# Initiation of Retarded Styrene Anionic Polymerization Using Complexes of Lithium Hydride with Organometallic Compounds

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ABSTRACT: The hydrogenolysis of poly(styryllithium) species leads to the in situ formation of lithium hydride, which is able to reinitiate styrene anionic polymerization at 100 °C. However, the slow addition rate of LiH to styrene with respect to propagation yields incomplete initiation. The presence of an organometallic derivative such as dibutylmagnesium or triisobutylaluminum was found to improve both the solubility and the reinitiation efficiency of lithium hydride. This behavior is explained by the formation of bimetallic complexes which slow down the propagation and favor the initiation. Following these findings, the use of hydrogen as chain transfer agent in the anionic retarded polymerization of styrene was investigated.

## Introduction

The retarded anionic polymerization has been recently investigated as a route to preserve the control of anionic polymerization of styrene at high temperature (>100 °C) and near the bulk, conditions close to those used in industry for styrene radical polymerization. The main goal of the anionic approach is to achieve the synthesis of polystyrene with improved characteristics and properties in conditions which can be economically competitive. This implies that besides the control of the polymerization parameters, low cost initiators, such as alkali-metal hydrides, and/or the development of catalytic-type processes based on the use of transfer agents have been in the meantime developed.

In a recent study[1] concerning the thermal decomposition of poly(styryllithium), at 150 °C, experimental data suggest that under specific conditions, LiH formed may initiate styrene anionic polymerization. The in situ generation of LiH by $\beta$-hydride elimination from PSLi chains leads to molecular nonaggregated LiH with a strongly enhanced reactivity compared to that of preformed LiH. In a quite similar way very active forms of lithium hydride[2a] were obtained by Ashby from in situ hydrogenolysis of *tert*-butyllithium or from *sec*-BuLi−TMEDA as described by Brandsma et al.[2b,c] Actually, the high lattice energy of alkali-metal hydrides (especially lithium hydride) is responsible for their insolubility in hydrocarbons which drastically reduces their reactivity.[1] To the best of our knowledge, very few papers deal with anionic polymerization of vinylic monomers initiated by metal hydrides. Williams briefly mentioned one styrene polymerization experiment initiated by NaH in hexane at 25 °C.[4] However, the initiation efficiency was very low and the conversion reached only 90% after 3 days. In 1969, Needles[5] studied sodium hydride initiated polymerization of vinyl monomers in aprotic polar solvent. Styrene was polymerized in DMSO at relatively low monomer/sodium hydride ratios yielding oils of low molar masses. In this case, however, it was assumed that the polymerization proceeds by attack of NaH onto DMSO and addition of the resulting dimsyl anion to styrene, followed by a rapid termination.

In this paper, the potential of in situ generated lithium hydride to initiate the polymerization of styrene either alone or combined with another metallic derivative was investigated. Besides, since $H_2$ reacts with PSLi to form inert PSH chains and LiH, which is able to initiate styrene polymerization, the use of $H_2$ as chain transfer agent was also explored.

## Experimental Section

**Materials.** *sec*-Butyllithium (1.3 M in cyclohexane from SAFC, Saint-Quentin Fallavier, France), *n*,*sec*-dibutylmagnesium (*n*,*sec*-$Bu_2Mg$, 1.0 M in heptane from SAFC), triisobutylaluminum (i-$Bu_3Al$, 1.0 M solution in toluene from SAFC) and 2,6-di-*tert*-butyl-*p*-cresol (BHT, 99% powder from SAFC) were used as received. Cyclohexane (99.5% from SAFC) was degassed over freshly crushed calcium hydride ($CaH_2$), stored over poly(styryllithium) oligomers and distilled before use. Styrene (99% from SAFC) was degassed over freshly crushed $CaH_2$, stored over *n*,*sec*-dibutylmagnesium, and distilled just before use.

**Synthesis of 2,6-di-*tert*-Butyl-4-methylphenoxybutylmagnesium (BuMgOBT).** BHT (0.900 g, $4.1 \times 10^{-3}$ mol) was placed in a graduated buret fitted with PTFE stopcocks and degassed under vacuum for 2 h at 50 °C before adding 30 mL of dry cyclohexane. Then, an equivalent molar amount of *n*,*s*-$Bu_2Mg$ solution, 1.0 M in heptane (0.568 g, $4.1 \times 10^{-3}$ mol), was added by syringe under argon flow. The mixture was allowed to react at room temperature for 1 day and kept until use.

