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Investigation of 1,1-diphenylethylene Oligomerization in the End-Capping Reaction of Poly(styryl)lithium

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Summary: The possible oligomerization of 1,1-diphenylethylene (DPE) in the end-capping reaction of poly(styryl)lithium (PSLi) was studied in hydrocarbon solvents using excess DPE ($\leq$16 mol-eq); the effect of addition of THF (30 mol-eq Lewis base) and extended times of reaction (8-24 h) were also investigated. The characterization of the polymers was made by size exclusion chromatography (SEC), proton nuclear magnetic resonance spectroscopy (1H NMR) and matrix-assisted laser desorption/ ionization time of flight mass spectrometry (MALDI-TOF MS). MALDI- TOF mass spectrometric results revealed the absence of DPE oligomerization under the reaction conditions used in this study.

Keywords: 1,1-diphenylethylene oligomerization; anionic polymerization; MALDI-TOF MS; polystyrene (PS)

Introduction

The use of 1,1-diphenylethylene (DPE) and its derivatives (i.e., polymeric chains) in living anionic polymerization offers a versatile approach for synthesizing well-defined homopolymers and copolymers that can be functionalized at specific points of the chain.[1–3] In particular, the addition of organolithium polymeric compounds to DPE and its derivatives (end-capping reaction) is a powerful method for the quantitative incorporation of various functional groups[1,4,5] (e.g., diphenol groups,[6] primary[7] and tertiary amine groups[8–10] and carboxyl group[11]). The addition of organolithium polymers [e.g., poly(styryl)-lithium] to substituted DPE compounds is a quantitative living functionalization reaction due to the formation of an active diphenylalkyllithium chain-end. After addition to one substituted DPE unit, the active functionalized polymeric chain-ends can be quenched with degassed methanol to obtain end- functionalized polymers or can react with a second monomer to obtain in-chain functionalized block copolymers [1,5]

The addition reaction of *n*-butyllithium (*n*BuLi) to DPE was previously studied using different DPE concentrations resulting in the synthesis of an adduct with one DPE unit incorporated using stoichiometric amounts of *n*BuLi and DPE.[12–14] In contrast, the use of a large excess of DPE in the reaction (5.4 fold-excess) promoted the formation of a diadduct by incorporation of two DPE units.[14] The yield of formation of the product with diaddition of DPE was very low (6–11%) although a large excess of the DPE was used in the reaction.[14] The addition of the second DPE unit was described as an equilibrium reaction which lies well towards the monoadduct, 1,1-diphenylhexyllithium, as shown in Scheme 1.

The products obtained in the reaction were separated by vacuum distillation of the high boiling point materials from a residual involatile, viscous compound. Three products were obtained and assigned as unreacted DPE, the monoadduct 1,1-diphenylhexane and the diadduct 1,1,3,3-tetraphenyloctane.[14] The molecular weights of the

