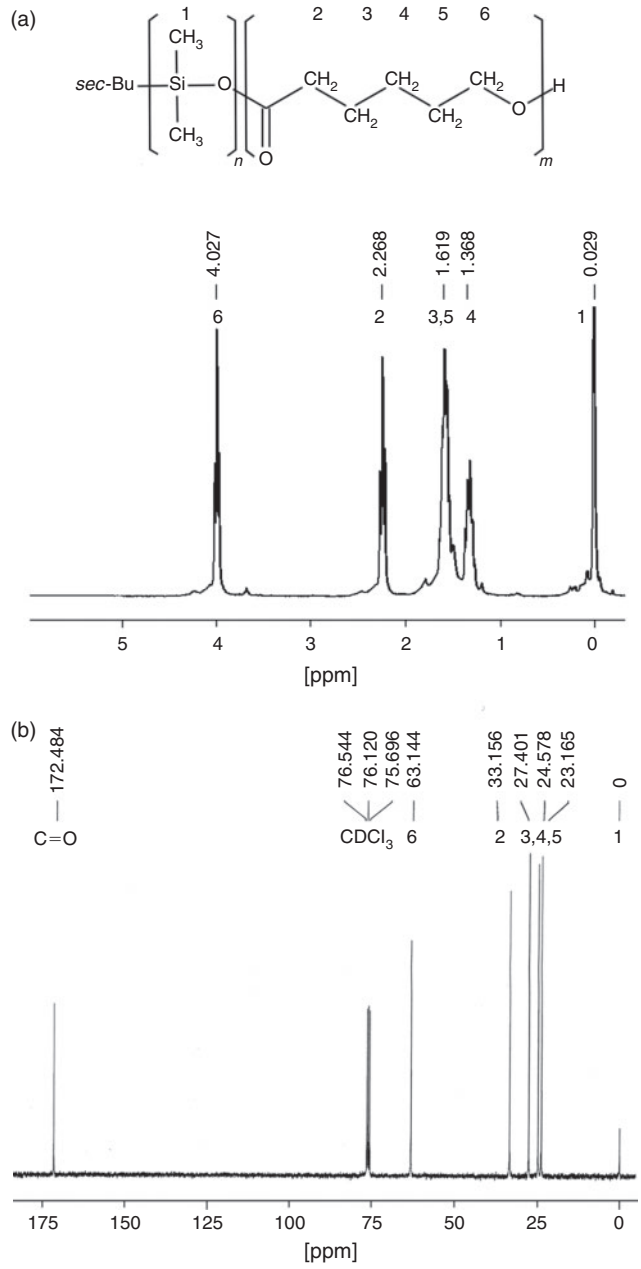


Fig. 3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra for the a-BC(130) copolymer.

favoured (especially in the case in which the LS is a macrosilanolate) because of the C–O σ-bond (free rotation) that would prevent the attack. Taking into account these assumptions, we proposed the reaction mechanism shown in Scheme 2 to obtain the PCL homopolymer by using *sec*-BuD^{-}Li^{+} as initiator.

The results obtained for the homopolymerization of ε-CL by using LS as initiators are shown in Table 1. The silanolate group successfully initiated the polymerization of ε-CL, and a near monodisperse PCL was obtained (PDI = 1.14). By taking into account this last result, we also attempted to open the ε-CL ring through a silanolate macroinitiator, as it was described in the experimental section and is shown in Scheme 2. In this test, the macroinitiator was PDMS^{-}Li^{+}, and therefore the final expected product was a PDMS-*b*-PCL copolymer. A sequential addition of monomers was employed in this case. In the first step, the PDMS^{-}Li^{+} macroinitiator was synthesized under the