**Polymerization.** Poly(styryllithium) seeds ($\overline{DP_n} = 20$, $[PSLi] = 7-8 \times 10^{-3}$ M) were prepared under argon in a graduated buret by addition of *s*-BuLi to styrene in cyclohexane solution. Then 30 mL of this PSLi solution was placed in a 150 mL glass flask equipped with a quartz cell and fitted with PTFE stopcocks. Hydrogen was then introduced at 1 bar pressure and the solution heated at 50 °C, thus generating LiH in situ. The intensity decrease of the PSLi band at 326 nm was monitored vs time. After complete disappearance of this peak, excess of $H_2$ was removed under vacuum. Styrene and a known amount of organometallic derivative were then added to obtain the required [Mt]/[LiH] ratio. Polymerizations were carried out under vacuum in cyclohexane at 100 °C. After styrene addition, the polymer conversion was measured by

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**Table 1. Polymerization of Styrene with in Situ Formed LiH in the Presence of Organometallic Additives (100 °C, Cyclohexane), $[M]_0 = 0.2-0.5$ mol·L$^{-1}$**

| additive | [Mt]/[Li] | $[Li]_r{}^a$ (mol·L$^{-1}$) | $k_{p,app}{}^b$ (L·mol$^{-1}$·min$^{-1}$) | $\bar{M}_{n,theor/Li}{}^c$ (g·mol$^{-1}$) | $\bar{M}_{n,exp}{}^d$ (g·mol$^{-1}$) | $I_p{}^e$ | eff (%)$^f$ |
|---|---|---|---|---|---|---|---|
|  | 0 | $5.8 \times 10^{-4}$ | *g* | 4700 | 79 500 | 1.4 | 6 |
| *n*,*sec*-$Bu_2Mg$[8] | 2.0 | $8.1 \times 10^{-3}$ | 1.0 | 5500 | 3700 | 1.1 | 150 |
| BuMgOBT[1] | 1.5 | $4.5 \times 10^{-3}$ | 1.9 | 4900 | 9800 | 1.3 | 50 |
| *i*-$Bu_3Al$[9] | 0.7 | $8.8 \times 10^{-3}$ | ~$2.9^h$ | 5200 | 5800 | 1.1 | 90 |

$^a$ Concentration in active species calculated from $[styrene]_0/\bar{M}_{n,expt}$. $^b$ $R_p = k_{p,app}[Li]_r[S]$. $^c$ $\bar{M}_n$ calculated from $[LiH]_0$ estimated from hydrogenolyzed $[PSLi]_0$ seeds. $^d$ $\bar{M}_n$ measured by SEC. $^e$ Polydispersity index estimated from SEC. $^f$ Initiation efficiency = $(\bar{M}_{n,theor/Li}/\bar{M}_{n,expt}) \times 100$. $^g$ Polymerization rate too high to be measured by the UV−visible technique. $^h$ 3 h induction period.

**Table 2. Polymerization of Styrene Initiated by PSLi Seeds in the Presence of Organometallic Additives (100 °C, Cyclohexane)**

| additive | $[M_t]/[Li]$ | $[PSLi]_0$ (mol·L$^{-1}$) | $k_{p,app}{}^a$ (L·mol$^{-1}$·min$^{-1}$) | $\bar{M}_{n,theor/Li}{}^b$ (g·mol$^{-1}$) | $\bar{M}_{n,theor/Li+Mg}{}^c$ (g·mol$^{-1}$) | $\bar{M}_{n,expt}{}^d$ (g·mol$^{-1}$) | $I_p{}^e$ |
|---|---|---|---|---|---|---|---|
| *n*,*sec*-$Bu_2Mg$ | 2 | $4.8 \times 10^{-3}$ | 6.0 | 12 000 | 4600 | 5000 | 1.1 |
| BuMgOBT | 1.3 | $7.5 \times 10^{-3}$ | 2.0 | 6900 |  | 8000 | 1.1 |
| *i*-$Bu_3Al$ | 0.8 | $7.4 \times 10^{-3}$ | 2.7 | 6400 |  | 6800 | 1.1 |

$[M]_0 = 0.5-0.6$ mol·L$^{-1}$. $^a$ $R_p = k_{p,app}[PSLi]_0[S]$. $^b$ $\bar{M}_n$ calculated from $[PSLi]_0$. $^c$ $\bar{M}_n$ calculated from $[PSLi + n,sec\text{-}Bu_2Mg]_0$. $^d$ $\bar{M}_n$ measured by SEC. $^e$ Polydispersity index estimated from SEC.

