

Lithium naphthalenides in non-polar or in low-polarity media: some insights regarding their use as initiators in anionic polymerizations

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Abstract The synthesis of bidirectional anionic initiators by the reaction between metallic lithium (Li) and naphthalene (Naph), under mild conditions, in non-polar (benzene) or low-polarity media (benzene/THF mixtures) is reported. The efficiency of these initiators to provide macromolecules with well-defined structures was demonstrated. Model linear homopolymers from styrene (S) or hexamethyl(cyclotrisiloxane) (D₃) monomers were synthesized using classical anionic polymerization (high-vacuum techniques). The model polymers obtained were analyzed using the conventional analytical techniques, and showed narrow molar mass distributions, a broad range of molar masses (from 3000 to 1,000,000 g/mol) and polydispersity indexes (M_w/M_n) lower than 1.1. High molar mass polymers were obtained using pure benzene as solvent, whereas lower molar masses were obtained in benzene/THF mixtures in which the concentration of THF was lower than 10 % v/v. The ratio [Li]/[Naph] and the nature of the reaction medium are the experimental parameters to be controlled to obtain the desired lithium naphthalenides.

Introduction

Since its discovery in the mid 1950s, anionic polymerization has captivated the attention of synthetic and theoretical chemists for two main reasons: (i) its unique efficiency for providing complex macromolecular structures and (ii) its particular

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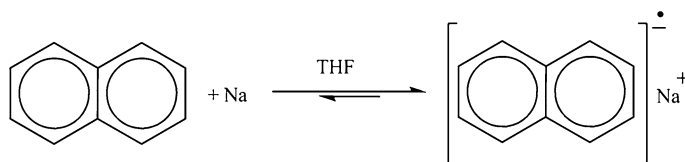
kinetic mechanism that produces polymer molecules of nearly the same size [1–4]. These two characteristics make anionic polymerization one of the most powerful methods for obtaining tailor-made polymer architectures [5, 6], as it can be deduced from the seminal papers published by Szwarc, Levy, and Milkovich [7–9]; to those by Morton and Fetters [10–12], Roovers and Bywater [13–15], Quirk and Hsieh [16, 17], Hadjichristidis et al. [18], and Uhrig and Mays [19], just to mention some.

Alkali metals/aromatic hydrocarbon complexes have been extensively used as initiators for anionic polymerization. This reaction was first described by Schlenk et al [20]. The reaction can be represented as an electron transfer from the metal to the aromatic compound in an equilibrium process, greatly favoring the complex formation (Scheme 1).

The reaction has been extensively used for the synthesis of block copolymers or cyclic homopolymers with well-defined structure [7, 8, 10–15, 21–23], and also as a source of oligomeric dianion initiators [24, 25]. This particular type of initiators can be efficiently formed in polar aprotic solvents, such as THF and glymes, which enhance both the rate of initiator formation and its solubility [26].

Recent works in the field of organometallic chemistry have demonstrated the feasibility of synthesizing lithium/naphthalene complexes with good yields and reactivity [27, 28]. Lithium metal is easy to handle, especially if it is used as metal chunks, and it is well known that organic lithium compounds offer a higher solubility in organic solvents compared to other metals in the periodic table. Moreover, it is well-documented that the synthesis of the corresponding dianion or radical anion can be controlled from the experimental conditions employed [28]. However, the report of experimental details regarding the synthesis of these complexes in non-polar or low-polarity media is not common, and the study of their performance as anionic polymerization initiators is even scarcer.

Taking into account the facts discussed above, this paper reports the synthesis of lithium/naphthalene complexes using mild reaction conditions and different reaction media. Their effectiveness as initiators for anionic polymerization is demonstrated. The effects of the reaction medium and the [Li]/[Naph] ratio are discussed. Furthermore, the efficiency of these bidirectional initiators to provide model poly(styrene) (PS) or poly(dimethylsiloxane) (PDMS) is demonstrated.



Scheme 1 Synthesis of sodium naphthalenide in THF

Experiment

Reagents

Most materials were purified by the standard anionic polymerization techniques, employing glass Pyrex[®] reactors. More details regarding these protocols may be found elsewhere [18, 19]. Purification procedures (which involve, briefly, freezing/thawing cycles and degassing in the vacuum line in all cases; and stirring over calcium hydride, vacuum distillation, and reaction with specific reagents depending on the particular solvent) were performed on benzene (Cicarelli), tetrahydrofuran (THF) (Cicarelli), and methanol (Química Industrial). The monomers employed: styrene (S) (Sigma-Aldrich) and hexamethyl-cyclotrisiloxane (D₃) (Sigma-Aldrich) were also purified by the standard anionic polymerization procedures. On the other hand, the polar aprotic solvents diethylether (Cicarelli) and anisole (Cicarelli) were employed without prior purification and after three freezing/thawing and vacuum degassing cycles. Finally, naphthalene (Naph) (Sigma-Aldrich, +99 %) and metallic lithium (Li, in granules, Fluka) were employed as received.