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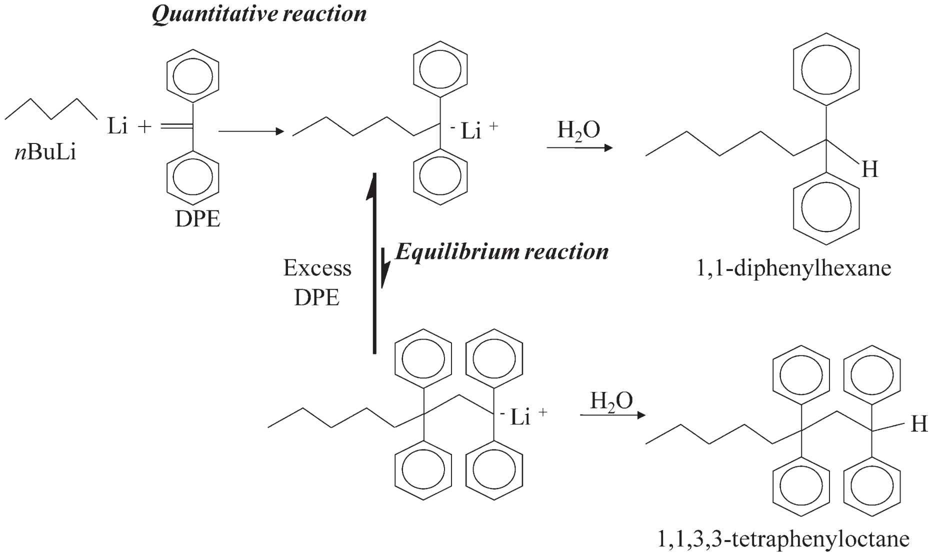
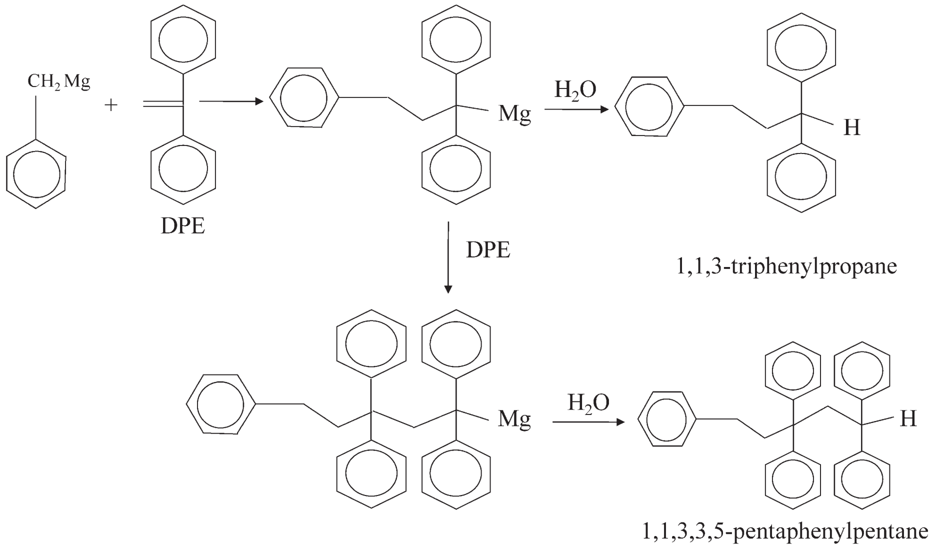


Scheme 1.
Addition reaction of DPE to *n*BuLi in the presence of a large excess of DPE.[14]

separated products were estimated cryoscopically in benzene.[14]

In a more recent study, Nakahama and coworkers[15] evaluated the addition reaction of DPE to dibenzylmagnesium. The presence of an oligomeric structure was characterized by GPC, ^{1}HNMR spectroscopy, melting point and mass spectrometry (MS). The reaction (Scheme 2) was performed under high vacuum using hexamethylphosphoramide (HMPA) as solvent. The results showed the presence of three products assigned as unreacted DPE, the monoadduct, 1,1,3-triphenylpropane, and



Scheme 2.
Addition reaction of dibenzylmagnesium to DPE.[15]

the diadduct, 1,1,3,3,5-pentaphenylpentane (Scheme 2), that were separated by preparative GPC.[15] The molecular weight obtained for the monoadduct, 1,1,3-triphenylpropane, was 272 g/mol (calc MW = 272 g/mol) and the observed integration ratio from the aromatic and aliphatic proton peaks of 15:5 was in agreement with the proposed structure of 1,1,3-triphenylpropane.[15] The molecular weight obtained for the diadduct, 1,1,3,3,5-pentaphenylpentane, was 452 g/mol (calc. MW = 452 g/mol) and the observed integration ratio from the aromatic and aliphatic proton resonance peaks of 25:7 corresponds to the proposed structure of 1,1,3,3,5-pentaphenylpentane compound.[15] In particular, a proton resonance at δ4.3 ppm that corresponds to the terminal methine in the monoadduct was shifted to higher field (δ~3.6 ppm) for the diadduct.[15] The reported data did not include the initial amounts of each compound and it is not clear if a large excess of DPE was necessary to observe the oligomeric DPE diadduct.

The objective of the study reported herein was to investigate different conditions in the end-capping reaction of polymeric organolithium compounds [i.e., poly(styryl)lithium] with DPE and evaluate, the possible formation of oligomeric DPE structure, using similar reaction conditions to those reported by George and Evans.[14] The characterization of the polymers was made by SEC, 1H NMR spectroscopy and MALDI-TOF mass spectrometry.

