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Well-Defined Synthesis of Poly(dimethylsiloxane) Homopolymers

Mario D. Ninago, Angel J. Satti, Jorge A. Ressia,
Andrés E. Ciolino, Enrique M. Vallés, Marcelo A. Villar

Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET)
Camino "La Carrindanga" Km. 7, (8000) Bahía Blanca, Argentina.
mvillar@plapiqui.edu.ar

In this work we present results on the controlled anionic ring-opening polymerization (AROP) of hexamethyl(cyclotrisiloxane) monomer (D_3) using *sec*–butyl lithium as initiator (*sec*-Bu^-Li^+), and classical anionic polymerization techniques in whole vacuum-sealed glass reactors. We explored different temperatures and reaction times in order to understand the influence of secondary reactions in order to obtain model poly(dimethylsiloxane) homopolymers (PDMS) with molar masses ranging from 10^3-10^5 g/mol, and polydispersity indexes less than 1.1.

Introduction

Poly(dimethylsiloxane) (PDMS) is a silicon-based homopolymer that can be regarded as derivative of inorganic silicates by partial substitution with methyl groups. This fact offers a wide spectrum of properties that cannot be covered by common organic polymers, which result from the combination of the polar Si–O backbone with the contribution of the organic groups. Among these properties, we can mention a low glass transition temperature, high gas permeability, usability over a wide range of temperatures, low chemical reactivity, and essentially a non-toxic nature (Lötters et al., 1997). Thus, PDMS is used in several applications such as rubbers, resins, dielectric multimedia, hydraulic or heat transfer fluids, lubricants, medical materials and surfactants among other.

The synthesis of PDMS usually starts with dichlorosilanes by hydrolysis and condensation, giving cyclic and linear polymers (Anderson, 1974). This method of synthesis results in a poor molecular weight control giving polymers that cannot be used as model material for special purposes. Therefore, in order to have a better control of the molecular parameters, the above mentioned method of synthesis was gradually replaced by ring opening polymerization (ROP) of cyclic siloxanes. Kinetically controlled polymerization of PDMS is based on anionic polymerization of hexamethyl(cyclotrisiloxane) (D_3). This method of synthesis allows the preparation of nearly monodisperse PDMS with tailored structures, and is based on a chain extension reaction in which a particular catalyst reacts with D_3 to yield short silanolate-ended

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chains that are able to attack other D_3 molecules to yield the desired polymer (Fessler and Juliano, 1972; Oulad-Hammouch et al, 1995).
Since the ring opening polymerization of D_3 is affected by several parameters (solvent, temperature, reaction time), in this work we present results that allows preparing model PDMS polymers with a precise control of molecular weight and narrow molecular weight distributions in the range of 10^3 – 10^5 g/mol.

Experimental

All materials were purified by standard anionic polymerization procedures. The initiator employed *sec*–butyl lithium (*sec*–Bu^-Li^+) was prepared *in vacuo* from *sec*–butyl chloride (Fluka) and lithium metal (Fluka) (Uhrig and Mays, 2005). The hexamethylcyclotrisiloxane monomer (D_3, Sigma-Aldrich) was purified according to conventional routines described elsewhere (Hadjichristidis et al, 2000). A mother solution of the monomer in pure distilled cyclohexane was collected, and its concentration was determined by ^{1}H-NMR. From this solution, exact volumes were collected in pre-calibrated ampoules in order to obtain precise D_3 quantities to perform the polymerization experiences. Tetrahydrofuran (THF) was used as promoter of D_3 polymerization whereas cyclohexane and degassed methanol were used as the solvent and terminating agent, respectively.

Synthesis of model PDMS homopolymer: All manipulations were performed under a high-vacuum glass line in glass reactors equipped with break–seals for the addition of the reagents and constrictions for removal of products (Uhrig and Mays, 2005; Morton and Fetters, 1975). A scheme of the polymerization apparatus used for the synthesis is shown in Figure 1. A description of the synthetic pathway employed is briefly described as follows.
The apparatus was connected to the vacuum line, checked for pinholes, flame-dried and pumped for 20-30 min in order to remove the volatile species. Then, 5 mL of concentrated *n*-Bu^-Li^+ 2 M solution in hexane (Aldrich) were injected through the lateral constriction into the purge section flask. The whole apparatus was pumped for additional 30 min in order to remove the hexane and air inserted during the injection, and an appropriate amount of pure cyclohexane (40-50 mL) was then distilled and degassed over 45 minutes. The apparatus was removed from the vacuum line by heat-sealing the constriction (VLC), and was washed with the diluted *n*-Bu^-Li^+ solution inside by gentle manual agitation. After washing, the purge section was removed by heat-sealing the middle constriction (MC) leaving the clean reactor with an appropriate amount of pure distilled solvent.
The break-seal of the D_3 monomer solution was first broken and the content was poured into the reactor flask, followed by addition of the *sec*–Bu^-Li^+ ampoule. Both ampoules were rinsed with the solution in order to remove any traces of initiator or monomer. The reaction between monomer and initiator was left to proceed for ~ 20 h at room temperature. Then, the reactor was placed in a water bath, which was set at the reaction temperature, and the THF ampoule was broken to promote D_3 polymerization. Samples of the resulting product were taken at different stages of the polymerization, and quenched with methanol. The final reaction product was precipitated in cold methanol;

re-dissolved in pure THF; and finally purified extracting the solvent by using a rotatory evaporator.