Glassware

A conventional vacuum line with a mechanical oil pump, a mercury diffusion pump, liquid nitrogen traps, upper and lower glass tube rigs, and stopcocks was employed in all the syntheses. Reactors and ampoules were prepared using glass-blowing techniques, employing Pyrex[®] glass and flasks.

Experimental procedure for the synthesis of lithium naphthalenide initiator in a non-polar aprotic solvent (benzene)

All manipulations were performed under high vacuum in glass reactors equipped with break seals for the addition of reagents and constrictions for the removal of products. An excess of Li metal over Naph was used in all the experiments. A scheme of the glass apparatus specially designed for the synthesis of these initiators is shown in Fig. 1.

The apparatus was attached to the vacuum line, checked for pinholes and flame-dried. After pumping during approximately 5 min (with the purpose of eliminating the air inside and humidity traces), a small quantity (3–5 mL) of $n\text{-Bu}^-\text{Li}^+$ solution 1.6 M in hexane (Sigma-Aldrich) was introduced through the septum (PC) with a syringe. After the removal of the hexane from the injected $n\text{-Bu}^-\text{Li}^+$ solution, constriction (PC) was heat sealed. Purified benzene (typically 20–30 mL) was distilled through the vacuum line into flask (b), and the reactor was sealed at constriction (VLC). The whole apparatus was washed with the dilute $n\text{-Bu}^-\text{Li}^+$ solution formed inside, to react with the impurities on the glass or over the surface of the Li metal, and was rinsed thoroughly by condensing benzene on the walls. Finally, benzene was distilled from flask (b) to flask (a), and the purge section was heat sealed at (MC). Afterwards, the break seal (N) was ruptured, and the ampoule

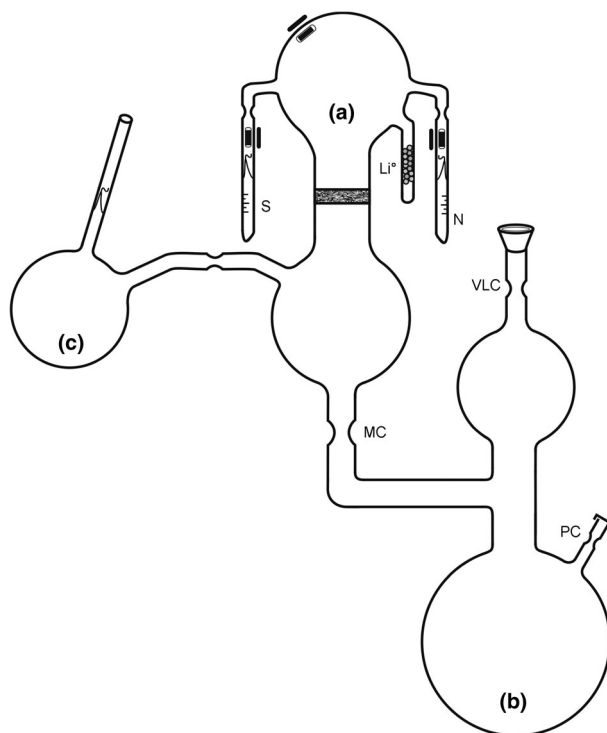


Fig. 1 Reactor for the synthesis of lithium naphthalenides. Li[°]: metallic lithium, N: solid naphthalene, S: THF ampoule, M: (a) reactor, (b) purge section, and (c) collection flask. VLC vacuum line constriction, MC middle constriction, PC septum constriction. In the reactor (a), the fritted glass filter appears between both flasks

was rinsed with the solvent to dissolve the solid Naph inside. Flask (a) was immersed overnight in an ice-water bath under continuous and vigorous stirring. The reaction mixture was then forced to pass through the glass filter to remove the unreacted Li metal, and the lithium naphthalenide solution in benzene was collected into the ampoule (c) for subsequent use (fractionation into pre-calibrated, glass vacuum-sealed ampoules).

Experimental procedure for the synthesis of model polymers using lithium naphthalenide initiators

Synthesized lithium naphthalenide initiators were tested regarding their efficiency for producing PS and PDMS by anionic polymerization of S and D₃ monomers, respectively. All manipulations were performed under high vacuum in glass reactors equipped with break seals for the addition of the reagents and constrictions for the removal of products. Details of the synthetic procedures can be found elsewhere [18, 19]. In most of the experiences performed, about 3–4 g of S or D₃ monomers were employed.

Polymerization reactions between S monomer and lithium naphthalenides were left to proceed during 24 h at room temperature. In the case of D₃ monomer, the first step involved the reaction of the monomer and the initiator for about 20 h at room temperature. Then, in a second step, THF was added to promote the D₃ polymerization during 24 h.

In all the cases, the final reaction product was precipitated in cold methanol, re-dissolved in pure THF, and finally purified by extracting the solvent using a rotary evaporator.