Experimental Part

Purification of Materials

Benzene (99.0%, EMD™), *tert*-butylbenzene (99.0%, Aldrich), styrene (reagentplus® > 99%, Sigma Aldrich), tetrahydrofuran (>99%, BDH®, 75-500 ppm BHT as preservative) and methanol (BDH®) were purified as described elsewhere.[16,17] *sec*-Butyllithium (*sec*-BuLi, FMC Corporation, Lithium division, 12 wt % heptane/cyclohexane) was used as received after titration with the Gilman double titration procedure.[18] 1,1-Diphenylethylene (DPE) (99%, Acros organics) was distilled into a second round-bottom flask with a lateral arm after being stirred over CaH_2 for 12 h with periodic degassing (freeze-evacuate-thaw). In the second round-bottom flask, a few drops of *n*-BuLi were added to titrate impurities until a persistent intense red coloration was observed. The required amount of DPE was distilled from the heated round- bottom flask at 65 °C under vacuum into a graduated ampoule via a short path distillation system[19] and diluted with several milliliters of solvent. The ampoule was flame-sealed from the line and stored at −20 °C.

Polymerization and End-Capping Reactions

The polymerizations were effected in an all-glass, sealed reactors under high vacuum as described elsewhere.[16,17,19] Styrene polymerization proceeded for 12 h at 30 °C and a base ampoule was taken for characterization. The DPE ampoule was opened and the end-capping reaction was allowed to proceed for 8 h at 30 °C. When THF was added into the reactor, the end- capping reaction was allowed to proceed for 1 h at 5–10 °C. Finally, the degassed methanol ampoule was opened to quench the reaction.

Characterization

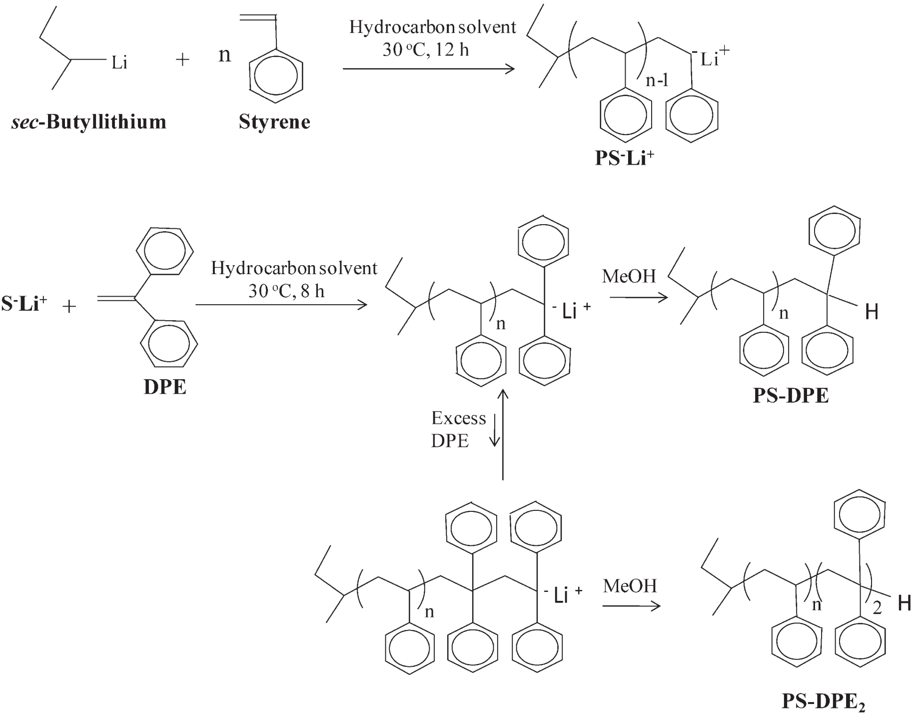
The polymers were characterized by size exclusion chromatography (SEC), proton nuclear magnetic resonance spectroscopy (1H NMR) and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS). SEC analyses were performed in a double detector Waters 510 chromatograph equipped with a Wyatt Dawn EOS multi-angle laser light scattering (MALLS) detector and a Waters 410 differential refractometer concentration detector. The system had three Waters Styragel® HR columns HR1, HR4E, HR5E with effective molecular weight ranges of 100 to 5,000, 50 to 100,000 and 2,000 to 4 × 106 g/mol, respectively. The instrument used THF as eluent at 35 °C at a flow rate of 1 mL/min.