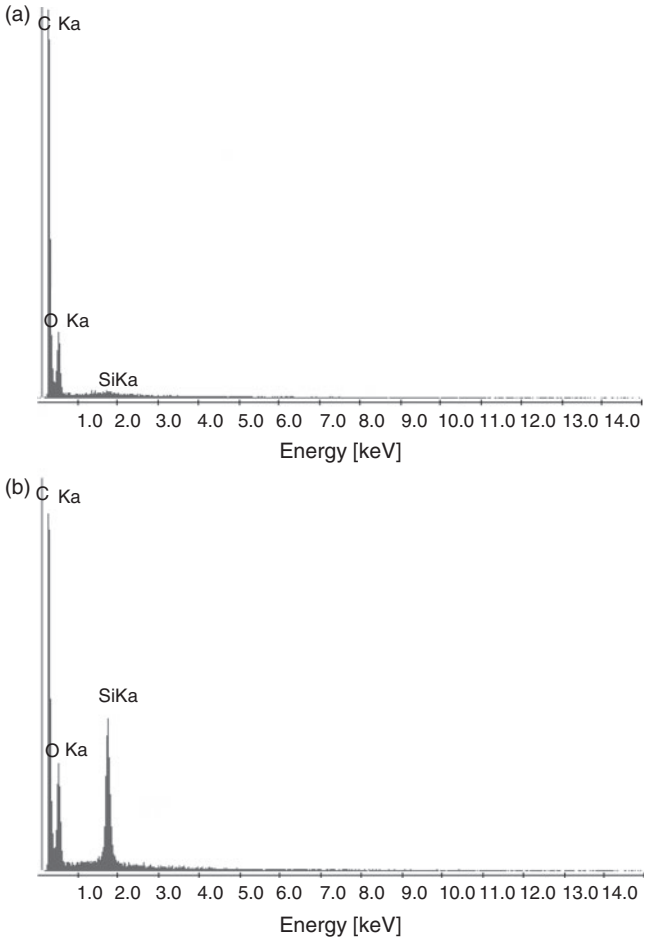


Fig. 4. EDX spectra for (a) a-PCL, and (b) a-BC(130).

experimental conditions already reported for the controlled synthesis of PDMS homopolymers.[31] Once PDMS^{-}Li^{+} was formed, the ε-CL monomer was added to the reaction medium to promote its co-polymerization, during 24 h.

Fig. 2 displays the SEC chromatograms of the obtained polymers. Samples of the PDMS^{-}Li^{+} macroinitiators were taken from the reactor before its copolymerization with ε-CL monomer. As it was expected, the PDMS precursor eluted first since it has a lower molar mass compared with the resulting block copolymer. For calculating the resulting molar masses of the block copolymers synthesized, ^{1}H NMR spectroscopy was used by taking into account the M_n values obtained for the PDMS block according to SEC (please refer to Table 1).

As an example, the ^{1}H and ^{13}C NMR spectra of a-BC(130) are shown in Fig. 3. The ^{13}C NMR spectrum shows both the signals related to the alkyl groups (CH_3, CH_2), and the signal corresponding to the carbonyl group of the PCL block, near 172 ppm. By following the same experimental procedure employed to synthesize a-BC(130), another block copolymer (with lower molar mass) was obtained (see Table 1). It is important to note that all syntheses were performed at 50°C, since we did not observe the AROP of the ε-CL monomer at lower temperatures. At the moment we do not have a proper explanation for this observation. It is possible that the reaction requires thermal activation as for the conventional synthesis using a stannous catalyst, and investigations are ongoing to elucidate this.

The EDX spectra of a-PCL homopolymer and a-BC copolymer are presented in Fig. 4. The homopolymer exhibited

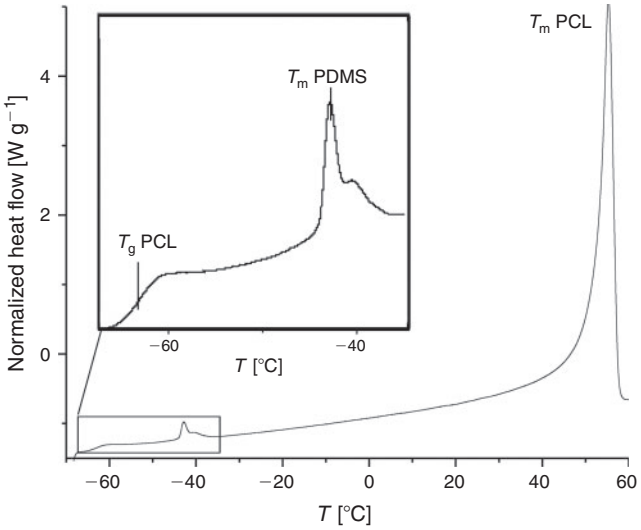


Fig. 5. DSC thermogram for a-BC(130).

characteristic peaks associated with C and O, both elements related to PCL. The presence of a weak peak corresponding to Si atoms from the silanolate chain-end is also evident. On the other hand, as it was expected, the copolymer sample shows a more significant Si signal, corresponding to the PDMS block.

Fig. 5 shows the DSC thermogram for the a-BC(130) copolymer (second heating). The glass transition temperature (T_g) of the PCL block is clearly defined at −63.3°C, which is in accordance with the results reported in the literature for a PCL homopolymer.[11] This result confirms that a-BC copolymer is truly a *block* instead of a *random* copolymer, in which a single T_g should be located between the corresponding T_g values for PDMS and PCL homopolymers.[36] The T_g for PDMS was not measured because the procedure employed was not able to decrease the temperature values near to −120°C. In a similar way, the melting peaks observed at −42.8 and +55.3°C are close to the values that correspond to the PDMS and PCL homopolymers' melting temperatures,[11] respectively. Although the major part of this block copolymer consists of a 0.69 molar fraction of semicrystalline PCL, the crystallinity of the copolymer is lower (33.7%) than that corresponding to a-PCL (54.7%). This result can be explained by the presence of the amorphous PDMS domains, which forms the other 0.31 molar fraction and decreases the crystallinity of the corresponding block copolymer.

