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Acetylene-Functionalized Lithium Initiators for Anionic Polymerization. Powerful Precursors for “Click” Chemistry

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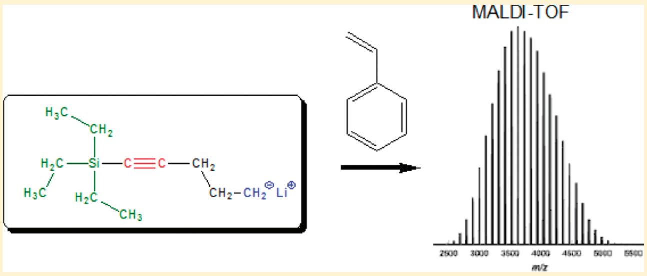
ABSTRACT: Two novel anionic acetylene-functionalized initiators, 5-trimethylsilyl-4-pentynyllithium (TMSPLi) and 5-triethylsilyl-4-pentynyllithium (TESPLi), were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, and GC-MS. TMSPLi was successfully used for the polymerization of styrene, but not for the polymerization of isoprene and butadiene. On the other hand, TESPLi exhibited all characteristics of an anionic initiator for the (co)polymerization of styrene, isoprene, and butadiene. TESPLi is ideal for the synthesis of living well-defined (co)polymers with acetylene end groups, perfect candidates for “click” reactions and at the same time possessing all the potential of living anionic polymerization for the synthesis of well-defined complex macromolecular architectures.



INTRODUCTION

The Cu-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) reaction between terminal alkynes and azide groups, or simply the CuAAC “click” reaction,[1−3] fulfills many requirements for the postpolymerization processing of polymers, since it is robust, general, insensitive, and orthogonal to most other chemistry used in polymer synthesis. These characteristics have contributed considerably to the popularity of “click” chemistry within the polymer and materials science communities.[4,5] Apart from the use of postanionic polymerization reactions to introduce active “clickable” groups with subsequent loss of the lithium site, cited in only a few publications,[6−14] “clickable” groups have never been simultaneously present with the Li-propagating sites. Such a species would have the potential to take advantage of both the lithium and active “clickable” sites, thereby combining two ideal methods, for the synthesis of well-defined complex architectures.

Lithium initiators functionalized[15] with hydroxyl, amino, and carboxylic moieties have been extensively used for anionic polymerization to introduce α-functional groups, with the requisite protection of the functional group in order to avoid reaction or association with the anionic sites. The same requirement is valid for the versatile “clickable” acetylene group, which can react with the anionic sites and thus should be protected.

Herein the synthesis and characterization of two new alkyllithium initiators, 5-trimethylsilyl-4-pentynyllithium (TMSPLi) and 5-triethylsilyl-4-pentynyllithium (TESPLi), with silyl-protected acetylene group are described. These initiators were tested for the polymerization of styrene, isoprene, and butadiene.

EXPERIMENTAL SECTION

Materials. The purification of styrene (Aldrich, 99%), isoprene (Aldrich, 99%), butadiene (Aldrich, 99%), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; Aldrich, 99%), and the solvents (Aldrich; hexane, tetrahydrofuran, methanol, and benzene) was performed using standard high-vacuum techniques reported elsewhere.[16,17] (5-Chloro-1-pentynyl)trimethylsilane (TMSPCl; Aldrich, 97%) and (5-chloro-1-pentynyl)triethylsilane (TESPCl; Oakwood Products, Inc., 97%) were dried over CaH_2 overnight, degassed, and distilled into calibrated ampules. Granular lithium with high sodium content (Aldrich, 99%) and other chemicals were used without further purification.

Synthesis of the Initiator 5-Trimethylsilyl-4-pentynyllithium (TMSPLi). The synthesis of TMSPLi was carried out in a specially designed all-glass apparatus (Figure 1). A 10-fold excess of lithium over the (5-chloro-1-pentynyl)trimethylsilane was used. The reactor was attached to the vacuum line, checked for pinholes, and flame-dried. The appropriate amount of lithium was subsequently placed in the apparatus through the side tube mouth (A) by breaking the vacuum for a short time. After the apparatus was heat-sealed at (A) and degassed, about 3 mL of *n*-BuLi solution in hexane (1.6 M) was introduced through septum (B) by a syringe. After removal of the hexane, constriction (C) was heat-sealed, purified benzene was distilled through the vacuum line into flask (D), and the reactor was sealed at (E). The reactor was purged with the *n*-BuLi solution and rinsed thoroughly with benzene to remove the excess *n*-BuLi and the reaction products of *n*-BuLi with impurities. The benzene was distilled from flask (D) to flask (F), and the purge section was removed by heat sealing at (G). The temperature of the flask (F) was adjusted at 50 °C, the break-seal (H) was ruptured, and the TMSPCl was introduced slowly into the flask (F) containing the lithium in benzene. The produced brown-green solution was left to react, under vigorous stirring, for 1.5 h at 50 °C and overnight at room temperature, before filtration through a medium porosity glass filter into the cylinder (I), which was removed by sealing off at (J). Since the filtrate