The software used was Wyatt ASTRA v 4.73.04. Prior to injection, the samples were filtered using a 0.45 μm pore size Teflon® filter. Matrix-assisted laser desorption/ionization time of flight mass spectrometric analyses (MALDI-TOF MS) were performed with a Bruker Reflex-III MALDI-TOF mass spectrometer (Bruker Daltonics, Billerica, MA) with a LSI model VSL-337ND pulsed 337 nm nitrogen laser, a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Polymers were analyzed in reflectron mode, using dithranol (1,8,9-trihydroxy-antracene) as matrix, and silver trifluoroacetate (CF_3COO^- Ag^+) or sodium iodide (NaI) as salts in a proportion of matrix:sample:salt equal to 10:2:1. 1H NMR spectroscopic analyses were performed using a 2 channel 500 MHz Varian NMR spectrometer equipped with auto-tune and auto-shim functions and a robotic arm for loading of the samples.

Results and Discussions

End-Capping Reaction of Poly(styryl)lithium with Excess DPE

The addition reaction of a polymeric organolithium compound to DPE is thermodynamically favored by the conversion of the π-bond to the resulting σ-bond and the formation of a more stable diphenylalkyl carbanion from a benzyl carbanion in the case of poly(styryl)lithium.[1–3] In particular, the end-capping reaction of poly(styryl)lithium using a stoichiometric amount of DPE in benzene is a quantitative addition reaction that was completed after 6 hours. The UV absorption peaks at λ_{max} of 440 nm for poly(diphenylalkyl)lithium chain-ends and 334 nm for poly(styryl)lithium chain-ends were followed to determine the required time for complete reaction.[1,2,5] In the presence of excess DPE, the reaction is expected to proceed as reported by George and Evans[14] for the



Scheme 3.
End-capping reaction of poly(styryl)lithium in the presence of a large excess of DPE.

Table 1.
Characterization of end-capped poly(styryl)lithium with different molar- equivalents of DPE.

EXPERIMENT	DPE (mol-eq)	M_n (g/mol)	M_w/M_n
Exp. No 1	1.05	2000	1.02
Exp. No 2	6.3	1700	1.02
Exp. No 3	11.0	1800	1.02
Exp. No 4	16.0	2200	1.02

addition reaction of *n*BuLi to DPE, taking into account an additional equilibrium reaction for the incorporation of a second DPE unit onto the growing polymeric chain. Scheme 3 shows the proposed reaction for the end-capping of poly(styryl) lithium in the presence of a large excess of DPE. In the present study, the end-capping reaction of poly(styryl)lithium was evaluated using different amounts of excess DPE (<16 mol-eq) in benzene for 8 hours at 30 °C. Poly(styryl)lithium samples reacted with 1.05, 6.3, 11 and 16 mol- eq of DPE in order to evaluate the limit at which the oligomeric DPE structure was noticed in the product obtained in the reaction as proposed in Scheme 3. The products were characterized by SEC, 1H NMR spectroscopy and MALDI-TOF MS. The properties of the prepared end-capped polystyrene samples are listed in Table 1.

In particular, the analysis of the polymers with MALDI-TOF MS was extremely useful to unambiguously distinguish between the products with one and two DPE units incorporated. The MALDI-TOF mass spectrometric analysis of the end-capped polymer ($M_n = 2200$ g/mol, $M_w/M_n = 1.02$, 2.25×10^{-3} mol) using 16 mol-eq of DPE (5 mL, 2.9×10^{-2} mol) is shown in Figure 1. In the amplified spectrum of the monomodal distribution (Figure 1), a representative monoisotopic mass peak observed at 1282.0 *m/z* corresponds to the polystyrene 9-mer with one unit of DPE incorporated into the polymeric chain C_4H_9-$(C_8H_8)_9$-