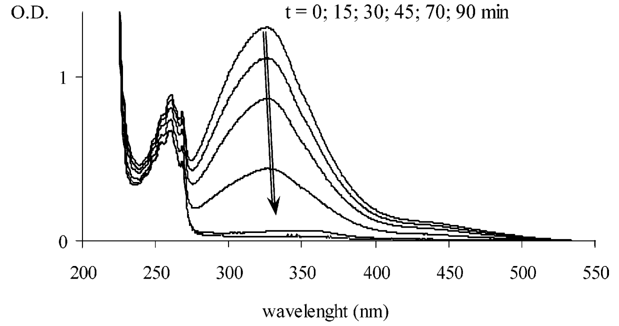


**Figure 1.** Evolution of the PSLi UV−visible spectrum under $H_2$ atmosphere (~1 bar) at 50 °C.

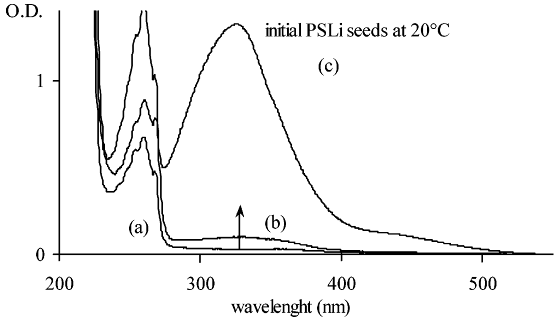


**Figure 2.** Evolution of the PSLi UV−visible spectrum in cyclohexane: (a) after 2 h at 50 °C under $H_2$ atmosphere (1 bar); (b) 20 min after $H_2$ degassing and addition of styrene at 100 °C, $[M]_0 = 0.5$ mol·l$^{-1}$; (c) initial PSLi seeds before hydrogenolysis.

following the decrease of the monomer concentration by UV−visible spectrometry. All polymerizations were stopped by adding methanol previously degassed under vacuum.

**Analytical techniques. UV—Visible Spectroscopy.** The absorption spectra were recorded on a UV−visible spectrometer Varian-Cary 3E using a quartz cell (0.01 cm path length) attached to the glass reactor; $\epsilon_{PSLi} = 13\,000$ L·mol$^{-1}$·cm$^{-1}$ at 326 nm, $\epsilon_{styrene} = 450$ L·mol$^{-1}$·cm$^{-1}$ at 290 nm.

**Polymer Characterization.** The average molar masses and polydispersity of the polystyrene samples were measured by size exclusion chromatography (SEC) in tetrahydrofuran at 20 °C. Measurements were performed using a JASCO HPLC-pump type 880-PU, a Varian apparatus equipped with refractive index/UV detection, and 4 TSK Gel columns (HXLG 2000, 3000, 4000 and 5000) calibrated with polystyrene standards.

The MALDI−TOF measurements were performed on a BIFLEX III instrument (Brüker Daltonik GmbH) in reflection mode using a dithranol matrix in THF and silver trifluoroacetate as cationizing agent.