Size exclusion chromatography (SEC)

The obtained polymer 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 at 25 °C flowing at a rate of 1 mL/min. The injection volume was 200 μL, and PS standards were used for calibration. The Mark–Houwink calibration constants used for each polymer were $K_{PS} = 0.012$, $\alpha_{PS} = 0.71$ for PS, and $K_{PDMS} = 0.020$, $\alpha_{PDMS} = 0.66$ for PDMS [29].

Lithium naphthalenide concentration

The concentration of lithium naphthalenide solutions obtained was calculated by a simple procedure already reported in the literature [18]. By taking into account the quantity of monomer employed in the polymerization reaction and the number-average molar mass obtained by SEC, the concentration of the initiator solution can be obtained, assuming 100 % monomer conversion, by the following expression:

$$C_s = \frac{v_m \times \delta_m}{\bar{M}_n} \times \frac{1000 \frac{\text{mL}}{\text{L}}}{v_s} \quad (1)$$

where C_s is the calculated concentration of the initiator solution (M); v_m (mL) and δ_m (g/mL) correspond to the volume and density of the monomer employed (S), respectively; \bar{M}_n is the number-average molar mass obtained by SEC (g/mol); and v_s is the volume of initiator solution employed (mL). Although the obtained values should be compared to those obtained by titration, this method provides quite good results, as it is reported in the previous works [18, 19].

Results and discussion

Effect of [Li]/[Naph] ratio in pure benzene

The solubility of lithium alkyls in hydrocarbon solvents is well-documented [30, 31]. Unlike sodium or potassium organometallics (salt-like compounds), lithium organometallics present a “bridging” aspect, due to the presence of

electron-deficient (multicentre bonded) covalent bonds [32]. Consequently, organic lithium compounds are more covalent (less ionic) than those of sodium and potassium and, therefore, much more soluble in organic solvents.

We explored the feasibility of the synthesis of lithium naphthalenide using benzene, a non-polar hydrocarbon solvent. According to Melero et al. [27, 28] when lithium naphthalenide salts are synthesized in THF by adding *N,N,N',N'*-tetramethylethylenediamine (TMEDA), the amount of lithium metal relative to naphthalene determines which species (lithium naphthalene radical anion, $[\text{Li}^+(\text{TMEDA})_2|\text{C}_{10}\text{H}_8^-]$; or lithium naphthalene dianion $[(\text{Li}^+\text{TMEDA})_2|\text{C}_{10}\text{H}_8^{2-}]$) is present in the reaction media. To evaluate if the relative amount of lithium affects the synthesis of lithium naphthalenide in benzene, different $[\text{Li}]:[\text{Naph}]$ molar ratios were studied. The synthesis of the corresponding lithium naphthalenides was performed during 24 h, under continuous and vigorous stirring. Once the synthesis was completed, the crude product was filtered from the reactor to the sampling ampoules by employing the fritted glass funnel (see Fig. 1). Then, the synthesized initiator was divided into sealed-glass ampoules. In all the cases, a pale yellow solution was obtained. Qualitatively, it was observed that more concentrated initiator solutions showed a more intense color.

For each $[\text{Li}]:[\text{Naph}]$ ratio studied, pure S monomer homopolymerization experiments were performed. In a typical synthesis, about 3.5 g of S monomer and 4 mL of initiator solution in benzene were employed. The synthesized PS was analyzed by SEC to test for polymerization control (evidenced by narrow molar mass distributions) and for the efficiency of the initiators (evidenced by the average molecular weight of the sample). Figure 2 and Table 1 show the obtained experimental results. By analyzing the data reported, three facts can be clearly appreciated: (i) all the PSs synthesized showed narrow molar mass distributions, without the appearance of secondary high or low molar mass peaks; (ii) regardless

Fig. 2 Chromatograms of PS obtained from different lithium naphthalenides in benzene for different $[\text{Li}]:[\text{Naph}]$ ratios. *a* [4:1], *b* [40:1], and *c* [400:1] (see Table 1)

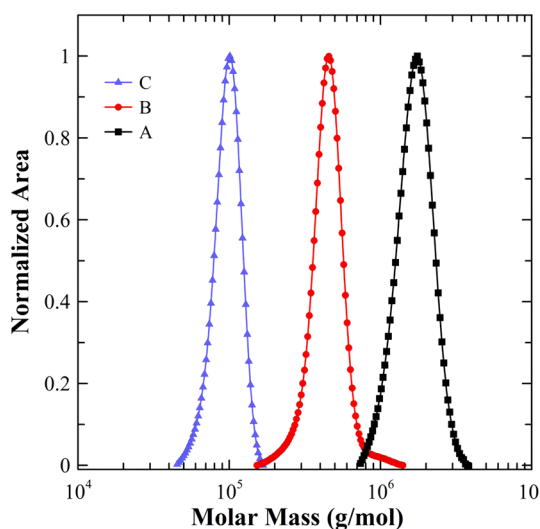


Table 1 Synthesis of model PS using lithium/naphthalene complexes as initiators

Sample	Naph (mmol)	[Li]:[Naph]	Styrene monomer (mL)	Polymer yield ^a (%)	M_n^b (g/mol)	$\frac{M_w^b}{M_n}$	C_s^c (mol/mL)
A	0.5	4:1	3.5	95.0	1,500,000	1.11	7.09×10^{-7}
B	0.8	40:1	3.7	98.5	450,000	1.05	2.55×10^{-6}
C	1.2	400:1	3.3	99.0	95,000	1.04	1.14×10^{-5}