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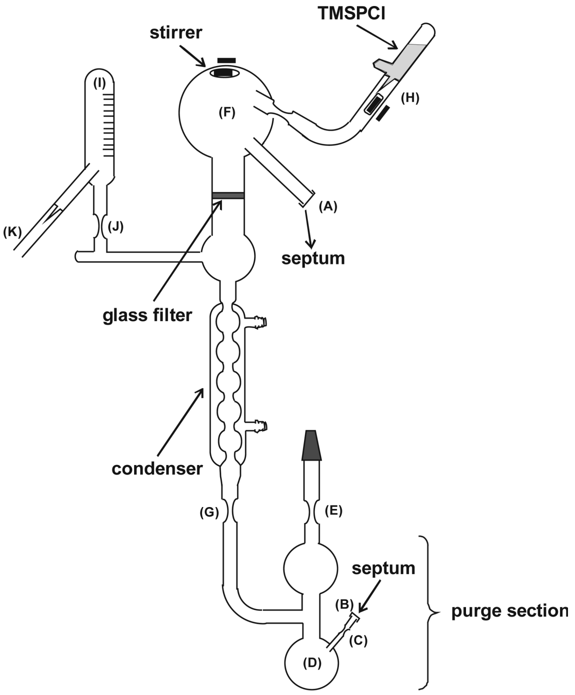


Figure 1. Apparatus for the synthesis of TMSPLi and TESPLi.

was not transparent the cylinder (I) was attached to a second apparatus (Figure 2) through the break-seal (K) and was passed through a fine porosity glass filter to afford a clear yellow solution. A small part of this solution was transferred into the methanol tube on the top of break-seal (M), the methanol tube was removed by heat sealing at (L), and the break-seal (M) ruptured to neutralize the initiator. The isolated initiator was used for structural analysis. The remaining initiation solution was split off in tubes (Figure 2).

Synthesis of the Initiator 5-Triethylsilyl-4-pentynyllithium (TESPLi). The synthesis of TESPLi, which was carried out in benzene, following the same procedure as in the case of TMSPLi, except for starting with (5-chloro-1-pentynyl)triethylsilane (TESPCl). This led to a transparent vivid red solution.

Synthesis of α-Acetylene-Functionalized Polymers. All polymerizations were carried out in benzene at room temperature and for 2 h, in the presence of TMEDA {[TMEDA]/[Li] = 4−5}, using well-known high-vacuum techniques.[16,17]

Characterization Methods. Size exclusion chromatography (SEC) experiments were conducted at 40 °C with a modular instrument consisting of a Waters model 510 pump, a U6K sample injector, a 401 refractometer, a 486 UV spectrometer, and a set of four μ-Styragel columns with a continuous porosity range of 10^6-10^3 Å. The columns were housed in an oven thermostatted at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The system was calibrated with seven PS standards having molecular weights between 2000 and 1 000 000.

Nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* at 25 °C with a Varian Unity Plus 300/54 NMR spectrometer.

Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer.

Gas chromatography−mass spectroscopy (GC-MS) experiments were contacted with a Carlo Erba model 5300 GC connected to a Hewlett-Packard model 6890 MS. The oven temperature was programmed from 70 to 270 °C at 10 °C/min.

Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were recorded using a Bruker Autoflex II model smart-beam equipped with a nitrogen laser (337 nm). Samples were dissolved in THF, dithranol was used as the matrix, and $(CF_3COO)Ag$ was used as the cation source (mixing ratio: matrix:sample:Ag 10:2:1).

■ RESULTS AND DISCUSSION

Synthesis and Characterization of 5-Trimethylsilyl-4-pentynyllithium (TMSPLi). TMSPLi was initially synthesized by lithiation of TMSPCl in hexane. When the final product of the reaction (dark-gray hexane solution) was used for the polymerization of styrene, in the presence of TMEDA (initiation accelerator), a polymer of very low yield (∼ 10%) and high molecular weight was obtained. It is very well documented[18−20] that pentynylalkyllithiums (like TMSPLi) undergo a very fast intramolecular cyclization at room temperature in hexane to give a strained cyclobutylidene organolithium (Scheme 1), which probably cannot satisfactorily initiate anionic polymerization. When the lithiation reaction was carried out in benzene, the final color of the solution was yellow, a first sign of the important role of the solvent in the synthesis of the organolithium compound. Probably the interaction of the lithium cation with the nonpermanent quadrupole benzene rings[21,22] inhibits the backbiting reaction and thus avoiding the formation of the cyclobutylidene compound. GC-MS was used to determine the structure of the synthesized initiator TMSPLi after neutralization with methanol. The gas chromatograph of TMSPH in hexane (Figure 3) showed three peaks: the main peak (∼ 70%) corresponds to TMSPH, while the other two peaks correspond to the unreacted TMSPCl and the Wurtz reaction product 1, 10-bis(trimethylsilyl)deca-1,9-diyne between TMSPCl and TMSPLi. At this point, it should be noted that the synthesis of TMSPLi was repeated many times in order to find the optimum time of heating the reaction mixture of TMSPCl and Li, since insufficient heating would lead to low reaction yield and consequently high percentage of the unreacted starting chloride, while extensive heating would favor the Wurtz reaction product and other byproducts, due to thermal degradation of the organolithium compound.