## Results and Discussion

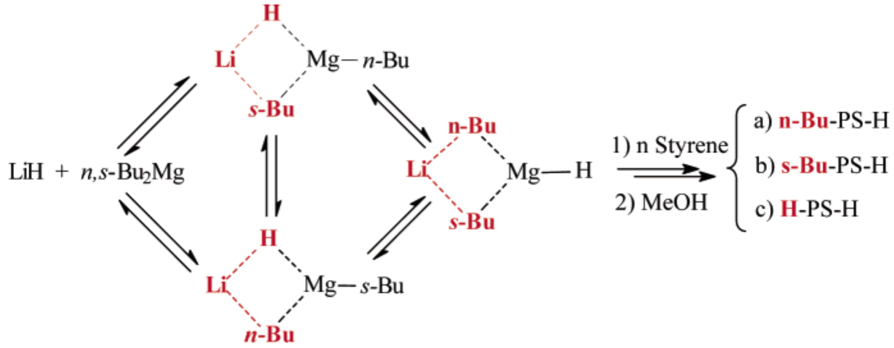
**PSLi Hydrogenolysis.** In this first paper dealing with the ability of alkali-metal hydrides to initiate styrene polymerization, LiH was generated in situ by deactivation of PSLi seeds with $H_2$ at 50 °C in cyclohexane. The reaction was monitored by UV−visible spectroscopy. Upon addition of $H_2$ (~1 bar) to the PSLi solution, the main absorption band of PSLi, initially located at 326 nm decreases and undergoes a slight batochromic shift likely due to specific interactions between the remaining PSLi and LiH, see Figure 1. Despite the low solubility of $H_2$ in hydrocarbons[6] ($[H_2] = 3.7 \times 10^{-3}$ mol·L$^{-1}$, at 20 °C, at $P = 1$ bar, in cyclohexane), almost a complete deactivation of PSLi was achieved within 1.5 h at 50 °C. In these conditions, the thermal decomposition of poly(styryllithium) yielding LiH is reported to be negligible,[7] as confirmed by the stability of the PSLi band in absence of $H_2$ with time. Generated in situ LiH remains soluble over several hours before aggregating, and then it finally precipitates.

The addition of an organometallic derivative such as magnesium or aluminum alkyls or alkoxy alkyl allows LiH to remain soluble, through the formation of bimetallic complexes. These mixed $R_2Mg/LiH$, $RMgOR/LiH$, and $R_3Al/LiH$ systems were tested as styrene polymerization initiator at 100 °C. All the polymerizations were stopped by adding methanol in order to yield PS chains with a terminal H atom. Results are collected in Table 1.

To compare, kinetic results obtained under similar conditions by direct initiation from PSLi seeds and metal−alkyls additives[8,9] are given in Table 2.

**Styrene Polymerization Initiated with LiH Alone ($PSLi/H_2$).** After complete hydrogenolysis of PSLi seeds by $H_2$ at 50 °C, indicated by the disappearance of the UV−visible PSLi signal, followed by hydrogen degassing, styrene was added to the system and the solution was heated to 100 °C: the solution turned rapidly to the orange color which is characteristic of PSLi species. The optical density (OD) increase of PSLi band at 326 nm (see Figure 2) confirmed the regeneration of PSLi species. However, this increase was quite low when

**Scheme 1. Formation of Ate Complexes between Lithium Hydride and *n,sec*-Dibutylmagnesium**[a]



[a] Parts in red are those where styrene insertion is assumed to take place in the complexes.

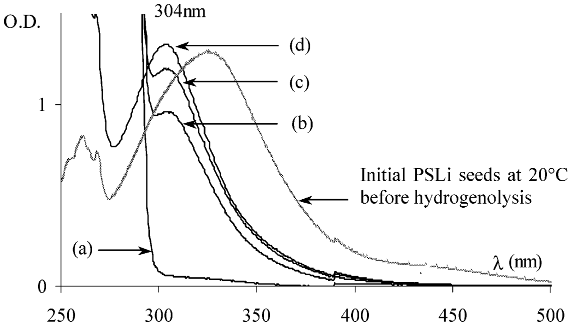


**Figure 3.** Evolution of the UV−visible spectrum of *n,sec*-$Bu_2$-Mg/LiH system after $H_2$ degassing and addition of styrene (cyclohexane, [Mg]/[Li] = 2). Reaction time at 100 °C: (a) after hydrogenolysis and before styrene addition, 0 min; (b) after 20 min; (c) after 60 min; (d) after 200 min.

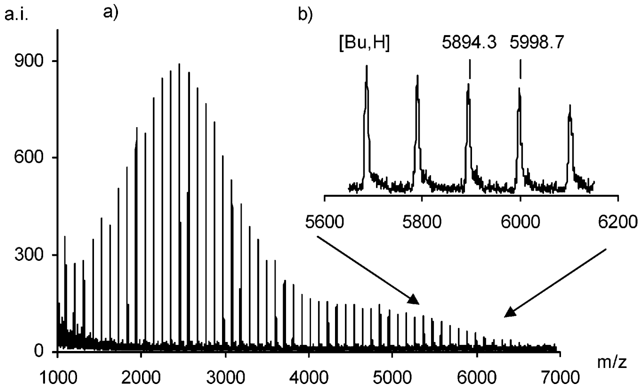


**Figure 4.** MALDI mass spectrum (a) of a polystyrene synthesized from *n,sec*-$Bu_2Mg$/LiH (cyclohexane, [Mg]/[Li] = 2, 100 °C); (b) enlarged part.