^a Calculated by gravimetric analysis

^b Data obtained from SEC analysis

^c Calculated from Eq. 1

of the [Li]:[Naph] ratio employed, all initiators were able to polymerize S monomer; and (iii) a range of molar masses between 10^4 to 10^6 g/mol was obtained.

The absence of shoulders of high or low molar masses in the SEC chromatograms may indicate that the initiators obtained presented a defined reactivity. With two or more species with a different reactivity, one would have expected a multimodal molar mass distribution. As may be observed, the chromatograms obtained are well defined, showing a monomodal distribution. In addition, their polydispersity indexes (M_w/M_n) are equal or less than 1.1, indicating that the initiators were successful in producing model homopolymers.

It is important to note that active lithium naphthalenide initiators were obtained for each [Li]:[Naph] ratio studied. It seems that each [Li]:[Naph] ratio produces the same reactive species, although an exhaustive analysis of the chemical nature of the resulting initiator should be performed to confirm this hypothesis.

Another fact that should be mentioned is that the final concentration of the resulting initiator increases as the [Li] increases. If one compares the relative concentrations shown in Table 1, it can be appreciated that the highest concentration was obtained when [Li]:[Naph] was 400:1. It seems that when more metallic lithium is present in the reaction media, the production of the corresponding lithium naphthalenide is higher, by a simple mass effect. Taking into account the heterogeneous nature of the reaction, the yields are similar to those obtained for the synthesis of lithium alkyls by the reaction between the corresponding alkyl chlorides and metallic lithium [30]. Nevertheless, more tests are required to confirm this assumption. One possibility would be performing simple halogen/lithium exchange reactions from polyhalogenated aromatic compounds [31] under the same experimental conditions.

Summarizing, model PS with molar masses between 10^4 and 10^6 g/mol was synthesized using lithium naphthalenides in pure benzene as reaction solvent. By carefully controlling the initial quantity of Li metal and solid Naph added to the reaction media, the final concentration of the lithium naphthalenide obtained might be conveniently tuned for using as bidirectional anionic initiator. However, it must be noticed that only high molar mass polymers are obtained, independently of the [Li]:[Naph] ratio employed (from 4:1 to 400:1). If lower molar masses are desired, another strategy has to be employed.

Effect of polar, aprotic additives in the reaction media

As it is reported in the literature, the synthesis of alkaline metal/aromatic hydrocarbon complexes is enhanced by the presence of polar, aprotic additives in the reaction medium [24]. Among the most employed ones, we can mention THF [33], dimethylether [34], anisole [10], TMEDA, and hexamethylphosphoramide (HMPA) [35, 36]. According to the published data, polar agents influence the rate of formation of the complexes, as well as their solubility and stability by changing their aggregate forms into more soluble species. Taking these facts into account, we explored the influence of the presence of three ethers of different chemical natures in the synthesis of lithium naphthalenide complexes in benzene: diethyl ether (DEE, an aliphatic ether), anisole (an aromatic-aliphatic ether), and THF (an alicyclic ether).

In a typical experiment, lithium naphthalenide complexes were synthesized in benzene by employing a ratio $[\text{Li}]:[\text{Naph}] = 4$. To replicate the experimental conditions, similar amounts of Li metal and Naph were employed in each experiment. After the rupture of the Li and Naph ampoules, 5 mL of the studied ether was added to the reaction media to obtain a concentration of approximately 10 % v/v. The synthesized lithium naphthalenides were tested regarding their efficiency as initiators of S polymerization. The results are shown in Fig. 3 and Table 2 below.