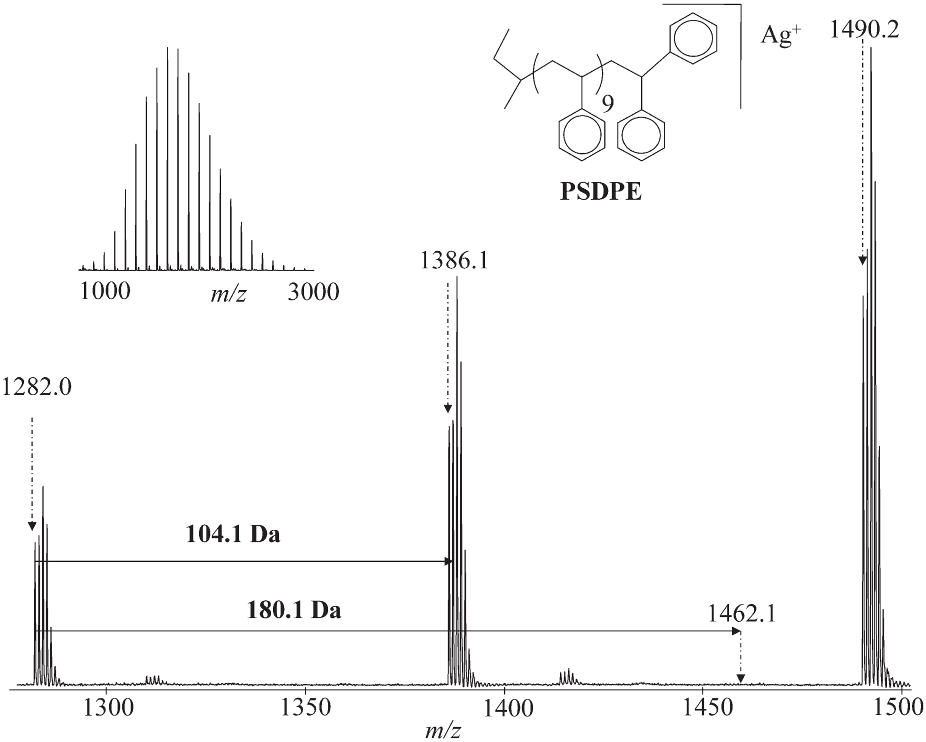


Figure 1.
MALDI-TOF mass spectrum of the end-capped polystyrene using 16 mol-eq of DPE.

$C_{14}H_{12}$–$H^{\bullet}Ag^{+}$; calculated monoisotopic mass = 1282.0 Da. The monoisotopic mass peak at 1462.1 *m/z* is not observed in the spectrum (Figure 1) for the polystyrene 9-mer with two DPE units incorporated into the polymeric chain C_4H_9-$(C_8H_8)_9$-$(C_{14}H_{12})_2$–$H^{\bullet}Ag^{+}$; calculated monoisotopic mass = 1462.1 Da.

Polystyrene end-capped with 16 mol-eq of DPE was analyzed using 1H NMR spectroscopy. The obtained spectrum was compared with the results obtained for the polystyrene end-capped in the presence of a stoichiometric amount of DPE (Figure 2). The chemical resonances present in both spectra were identical and the proton resonance for the terminal methine proton was observed at δ 3.6 ppm.[2] The observed integration ratios between the methyl protons of the initiator unit and the terminal methine proton at δ3.6 ppm is 6.0/1.0 for the polymer end-capped in the presence of 16 mol-eq of DPE.

Prolonged times of reaction were evaluated to observe if the addition of polymeric carbanions to the second DPE was slower than the addition to the first DPE unit that is completed after 6 hours.[2] This behavior was observed in the addition of *n*BuLi to excess DPE that was followed by the reduction of volume during the reaction.[14] The rate of volume reduction was very slow after complete formation of the monoadduct.[14] For this reason, the end-capping reaction was allowed to proceed for 8 hours and a sample was taken for analysis. After 24 hours (4 times the required time for DPE monoaddition),