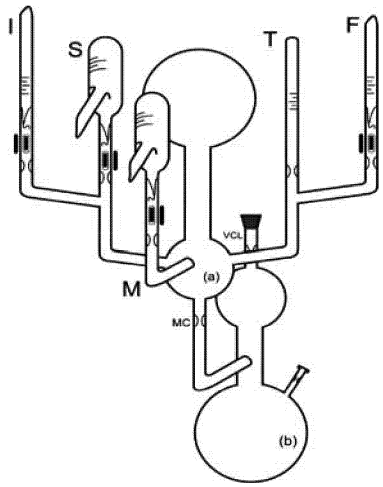

Figure 1. *Polymerization apparatus for the synthesis of model PDMS homopolymers. References:* ***I****: sec–Bu*$^{-}$*Li*$^{+}$ *ampoule,* ***S****: THF ampoule,* ***M****: D_3 monomer ampoule,* ***T****: sampling ampoule,* ***F****: methanol ampoule.* ***(a)****: reactor,* ***(b)****: purge section.* ***VLC****: vacuum line constriction,* ***MC****: middle constriction.*

Chemical Characterization

Size Exclusion Chromatography (SEC). SEC experiments were performed on a system built with a Waters 515 HPLC pump and a Waters model 410 refractive index detector, equipped with 4 columns with a porosity range within 10^2-10^6 Å. Toluene was used as solvent, at room temperature with a flow rate of 1 mL/min. Polystyrene standards were used for calibration. *Nuclear Magnetic Resonance (^{1}H–NMR).* ^{1}H-NMR spectra of the solution of D_3 in cyclohexane and PDMS homopolymers were recorded on a Bruker 300 MHz instrument using deuterated chloroform as solvent.

Results and Discussion

Despite the molar masses desired, the general experimental procedure used for synthesizing the model PDMS homopolymers could be rationalized as a two-step methodology. In the first step, the equilibration reaction between D_3 monomer and *sec*-Bu^{-}Li^{+} was left to proceed during ~ 20 h at room temperature. Under these circumstances, the reaction of *sec*-Bu^{-}Li^{+} with D_3 monomer in hydrocarbon media proceeds yielding the following species: *sec*-BuD^{-}Li^{+}, *sec*-BuD$_2^{-}$Li^{+}, and *sec*-BuD$_3^{-}$Li^{+} in which D refers to $(CH_3)_2SiO^{-}$ adduct (Fessler and Juliano, 1972; Zundel et al., 1998). Once we ensured that *sec*-BuD^{-}Li^{+} initiating specie was obtained, the polymerization apparatus was immersed in a water bath at the chosen reaction temperature. The THF ampoule was broken in order to promote the polymerization of the D_3 monomer present in the reaction media. Samples of living PDMS were taken at different times for monitoring the polymerization reaction.

Table 1. Molecular characterization of model PDMS homopolymers

	20 °C		30 °C		40 °C		50 °C	
t (h)	**X (%)**	**PD***	**X (%)**	**PD***	**X (%)**	**PD***	**X (%)**	**PD***
4	17	1.09	28.5	1.07	36	1.05	42	1.08
8	28	1.07	48	1.06	55	1.09	64	1.06
24	59.5	1.05	90.5	1.08	85	1.09	80	1.13
32	-	-	100	1.10	-	-	98	1.15
72	-	-	-	-	-	-	100	1.13
96	100	1.12	-	-	-	-	-	-

*PD determined by SEC at room temperature using toluene as solvent

Synthesis of model PDMS homopolymers with $M_n < 10^5$ g/mol. Monomer conversion (X%) as a function of time is presented in Table 1. As can be expected, conversion increases as temperature increases. Higher conversions at the first stages of the polymerization are reached at the highest temperature studied (50 °C). After a reaction time of ~ 24 h, almost all experiences above ambient temperature reached a similar conversion value.

Table 1 also displays the polydispersity index (PD) data obtained for the model PDMS synthesized at different temperatures and reaction times. It can be seen that independently of the experimental conditions employed, for longer reaction times (above 80 % of conversion) the values of the PD are higher than 1.1 at any temperature. This fact could be explained taking into account monomer concentration in the media and a temperature-kinetic effect.

The probability of occurrence of secondary reactions increases when monomer concentration in the reaction media decreases. For lower monomer concentration in the media, the living PDMS chains could suffer backbiting, reshuffling or redistribution reactions instead of the desired propagation reaction. On the other hand, it is well established that the kinetics of chemical reactions increases as well as temperature increases.