According to the data reported in Table 2, model PSs ($M_w/M_n < 1.1$) were obtained in all the experiments. Since in anionic polymerization, the final number-average molar mass M_n depends on the mass of the monomer and the concentration of the initiator, SEC chromatograms with higher molar mass peaks indicate low initiator concentration, and vice versa. These facts can be clearly appreciated in the SEC chromatograms, as shown in Fig. 3. The lower molar mass distribution was obtained when THF was added, whereas polymers with higher molar masses are

Fig. 3 SEC chromatograms of the PS obtained in benzene (g), and PS obtained in benzene/ether mixtures: benzene/THF (d), benzene/DEE (e), and benzene/anisole (f) (see Table 2)

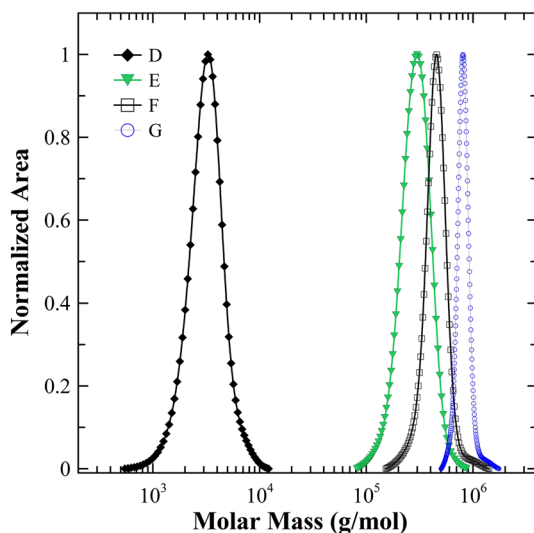


Table 2 Synthesis of model PS using lithium/naphthalene complexes as initiators and different aprotic polar agents in the reaction medium

Sample ^a	Polar aprotic additive	Styrene monomer (mL)	Polymer yield (%) ^b	M_n (g/mol) ^c	$\frac{M_w}{M_n}$ ^c	C_s^d (mol/mL)
D	THF	3.5	99.9	3000	1.08	3.65×10^{-4}
E	DEE	3.7	99.0	400,000	1.02	2.09×10^{-6}
F	Anisole	3.4	98.5	360,000	1.04	2.46×10^{-6}
G	–	3.5	99.0	840,000	1.04	1.04×10^{-6}

^a [Li]:[Naph] = 4:1 in all cases

^b Calculated by gravimetry

^c Calculated from SEC analysis

^d Calculated from Eq. 1

obtained in the case of the other ethers. Furthermore, the highest molar mass corresponds to the PS obtained using the initiator without adding any aprotic polar solvent in the reaction media (pure benzene as solvent). A tentative explanation for these results is discussed below.

As it was pointed out above, the presence of polar, aprotic reagents increases the initiator concentration. According to the data obtained, DEE and anisole produce a similar active concentration of the initiator, whereas higher concentration results when THF is employed. There are several possible explanations for this behavior. The dielectric constant of THF ($\epsilon = 7.58$) is higher than those of anisole and DEE ($\epsilon \cong 4.33$) [37]. Since a higher dielectric constant value means a more polar solvent, then the more polar THF provides a better solubility of the complexes that leads to a higher concentration and, as a consequence, to a lower molar mass polymer. This behavior may be observed in Table 2. These results may also be explained by considering steric factors in the coordinating solvent [38], as well as the formation of contact-ion pairs that is more likely in solvents of low polarity and coordinating ability [39].

In situations where all alkaline metal cations form contact-ion pairs, lithium binds more strongly to the anions. However, in other, not uncommon cases, Li^+ compounds are solvent-separated ion pairs, while their Na^+ , K^+ , or Cs^+ counterparts form contact-ion pairs [40]. For example, the sodium salt of the naphthalene radical ion in THF is a contact-ion pair, whereas the corresponding lithium compound exists almost completely as a solvent-separated ion pair [41]. This can be rationalized by taking into account the solubility characteristics of the organic lithium compounds and the Lewis-base nature of the polar solvents, because they become an integral part of the organolithium aggregate [42]. From the analysis of the results obtained, it is possible to conclude that THF presents a better coordination ability towards Li^+ than DEE or anisole, even when it is used at low v/v concentrations.

The bulky aryl substituent in anisole and the short alkyl ethyl chain in DEE are not able to conveniently coordinate with the Li^+ ion. Consequently, it is reasonable to assume that in these situations, part of the lithium naphthalenides remains in the

aggregate form, and hence, its reactivity is diminished. However, the final molar masses obtained using anisol or DEE in the reaction media are half the value obtained in the non-polar medium. This fact might denote a higher solubility of the lithium naphthalenides in the presence of these ethers in the reaction medium, although the final relative concentration obtained is lower than in the case of THF.

When THF is the coordinating agent, the coordination ability (even at low concentrations) is enhanced, since it is a better electron-donor solvent than the others [43]. This enhanced coordination may favor the generation of solvent-separated ion pairs, and consequently, the solubility of the lithium naphthalenide is increased. This higher reactivity may be assumed to lead to a higher concentration of the initiator in the reaction medium, which yields polymers with lower molar masses. As reported in the literature, ion pairing is an important, though not well defined, part of the reactions of radical anions. This is particularly the case in reactions forming dianions and in polymerization [44].