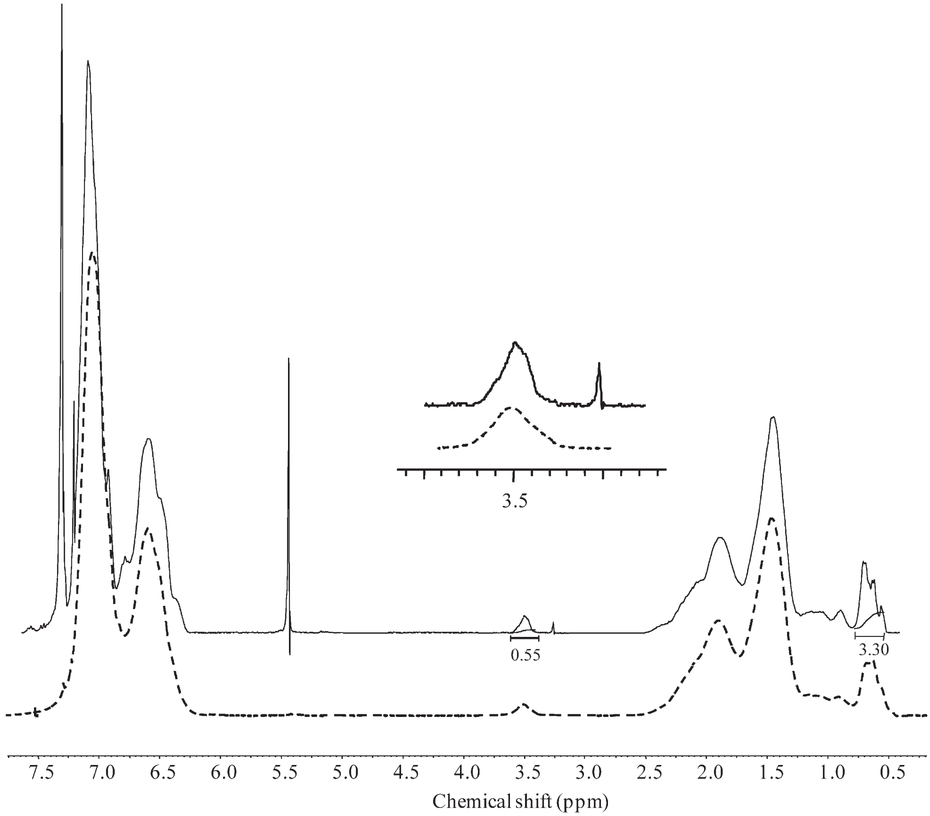


Figure 2.

^{1}H NMR spectra of poly(styryl)lithium end-capped with stoichiometric and excess amount of DPE. Polystyrene end-capped in the presence of 1.05 mol-eq of DPE is represented with the dotted line and polystyrene end-capped in the presence of 16 mol-eq of DPE is represented with a solid line.

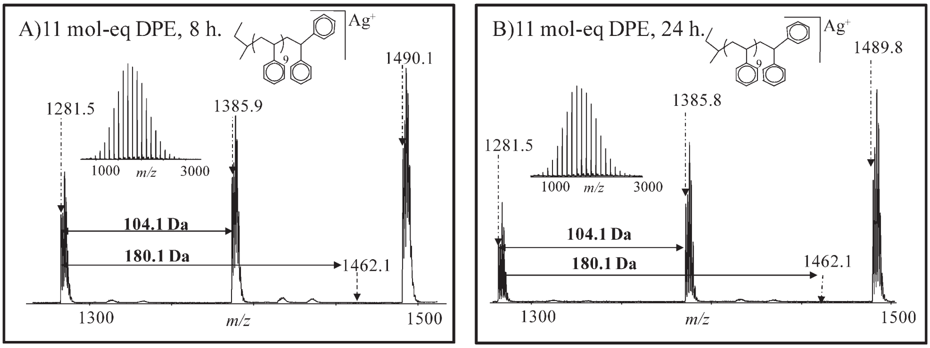


Figure 3.
MALDI-TOF mass spectra of the end-capped polystyrene using 11 mol-eq of DPE: A) after 8 h of reaction and B) after 24 h of reaction.

the reaction was terminated and the product was again analyzed. The MALDI-TOF mass spectra of a poly(styryl)lithium end-capped in the presence of 11 mol-eq of DPE are shown in Figure 3. Both spectra show a monomodal distribution that corresponds to polystyrene end-capped with only one unit of DPE; the calculated monoisotopic mass of the polystyrene 9-mer with one DPE is 1282.0 Da and the observed *m/z* for the first peaks in the spectra were 1281.5 *m/z* after 8 hours of reaction and 1281.5 *m/z* after 24 hours of reaction. The calculated monoisotopic mass for the polystyrene 9-mer with two DPE units incorporated, C_4H_9-$(C_8H_8)_9$-$(C_{14}H_{12})_2$-$H^{\bullet}Ag^+$; is 1462.1 Da which was not observed in the mass spectra (Figure 3).