^{1}H NMR and ^{13}C NMR spectroscopy was also used for the characterization of the synthesized TMSPLi (Figure 4). Apart from the presence of some minor peaks (^{1}H NMR: 2.8 ppm), due to the aforementioned byproducts, the two NMR spectra appear to be those expected (^{1}H NMR: $-Si(\mathbf{CH_3})_3$ 0.2 ppm, *s*; $-\mathbf{CH_3}$ 1.0 ppm, *t*; $-\mathbf{CH_2}$ 1.6 ppm, *m*; $-\mathbf{CH_2}$ 2.3 ppm, *t*. ^{13}C NMR: $-Si(\mathbf{CH_3})_3$ 0 ppm; $-\mathbf{CH_3}$ 14 ppm; $-\mathbf{CH_2}$ 22 ppm; $-\mathbf{CH_2}$ 23 ppm; $-\mathbf{C{\equiv}C}-$ 85, 108 ppm). More interestingly, there is no sign of the existence of the cyclic byproduct.

TMSPLi was used for the polymerization of styrene in benzene. Upon mixing TMSPLi and TMEDA, precipitation of LiCl was observed due to the Wurtz reaction (favored in polar media) between TMSPLi and the remaining starting chloride. Thus, the produced benzene solution of TMSPLi and TMEDA does not contain, apart from TMSPLi, other compounds that could affect the polymerization. When styrene was added into the initiator solution (high-vacuum techniques), the color of the solution immediately turned dark red. After 20 h the color of the solution became much lighter, an indication that termination reactions took place. The SEC chromatography of the terminated with methanol polystyrene (PS) (Figure 5a) reveals only a narrow and symmetrical molecular weight distribution peak, which means that the termination reaction took place after the complete consumption of the monomer. This is probably due to the reaction of part of living end with the liable proton of the

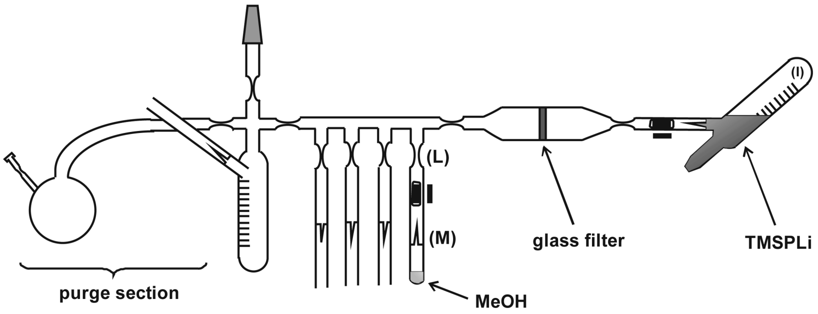


Figure 2. Apparatus used for the second filtration of TMSPLi and the split-off of TMSPLi and TESPLi solutions in tubes.