As it is well known, the ROP of ε-CL is usually mediated by tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) catalyst in the presence of active hydrogen compounds such as alcohols.[37,38] Hydroxy-functionalized macromolecules can also be conveniently used as macroinitiators for the ROP of ε-CL, yielding block copolymers as product.[39,40] Taking this into account, we explored the plausible synthesis of PDMS-*b*-PCL through the ROP of ε-CL by means of a direct reaction with a ω-hydroxy-terminated anionic PDMS (PDMS-OH) in the presence of $Sn(Oct)_2$ as catalyst. The PDMS-OH chains were quantitatively chain extended with PCL, resulting in well defined PDMS-*b*-PCL diblock copolymers (c-BC sample), as is summarized in Table 1 and shown in the SEC chromatograms of Fig. 2d.

While the method to obtain c-BC is an alternative, cost-effective, and convenient method to produce PDMS-*b*-PCL, the high temperature together with long reaction times required in this synthesis can result in an increase in polydispersity due to

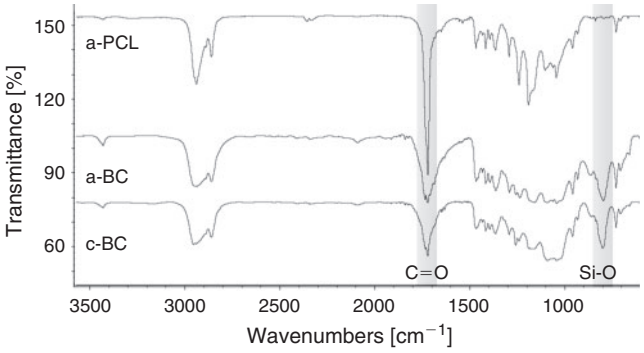


Fig. 6. FTIR spectra for all the synthesized polymers.

inter- and intramolecular transesterification reactions.[35] This drawback might be minimized by the AROP method employed in this work, since the reaction temperature is lower. In addition, the latter methodology is certainly more suitable for high molar mass polymers, as well as for the production of model diblock copolymer systems. On the other hand, comparing the yields of the polymerizations, both methods showed a near 100% conversion of ε-CL. These results can be compared with another interesting approach for the synthesis of PDMS-*b*-PCL from a hydroxy (aliphatic)-terminated PDMS block and further functionalized with $EtAl_3$, as it was reported by Viville et al. ($M_n = 8000$ g mol^{-1}).[20] However, it should be pointed out that in that work ε-CL propagation was followed at 0°C.

Fig. 6 shows the FT-IR spectra for all the synthesized materials. The characteristic stretching vibration mode of the carbonyl groups from the PCL block is observed at 1730 cm^{-1}, and the typical Si–C stretching vibration from the PDMS block is detected at 800 cm^{-1}.[16]

Conclusions

In this work, a new approach for the synthesis of ε-CL homopolymers and copolymers through AROP by employing lithium silanolates and high vacuum techniques is reported. The *sec*-BuD^-Li^+ species formed from the reaction between D_3 and *sec*-butyllithium provided nucleophiles that are able to attack the carbonyl group of the ε-CL monomer prompting the acyl-oxygen bond scission and the formation of the alkoxide propagating species.

This strategy proved to be successful for the AROP of ε-CL, yielding polymers with low polydispersity indexes and good yields. In the case of the PCL homopolymer, the *sec*-butylsilanolate chain-end was identified in the EDX spectrum. The broad scope of the herein reported approach was further confirmed for the synthesis of PDMS-*b*-PCL copolymers by using poly(dimethylsiloxanyl) lithium as macroinitiator. This strategy promoted the extension of the anionic PDMS chains to provide the corresponding PCL block. In this case, the EDX spectrum of the copolymer had indeed shown a more significant Si related band, assigned to the presence of the PDMS block.

The synthetic strategy reported in this paper provides a new initiator for the living AROP of ε-CL and for the synthesis of PDMS-*b*-PCL copolymers with controlled molar masses and homogeneity. These copolymers have many interesting properties, since they combine a biodegradable polyester and a biocompatible silicon-based polymer. This preliminary approach prompted us to explore in more detail the kinetic mechanism of this reaction, and further investigations regarding

this subject are on the way. It is also important to mention that the copolymers synthesized in this work are able to nanoprecipitate and can be used as additives against wear rate. These preliminary approaches have been reported by our group in recent symposiums related to polymer chemistry.[41,42]

Acknowledgements

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