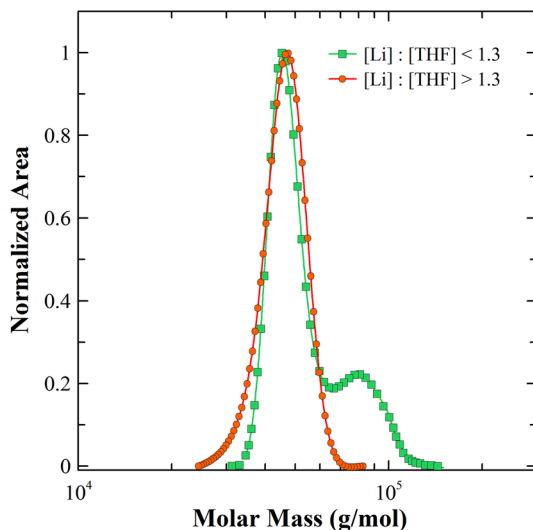
Effect of THF concentration in the reaction media

Since the addition of THF in the reaction medium improves the yield of lithium naphthalenides, we performed several experiments in which the synthesis of the initiator was carried out with different concentrations of THF in the reaction medium. As before, lithium naphthalenide initiators obtained were used to polymerize S monomer, and the molecular characteristics of the polymers were used to infer the activity and concentration of the initiator. In all the experiments, the concentration of THF was carefully controlled, and a ratio [Li]:[Naph] = 4 was employed.

By analyzing the SEC chromatograms obtained in these experiments, it can be concluded that the concentration of THF in the reaction media affects noticeably the behavior of the resulting initiator. When THF is exclusively the solvent employed for the synthesis, the resulting initiator produced a bimodal PS. On the other hand, when a mixture of benzene/THF is employed, the modality of the population of the resulting polymers depends on the concentration of THF in the mixture. An example is shown in Fig. 4. Several facts reported in the scientific literature should be kept in mind to explain these results, and they will be discussed as follows.

If THF was present in the reaction medium, a characteristic change in color was observed when the reaction between Li metal and solid Naph took place. At the beginning of the reaction, a green solution was observed, and then, as stirring continued, the green color slowly changed to a deep purple. According to the data reported in the literature [44], the green solution corresponds to the formation of the mononegative ion of naphthalene (radical anion), whereas the deep purple solution indicates the presence of the naphthalene dianion. This color change was observed in all the experiments performed, regardless of the concentration of THF used. Consequently, it is possible to conclude that a significant quantity of the naphthalene dianion was present in all the syntheses performed. The question to answer is how much of this species is present in the reaction medium, since one should not discard the presence of the radical anion in equilibrium with the dianion [38]. This is not a

Fig. 4 SEC chromatograms of the PS ($M_n = 52,000$ g/mol) obtained from different benzene/THF v/v mixtures. Symbols (filled circle) monomodal, and (filled square) bimodal, with a shoulder peak around 90,100 g/mol



minor concern, since both species could account for a significant portion of the chemical activity.

Considering the previous work reported in the literature [45–47], the chemical nature of the solvent is important in the equilibria between radical anions and their corresponding species. Solvents that form strong associations with the cations favor the formation of free radical anions (which do not disproportionate), whereas less polar solvents do not bind strongly with the cation, so the dianion formation is more favorable [38]. Besides these equilibria, it must be considered that these species exist in solution in at least two forms: as ion pairs and as free ions. However, other associations, such as contact-ion pairs and solvent-separated pairs, triple ions, dimeric ion pairs, etc., may also be encountered. Each of these species has its own characteristics, and usually differs from the others in reactivity [48].

From the analysis of SEC chromatograms shown in Fig. 4, and taking into account the reported data already discussed, it seems logical to assume that the presence of THF in the reaction media strongly affects the solubility and the dissociative equilibria between lithium naphthalenide species. Moreover, we found that the initial [Li]:[THF] ratio is crucial: for [Li]:[THF] > 1.3, the synthesized lithium naphthalenide yielded model PS (more lithium, less THF content, $M_w/M_n < 1.1$) with monomodal molar mass distributions found by SEC, whereas for lower values (less lithium, higher THF content), bimodal molar mass distributions were obtained (Fig. 4).

At this point, it is worth mentioning that the ratio [Li]:[THF] > 1.3 is a partial result obtained from this preliminary work, and should not be considered as a definitive limit until an exhaustive research is performed. Although we do not have a clear explanation for these results, it is evident that the [Li]:[THF] ratio affects the performance of the resulting lithium naphthalenide complexes. Coordination factors and concentration effects over the above-mentioned equilibria might be presented as

tentative explanations for this fact. This is not surprising, because the literature reports dramatic changes in the equilibrium constants of species by changing the amount of THF in the media [49]. Nevertheless, more experiments should be performed to corroborate the activity of these initiators. This is not a minor undertaking. As reported in the scientific literature, many groups have worked on it during several years [45–55].

Polymerization of D₃ monomer

The efficiency of lithium naphthalenide complexes for performing the homopolymerization of D₃ monomer was also checked. According to the literature, both S and D₃ monomers may be homopolymerized using alkaline metals/aromatic hydrocarbon complexes [56, 57]. In the experiments performed in this work, the lithium naphthalenide synthesized with a small amount of THF in the reaction medium was employed as initiator. The results are shown in Table 3.