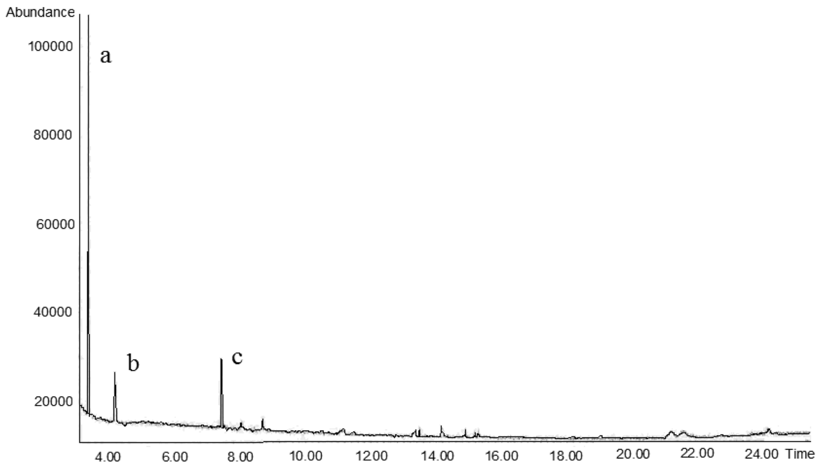
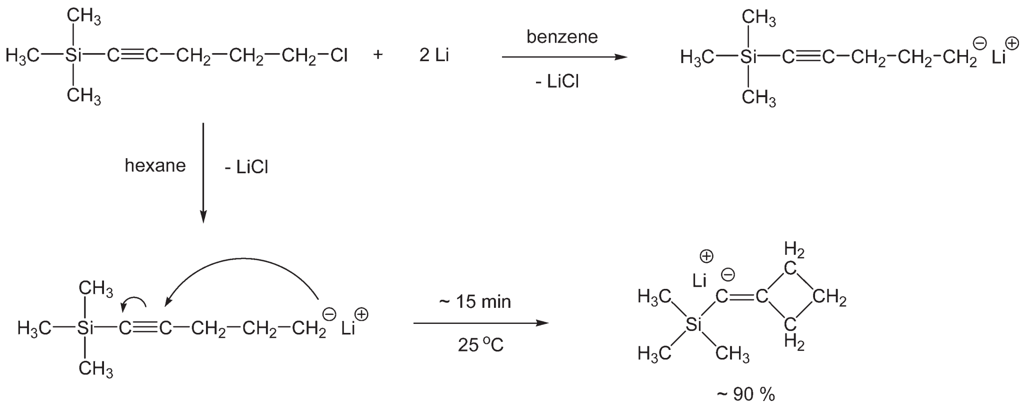


Figure 3. Gas chromatogram of the TMSPLi solution after neutralization with methanol. Peaks: (a) TESPH, (b) Wurtz reaction product, and (c) unreacted starting chloride.

Scheme 1. General Reactions for the Synthesis of TMSPLi



methylene next to the acetylene group,[23] which deactivates the living chains without changing the molecular weight. This was confirmed by adding isoprene to the living polystyrene solution, where a big part of the initial PS did not polymerize isoprene (Figure 5b). Moreover, the trace of the produced diblock copolymer seems to be broad and unsymmetrical. Attempts to homopolymerize isoprene and butadiene failed to yield any polymer. The difference in behavior between the styrene and the dienic monomers may be due to (a) the higher reactivity of dienic living chains toward the proton next to the acetylenic group (less steric hindered macroanions) than that of styrene and (b) the π-coordination of the first formed dienyllithium with the acetylenic moiety[24] of the initiator, which prevents the polymerization. The increased steric hindrance of styryllithium due to the phenyl group probably discourages this π-interaction, enabling the full consumption of the monomer and the preparation of well-defined PS. The ability of α-TMS-PSLi to polymerize dienes may well be due to the shielding of the acetylene group by