Taking into account the observations described above, we hypothesize that in order to synthesize narrow PDMS samples with PD strictly lower than 1.1 and molar masses less than 100,000 g/mol, an increase in the reaction temperature would favor conversion shortening reaction times. It can be deduced that following this strategy a wide range of molar masses, 10^3-10^5 g/mol, can be obtained with good yields (~ 90 %) by simply tuning temperature and reaction time without making additional manipulations. Figure 2 displays SEC chromatograms of selected PDMS samples with PD strictly less than 1.1 obtained at different temperatures during D_3 polymerization.

Synthesis of model PDMS homopolymers with $M_n > 10^5$ g/mol. Figure 3 displays the SEC chromatograms obtained for the synthesis of a model PDMS homopolymer with a molar mass > 10^5 g/mol. The reaction temperature for this experience was 50 °C. The first two chromatograms correspond to the samples obtained at 4 h, the third one at 8 h, and the last one corresponds to the final product obtained at ~ 30 h and 100 % conversion. It can be easily noticed that a long reaction time provides a poor control of the polymerization process, and a SEC chromatogram with shoulders at low

and high molar masses ranges is obtained. This result is identical to those obtained in a previous work (Ressia et al, 2001), and agrees well with the observation reported by Zillioux et al. (1972) for the synthesis of PS-*b*-PDMS copolymers. On the contrary, when the reaction was finished at 4 or 8 h of propagation, narrow SEC chromatograms were obtained. Nevertheless, conversion decreases up to 65 %. Finally, the SEC chromatogram of the sample obtained by the two-step procedure described by Bellas et al. (2000) shows no appreciable differences with the sample obtained without cooling. Although this result does not agree with the mentioned paper, it would prove that the additional cooling step is not necessary for this case since M_n value did not improve significatively. The above-discussed results seem to prove that high molar masses model PDMS homopolymers could be obtained by using temperatures higher than ambient, and high-vacuum anionic polymerization techniques. Although the conversion reached would be far from 100 %, this experimental tip would provide model PDMS homopolymers with $M_n > 10^5$ g/mol and PD strictly less than 1.1.

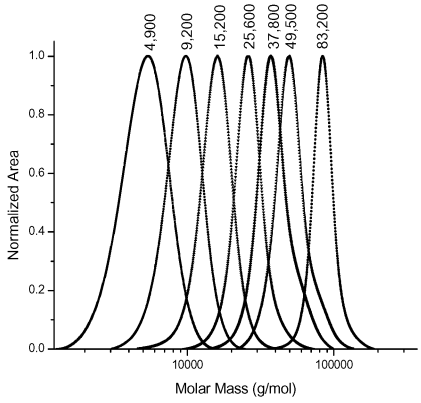

Figure 2. *Model PDMS with PD < 1.1 and Mn < 10^5g/mol. References: T = 20 °C, M = 9,200, M = 15,200, and M = 83,200 g/mol; T = 30 °C, M =4,900, M = 25,600, and M = 49,500 g/mol; T = 40 °C, M = 37,800 g/mol.*

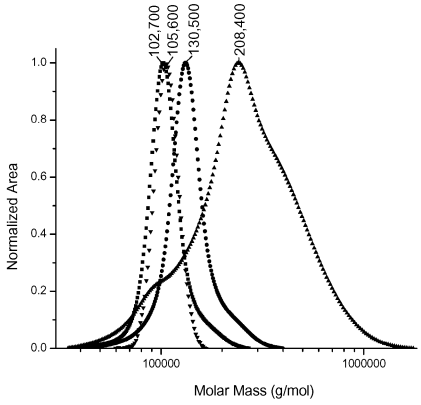

Figure 3. *Model PDMS synthesized at T = 50 °C, Mn > 10^5g/mol. References: (■) t = 4 h, M = 102,700 g/mol (PD = 1.05), (▼) t = 4 h plus 5 days at T = –20 °C, M = 105,600 g/mol (PD = 1.02), (+) t = 8 h, M = 130,500 g/mol (PD = 1.08), (▲) t = 28 h, M = 208,400 g/mol (PD = 1.4).*

Conclusions

The controlled synthesis of PDMS homopolymers using *sec*-Bu^-Li^+ as initiator, and high-vacuum anionic polymerization techniques was studied using different experimental conditions. It was observed that polydispersity indexes and conversion strongly depend on temperature and reaction times. For model PDMS with molar masses below 100,000 g/mol, high conversion (> 90 %) and PD < 1.1 can be achieved at long reaction times (24 hours) and mild conditions. On the other hand, to obtain model PDMS with molar masses higher than 100,000 g/mol and PD < 1.1 it is necessary

to increase the temperature (50 °C) and decrease the reaction time (8 hours). However, under these circumstances, conversion decreases (up to 65-70 % conversion is achieved). Apparently, the competition between propagation and secondary reactions (redistribution, backbiting, and reshuffling) depends on the molar masses desired. According to the results obtained in this study, when temperature increases the propagation reaction is favored when the expected molar masses are low (M_n < 100,000 g/mol), whereas secondary reactions seem to be important for higher molar masses (M_n > 100,000 g/mol) at long reaction times. Nevertheless, model PDMS homopolymers with high molar masses can be obtained increasing the temperature and shortening reaction times. The combined effect of these two facts would favor propagation against secondary reactions providing model PDMS homopolymers with molar masses close to the expected ones.

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