compared to the initial concentration of PSLi seeds (<10%). Nevertheless, it is in agreement with the efficiency calculated from the experimental molar masses, see Table 1. These results show that soluble LiH is an active initiator for styrene polymerization at high temperature. The low efficiency of LiH may result from both its incomplete solubility and the high reactivity of PSLi species at 100 °C; the propagation is too fast to enable complete initiation before total monomer conversion since styrene is completely consumed within a few minutes at 100 °C.

These results led us to examine the combination of LiH and organometallic additives in order to strongly decrease the styrene propagation rate and to get an higher reinitiation efficiency.

**Initiation from *n,sec*-$Bu_2$Mg/LiH (PSLi/$H_2$).** The system *n,sec*-$Bu_2$Mg/LiH was obtained by addition of *n,sec*-$Bu_2$Mg to LiH generated in situ by hydrogenolysis of PSLi as previously described. After addition of styrene, the temperature of the system was raised to 100 °C and the regeneration of PSLi/*n,sec*-$Bu_2$Mg species ($\lambda$ = 304 nm) was monitored by UV−visible spectroscopy. As shown by the rapid increase of the OD vs time (Figure 3) the efficiency of the initiation is much higher than that obtained with LiH alone. Most of the new PS active species are formed within 60 min.

However, in contradiction to expected from an hydride initiation (Scheme 1c) the MALDI−TOF mass spectrum of the polymer shows that all the chains formed by the new initiation process possess a butyl headgroup (Figure 4) indicating that chains were not initiated with Mt−H bonds. This may be related to the *n,sec*-$Bu_2$Mg ability to form PS chains in the presence of alkyllithium species:[8] through formation of bimetallic complexes, *n,sec*-$Bu_2$Mg exchanges or shares its ligands with LiH to yield in the complex BuMgH and BuLi moieties, likely *sec*-BuLi, which are able to reinitiate styrene polymerization (Scheme 1a,b). As indicated by the kinetic data reported in Tables 1 and 2 the newly formed PSLi/BuMgH complex exhibit a higher retardation effect than PSLi/*n,sec*-$Bu_2$Mg[8] ($k_{p,app}$ PSLi/*n,sec*-$Bu_2$Mg> $k_{p,app}$ PSLi/BuMgH).

According to the number of PS chains formed estimated from the ratio $[\text{styrene}]_0/\bar{M}_{n,\text{exp}}$, the reinitiation corresponds to the formation of 1.5 PS chains per initial LiH formed (based on $[\text{PSLi}]_0$ seeds before hydrogenolysis). In other words, 37% of Bu−Mg bonds (probably 75% of *sec*-Bu−Mg bonds[8]) were activated by LiH and contribute to the growth of new PS chains ([Mg]/[Li] = 2.0).

**Initiation from BuMgOBT/LiH (PSLi/$H_2$).** To force initiation into Li−H bonds, *n,sec*-$Bu_2$Mg was replaced by another retarding agent, BuMgOBT. Contrary to the behavior of *n,sec*-$Bu_2$Mg this magnesium derivative does not contribute to the formation of new PS chains in the presence of PSLi, at 100 °C, in cyclohexane. This is in agreement with the lower tendency of alkylalkoxymagnesium derivatives to exchange their alkyl ligands with lithium species. Nevertheless, BuMgOBT and PSLi form strong 1:1 complexes which afford an important retarding effect,[1] even at low [Mg]/[Li] ratios.

The UV−visible absorption spectrum of the BuMgOBT/LiH system in cyclohexane (Figure 5) after styrene addition, is very similar to that observed with BuMgOBT/PSLi except a slight hypsochromic shift of the absorption band from 330 to 328 nm. The formation of the new PS species is slow and incomplete as shown by the OD increase with time. These results agree with the reinitiation efficiency calculated from the number of PS