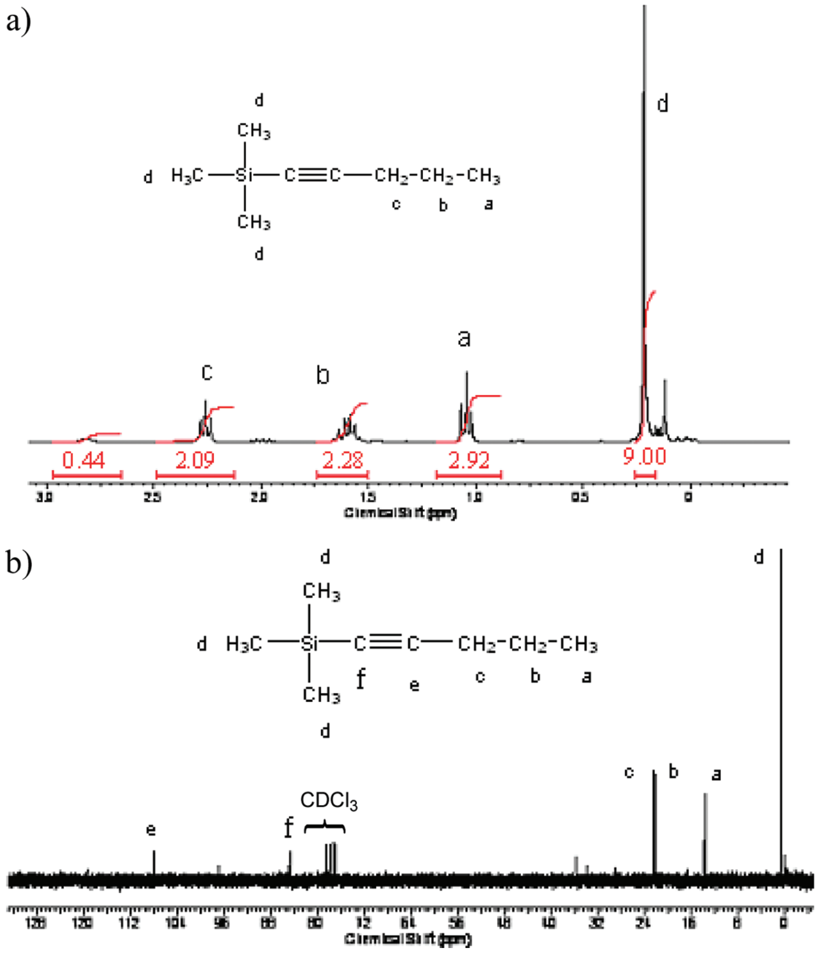


Figure 4. (a) ^{1}H NMR and (b) ^{13}C NMR of the TMSPH.

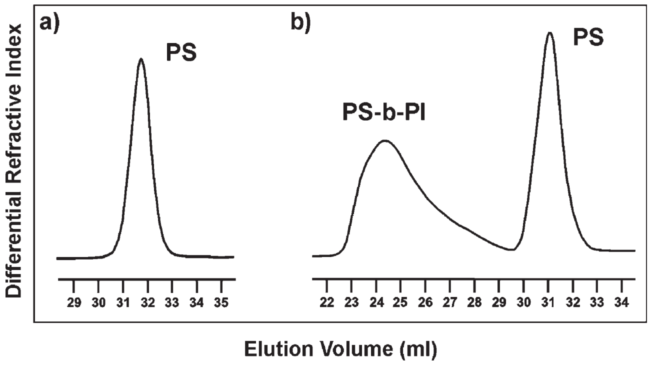


Figure 5. (a) SEC trace of *a*-(TMS-acetylene)-PS (M_n = 3000, I = 1.04) and (b) effort for preparing the diblock copolymer PS-*b*-PI.

the PS block. The breadth of the MWD of the block copolymer may result from the imperfect protection by the PS block.

In the MALDI-TOF mass spectrum of *a*-(TMS-acetylene)-PS (Figure 6a), two peaks are present, with a line-to-line mass increment of 104.152 g mol^{-1} corresponding to the molar mass of styrene monomeric unit. The main peak is attributed to the expected product with the following chemical structure: TMS—Si—C≡C—$(CH_2)_3$—$(styrene)_{25}$—H—Ag (Figure 6b, expanded). The other peak corresponds to the structure H—C≡C—$(CH_2)_3$—$(styrene)_{26}$—H—Ag (Figure 6b); in other words, it corresponds to the "deprotected" product. This species could not coexist from the beginning; otherwise, termination reactions due to acetylenic acidic proton would have taken place during polymerization, and the final distribution would be much higher. Consequently, removal of the TMS group from the chain-end acetylene—polystyrene probably took place during the ionization of the sample for the MALDI-TOF mass spectrometry experiment.

By performing preliminary polymerization experiments and analyzing the polymers obtained at different times, we decided to leave all polymerization for 2 h.

In conclusion, the synthesized acetylene-functionalized anionic initiator TMSPLi, although not highly pure, was successfully used for the polymerization of styrene. However, TMSPLi failed to (co)polymerize dienic monomers, suggesting that the lack of sufficient "protection" of acetylene from the TMS group caused the anionic site of TMSPLi to malfunction. For this reason, the synthesis of a second initiator containing the bulkier triethylsilyl (TES) protecting group was decided.

Synthesis and Characterization of 5-Triethylsilyl-4-pentynyllithium (TESPLi). The strategy followed for the preparation of TESPLi was the same as that for TMSPLi, with the only variation being the starting chloride, which was (5-chloro-1-pentynyl)triethylsilane (TESPCl) instead of TMSPCl. After neutralization of TESPLi with methanol, the initiator was