As it can be seen, even though the polydispersity indexes in this case are a little bit higher than 1.1, they are still acceptable for considering the polymers as homogeneous samples. We can mention two facts as a tentative explanation for these “apparently” higher polydispersity indexes: (i) the presence of THF in the initiator solution (that might accelerate the propagation reaction) and (ii) the reaction temperature (20 °C). As it is reported in the literature [58], PDMS polymerization is performed in two steps. In the first one, the lithium alkyl employed as initiator reacts with the D₃ monomer in a ring opening reaction. However, this first step is always conducted in a non-polar medium, to ensure the opening of the ring without polymerization of the remaining monomer. In the second step, THF is added as promoter of the polymerization. On the other hand, although an increase in the reaction temperature might favor polymerization rate [59], it should be kept in mind that an increase in this parameter might affect the stability of lithium complexes [38].

Finally, we would like to mention some preliminary results that might offer the possibility for obtaining telechelic polymers from the lithium/naphthalene complexes obtained in this work. Just to explore the possibility of obtaining a methacryloyl-terminated PDMS, a living PDMS was terminated using glycidyl methacrylate as terminating agent [60]. We expected the ring opening of the oxirane ring to introduce the methacrylic groups at both ends of the polymer chain, as it is shown in Scheme 2.

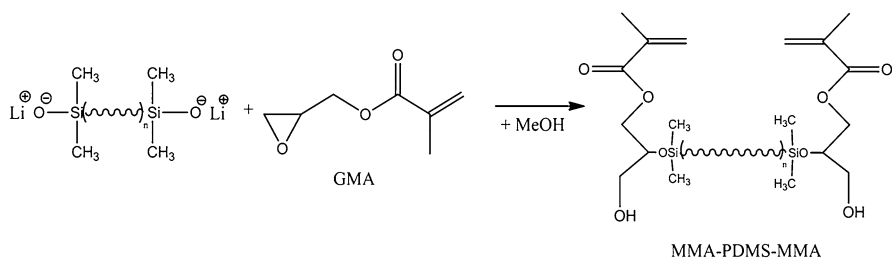
Table 3 Synthesis of *model* poly(dimethylsiloxane)s using lithium/naphthalenide complexes as initiators

Sample	Aprotic additive ^a	Polymer yield (%) ^b	M_n (g/mol) ^c	$\frac{M_w}{M_n}$ ^c
PDMS 1	THF	70	6000	1.26
PDMS 2B	THF	75	23,300	1.19

^a Benzene: THF 90:10 v/v

^b Calculated by gravimetry

^c Calculated from SEC analysis



Scheme 2 Synthesis of α,ω -methacryloyl-terminated PDMS using lithium/naphthalene complex as initiator and glycidylmethacrylate (GMA) as terminating agent

Although this reaction is far from being considered as 100 % efficient (despite its weakness, the poly(dimethylsiloxanyl)lithium base is able to open the oxirane ring by preserving the integrity of the double bond), a liquid methacryloyl-terminated PDMS was isolated. This macromonomer was subsequently co-polymerized with methyl methacrylate under the conventional radical polymerization reactions (toluene as solvent, 80 °C, benzoyl peroxide as radical initiator). A new solid material was obtained, and after its purification (using selective solvents for each block), the resulting sample was compared with the methacryloyl-terminated PDMS. The FTIR spectra of both samples are shown in Fig. 5.

As it can be observed, a broad absorption band between 3000 and 3500 cm^{-1} appears in the α,ω -methacryloyl-terminated PDMS (assigned to O–H bond stretching), whereas a strong narrow band around 1750–1700 cm^{-1} (assigned to the stretching of the C=O bond) appears in the copolymer spectrum [61]. In addition, a $^1\text{H-NMR}$ spectrum of this material was also recorded. The characteristic peaks of the functional groups of the copolymer are also observed on this spectrum, as shown in Fig. 6. The signals observed in the spectrum will be discussed as follows. Around 2.5 ppm, a multiple signal of low intensity due to a CH group left after the double bond opening of the methacryloyl-terminated PDMS can be

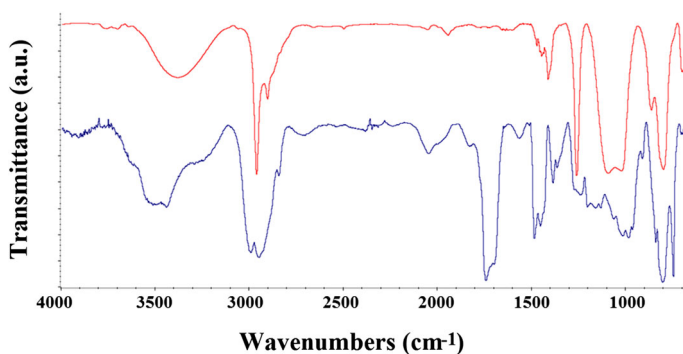


Fig. 5 FTIR spectra of α,ω -methacryloyl-terminated PDMS (upper, red) and the block copolymer obtained after copolymerization (conventional radical polymerization) with methyl methacrylate (lower, blue) (color figure online)