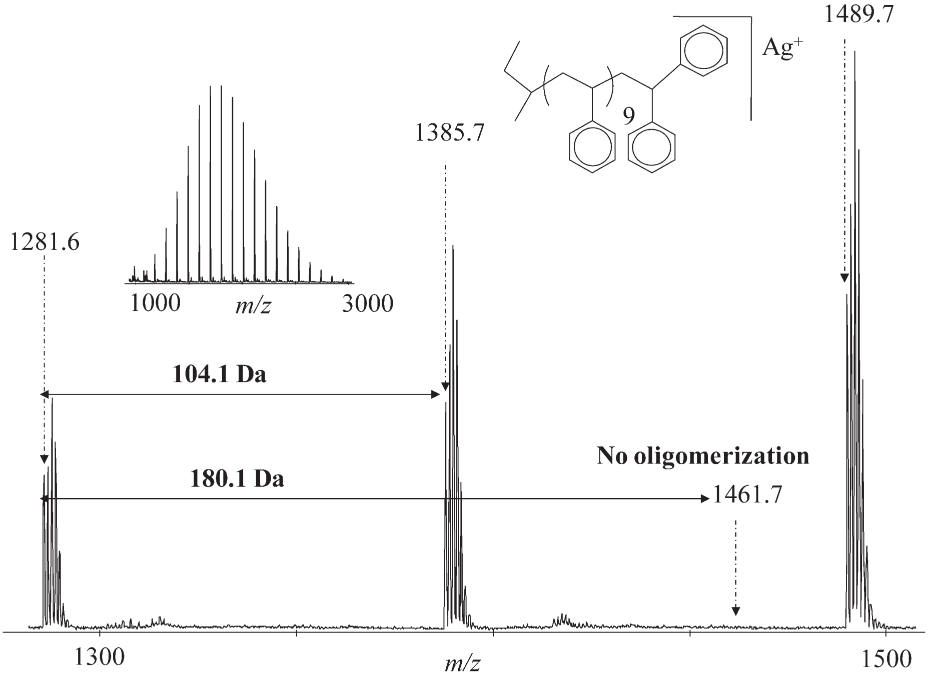


Figure 4.
MALDI-TOF mass spectrum of polystyrene end-capped with 3.4 mol-eq of DPE in the presence of 30 mol-eq of THF for 8h at 5 °C.

End-Capping Reaction of Poly(styryl)lithium with DPE in the Presence of THF (Lewis Base)

The degree of aggregation of the 1,1-diphenylalkyllithium compounds is dimeric in hydrocarbon solvents.[3] In order to increase the reactivity of the 1,1-diphenylalkyllithium chain-ends, a few molar-equivalents of Lewis base (30 mol-eq of THF) was added into the reaction. The Lewis base interact with the stable 1,1-diphenylalkyl carbanion and shift the equilibria in the Winstein spectrum (i.e., aggregated, non-aggregated and complexed ion pairs) towards a more reactive species.[20] It was reasoned that increasing the reactivity of the 1,1-diphenylalkyl carbanion might shift the proposed equilibrium reaction towards the addition of a second DPE unit (Scheme 3). MALDI-TOF mass spectrometric analysis of the products from this reaction is shown in Figure 4. The monomodal distribution corresponds to polystyrene end-capped with one unit of DPE. The observed peak at 1281.6 *m/z* corresponds to the monoisotopic mass of the polystyrene 9-mer with one DPE unit, C_4H_9-$(C_8H_8)_9$-$C_{14}H_{12}$-H]$Ag^+ = 1282.0$ Da. The calculated monoisotopic mass of polystyrene 9-mer with two units of DPE, C_4H_9-$(C_8H_8)_9$-$C_{14}H_{12}$-$H^{\bullet}Ag^+$, is 1462.1 Da. This peak is not observed in the spectrum and indicates that the oligomerization was not promoted by the addition of a few molar-equivalents of THF in the presence of 3.4 mol-eq of DPE as expected.

Conclusion

The addition of a second unit of DPE in the end-capping reaction of poly(styryl)lithium in the presence of a large excess of DPE (<16 mol-eq) was not observed. The characterization of the polymers made by MALDI-TOF MS indicates that the oligomerization of DPE was not observed under the investigated reaction conditions. The addition of a few molar-equivalents of Lewis base did not have an effect on the lack of oligomerization observed in the end-capping reaction of poly(styryl)lithium and excess DPE. Since oligomerization of DPE has previously been observed in the reaction with *n*-butyllithium, it is concluded that steric effects affect this reaction. Investigation of other, less sterically hindered chain-ends, are currently underway.

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