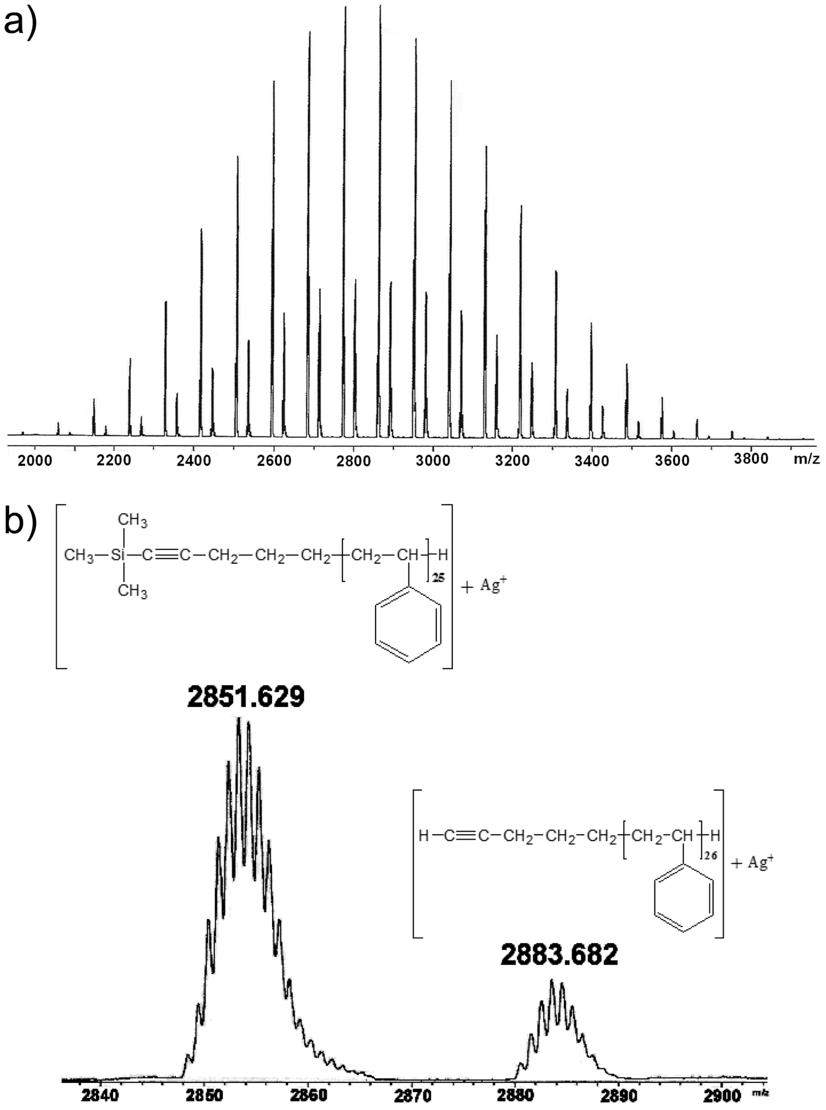


Figure 6. (a) MALDI-TOF mass spectrum of the synthesized *a*-(TMS-acetylene)-PS and (b) the expanded spectrum, focusing on the two main peaks.

thoroughly characterized. GC-MS analysis (Figure 7) revealed high purity of the synthesized organolithium compound, with both the starting chloride (originally appeared at 12.2 min) and Wurtz product peaks being absent and no other product present. NMR analysis (Figure 8, ^{1}H NMR: $-\mathrm{Si}(\mathbf{CH_2}\mathrm{CH_3})_3$ 0.1 ppm, *q*; $-\mathrm{Si}(\mathrm{CH_2}\mathbf{CH_3})_3$ 1.0 ppm, *m*; $-\mathbf{CH_3}$ 1.0 ppm, *m*; $-\mathbf{CH_2}$ 1.5 ppm, *m*; $-\mathbf{CH_2}$ 2.2 ppm, *t*. ^{13}C NMR: $-\mathrm{Si}(\mathbf{CH_2}\mathrm{CH_3})_3$ 5 ppm; $-\mathrm{Si}(\mathrm{CH_2}\mathbf{CH_3})_3$ 8 ppm; $-\mathbf{CH_3}$ 14 ppm; $-\mathbf{CH_2}$ 22 ppm; $-\mathbf{CH_2}$ 23 ppm; $-\mathbf{C}{\equiv}\mathbf{C}-$ 82, 109 ppm) confirmed the GC-MS results.

In the next step, polymerization of styrene took place using TESPLi in the presence of the appropriate amount of TMEDA. The SEC trace of the synthesized polymer was symmetrical and monomodal, looking similar to the chromatograph of Figure 5a. MALDI analysis revealed a single and narrow distribution (Figure 9a). Focusing on a specific peak of the spectrum (Figure 9b), it can be seen that this peak is attributed to the expected product with the following chemical structure: $\mathrm{TES{-}Si{-}C{\equiv}C{-}(CH_2)_3{-}(styrene)_{24}{-}H{-}Ag}$. Taking into account that the line-to-line mass increment is 104.152 g mol^{-1}, it is easy to conclude that the peak corresponds to α-(TES-acetylene)-polystyrene with a degree of functionality 100%. Moreover, in the present sample no cleavage of the TES group took place during MALDI-TOF mass spectrometry analysis, probably due to the much slower rate of cleavage of the TES in regard to the TMS group.[25]