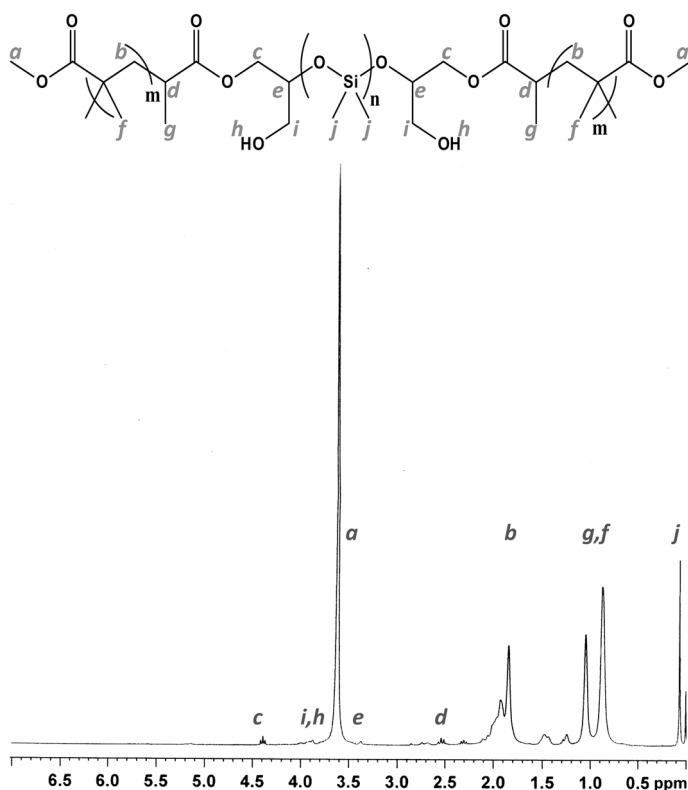


Fig. 6 ^1H -NMR spectrum of PMMA-*b*-PDMS-*b*-PMMA copolymer obtained

observed. In addition, the peaks from CH_2 , CH , and OH after the oxyane ring opening are located between 3.6 and 4.0 ppm. The absence of signals around 6.5 ppm related to double bonds confirms the copolymerization with the MMA monomer. Although a more detailed analysis is evidently called for these exploratory tests can be thought of as a partial evidence of the functionalization of the PDMS precursor and might suggest that the lithium/naphthalene complex employed as initiator has the potential to be used for synthesizing triblock copolymers by chemical functionalization or sequential addition of monomers. Further research in this direction is on the way.

Conclusion

The synthesis of lithium/naphthalene complexes to produce effective anionic polymerization initiators using mild reaction conditions and different reaction media was studied. When pure benzene was employed as solvent, synthesized poly(styrene)s (PS) showed narrow molar mass distributions, without the appearance of high or low molar mass peaks. Regardless of the $[\text{Li}]:[\text{Naph}]$ ratio

employed, all initiators can polymerize styrene monomer, and a range of molar masses between 10^4 and 10^6 g/mol was obtained.

When adding polar aprotic solvents, such as DEE and anisol, lower molecular weights were obtained if compared to pure benzene under the same [Li]:[Naph] ratio, probably due to a better dissociation of the lithium naphthalenide. Nevertheless, when THF was added in the same reaction medium, monomodal or bimodal SEC chromatograms were obtained for the synthesized PS, depending on the amount of THF added. Apparently, the presence of THF affects the solubility and the dissociative equilibria between the lithium naphthalenide species more strongly than the other ethers, leading to lower molecular weight values. We found that the initial [Li]:[THF] ratio seems to be crucial, and for [Li]:[THF] >1.3, the synthesized lithium naphthalenides yielded a model PS (PD <1.1) with a monomodal molar mass distribution, whereas for higher values, bimodal SEC chromatograms were observed.

The efficiency of lithium naphthalenides for performing the homopolymerization of hexamethyl-cyclotrisiloxane monomer (D_3) was also studied. In this case, two types of polymers were synthesized. One was poly(dimethylsiloxane) (PDMS). The other one was an α,ω -methacryloyl-terminated PDMS that was synthesized by reacting a living PDMS with glycidyl methacrylate (GMA). The corresponding macromonomer was subsequently co-polymerized with methyl methacrylate under the conventional radical polymerization reactions, and a new solid material was obtained. This last result can be thought of as a good evidence of the functionalization of the PDMS precursor, and might suggest that lithium/naphthalene complexes employed as initiators have the potential to be used for synthesizing model triblock copolymers. Further experiments to confirm this possibility are under way.

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