TESPLi was also used for the polymerization of isoprene. Interestingly, upon addition of the monomer to the initiator solution, the color turned from red into yellow, indicating the initiation of the isoprene polymerization. After 2 h, the polymerization reaction was terminated. SEC chromatography (Figure 10a, M_n = 12 200, I = 1.10) of the neutralized macroanion confirmed the successful synthesis of PI. Furthermore, by using TESPLi, it was possible to synthesize well-defined poly(styrene)-*b*-poly(isoprene) and poly(styrene)-*b*-poly(butadiene). The polymerization of polystyrene was followed by the addition of isoprene (or butadiene); however, the color of the solution did not change immediately in both cases from red (the color of polystyrenyllithium) to yellow (the color of polyisoprenyllithium or polybutadienyllithium), taking about 7 min for the complete color shift. After a total 4 h reaction period the polymer was precipitated and analyzed by SEC chromatography. As an example, the SEC of poly(styrene)-*b*-poly(isoprene) given in Figure 10b confirms the successful synthesis of the block copolymer (M_n = 8500, I = 1.09).

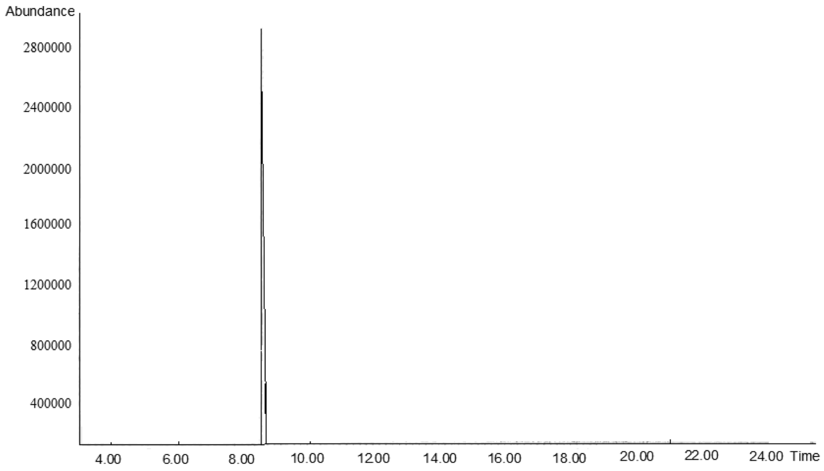


Figure 7. Gas chromatograph of the TESPLi solution after neutralization with methanol. The only peak that appears corresponds to TESPH.

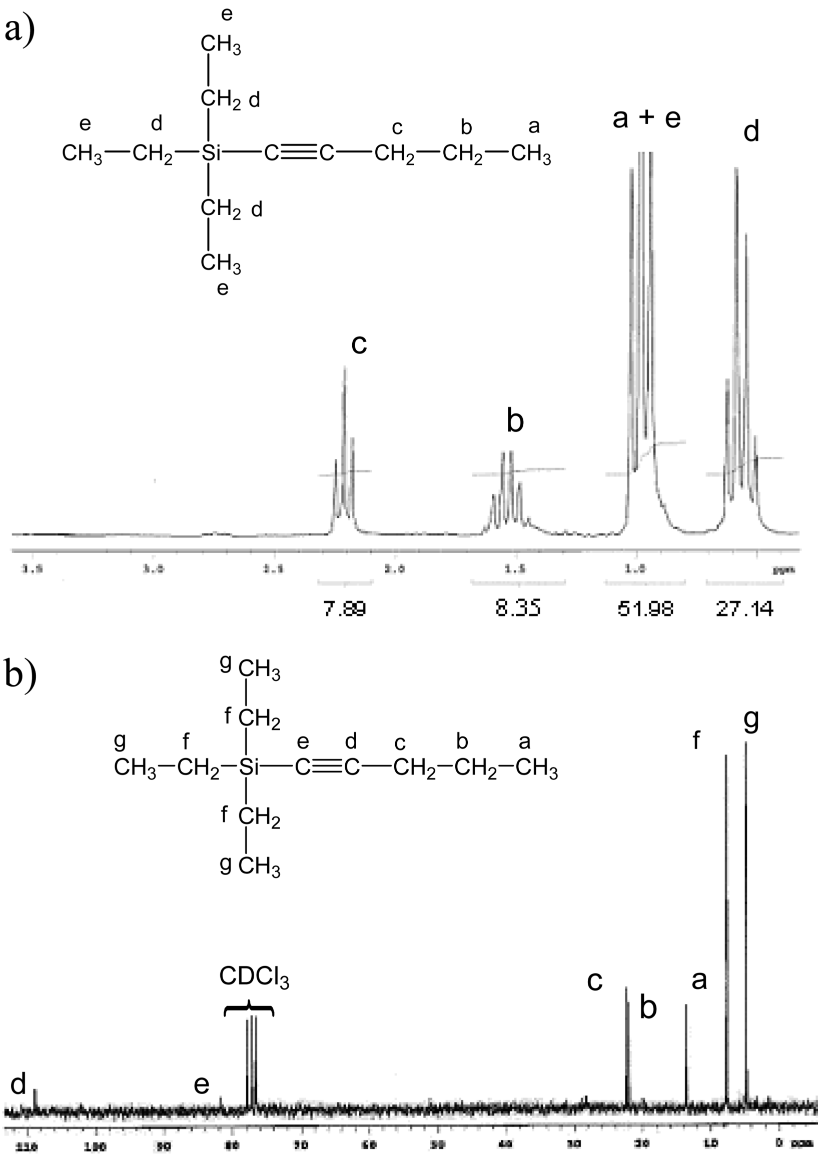


Figure 8. (a) ^{1}H NMR and (b) ^{13}C NMR of the TESPH.

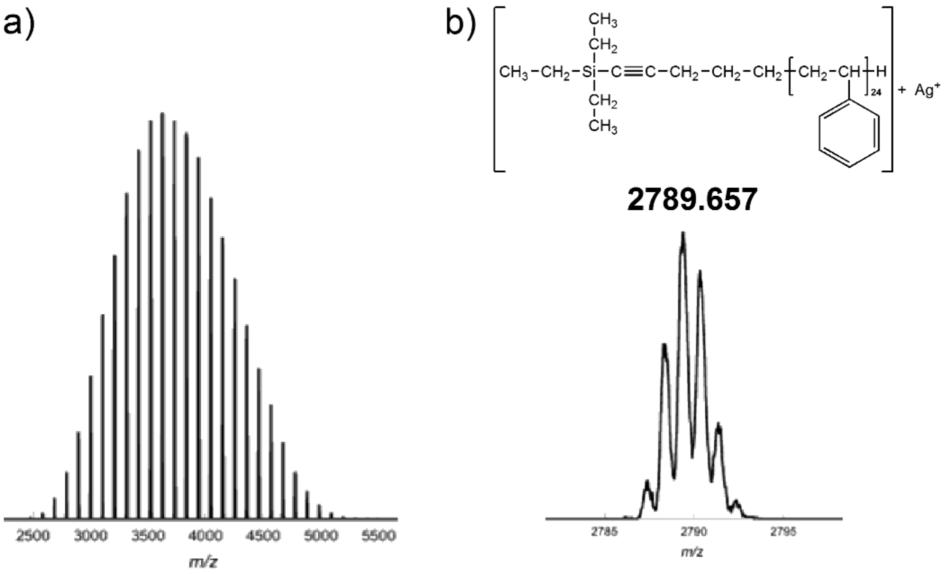


Figure 9. (a) MALDI-TOF mass spectrum of the synthesized *a*-(TES-acetylene)-PS and (b) the expanded spectrum, focusing on a peak of the distribution.

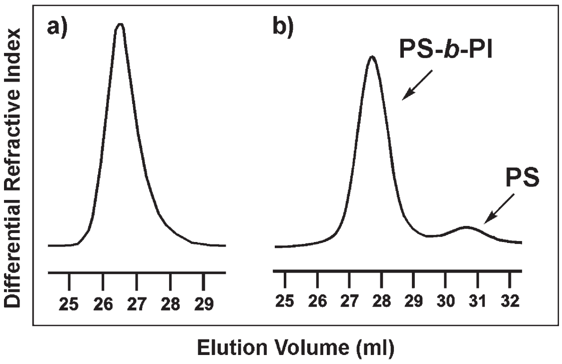


Figure 10. SEC trace (a) of *a*-(TES-acetylene)-PI (M_n= 12 200, *I* = 1.10) and (b) of diblock copolymer *a*-(TES-acetylene)-PS-*b*-PI.

Comparing the experimental results of the two synthesized functional initiators, it is easy to conclude the favorable characteristics of TESPLi both during the preparation of the organolithium compound and the anionic (co)polymerization of styrene, butadiene, and isoprene. Consequently, the improved properties of TESPLi are exclusively due to the bulkier TES group, which better "protects" the terminal alkyne.

CONCLUSIONS

Two novel acetylene-functionalized anionic initiators, 5-trimethylsilyl-4-pentynyllithium (TMSPLi) and 5-triethylsilyl-4-pentynyllithium (TESPLi), were synthesized and characterized. TMSPLi showed many drawbacks during the anionic polymerization of dienes, while it was successfully used for the polymerization of styrene. TESPLi was found to be an effective initiator for styrene, isoprene, and butadiene, affording well-defined (co)polymers with 100% functionality in the acetylenic moiety, enabling the further processing of the polymers through "click" chemistry and the preparation of complex macromolecular architectures by combining two ideal methods: anionic polymerization and "click" chemistry. The use of these acetylenic polymers to produce cyclic and multiblock polymers will be reported in a forthcoming paper.

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