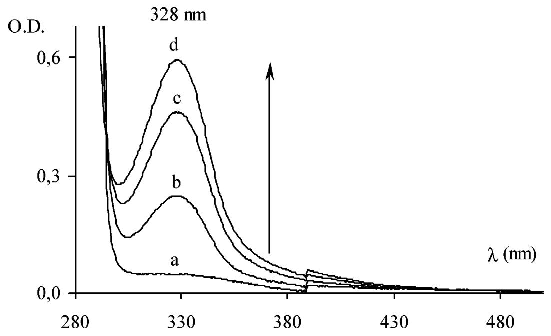
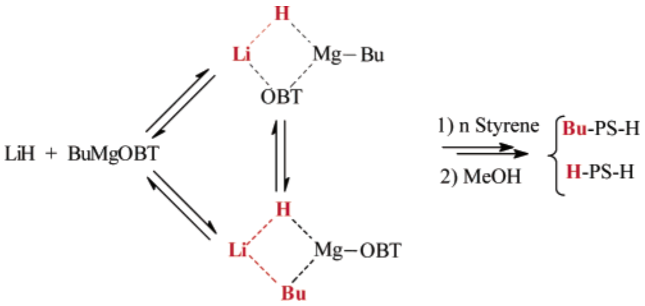


**Figure 5.** Evolution of the UV–visible spectrum of BuMgOBT/LiH system after $H_2$ degassing and addition of styrene (cyclohexane, [Mg]/[Li] = 1.5). Reaction time at 100 °C: (a) PSLi hydrogenolyzed before styrene addition, $t = 0$ min; (b) $t = 20$ min; (c) $t = 90$ min; (d) $t = 220$ min.

**Scheme 2. Formation of Ate Complexes between Lithium Hydride and 2,6-Di-*tert*-butyl-4-methylphenoxybutylmagnesium**[a]



[a] Parts in red are those where styrene insertion is assumed to take place in the complexes.

chains recovered after reaction. Only 50% of the potentially active species corresponding to the initial PSLi seeds are formed within the polymerization time (5 h for total styrene conversion). In addition, samples exhibits a larger polydispersity index than those measured on samples obtained with *n*,*sec*-$Bu_2Mg$ additives, in agreement with a slower initiation step.

The MALDI mass spectrum, Figure 6, shows that among PS chains formed by BuMgOBT/LiH initiation, 50% possess a butyl headgroup and 50% a H headgroup. This indicates that two initiation mechanisms are able to coexist: a ligand exchange between Li and Mg to form BuLi moieties and direct insertion into Li–H bonds (see Scheme 2). In the range 2000–3000 g·mol$^{-1}$, the proportion of chains with a butyl headgroup is largely predominant with respect to chains with a H headgroup and corresponds to terminated PSLi seeds used to generate LiH in situ.

The formation of HMgOBT affects noticeably neither the UV–visible spectrum of active species nor the retardation effect with respect to the BuMgOBT/PSLi system. This could indicate that complexation mainly involves PS–Li and Mg-phenoxy bonds.

**Initiation from *i*-$Bu_3Al$/LiH (PSLi/$H_2$).** A similar study was performed with *i*-$Bu_3Al$ as additive ([Al]/[Li] = 0.7). Contrary to other systems, the lithium derivative was used in excess with respect to *i*-$Bu_3Al$ since it has been previously shown that retardation is already important at [*i*-$Bu_3Al$]/[PSLi] < 1, the system being practically inactive toward styrene polymerization at [*i*-$Bu_3Al$]/[PSLi] ≥ 1.[9] The retardation was explained by the formation of a 1:2 *i*-$Bu_3Al$:PSLi complex which transforms into a 1:1 *i*-$Bu_3Al$:PSLi inactive complex upon increasing the [Al]/[Li] ratio; see Scheme 3. Addition of *i*-$Bu_3Al$ to LiH formed in situ in cyclohexane yields an uncolored, slightly turbid solution. Since 1:1 complexes between *i*-$Bu_3Al$ and LiH are soluble in cyclohexane, it is believed that either 1:2 (Al:Li) complexes or some uncomplexed LiH are responsible for this turbidity. After $H_2$ degassing and styrene addition, the solution turned to yellow but some insoluble particles remained until the end of the polymerization.

Kinetic studies performed by UV–visible spectroscopy shows that the propagation reaction only starts after an induction period of about 3 h at 100 °C. During this induction period, the formation of a peak shoulder at 300–350 nm is observed (Figure 7). This band corresponds to the first insertion of styrene molecule into LiH bonds yielding $HCH_2CHPhLi$ species complexed with *i*-$Bu_3Al$. The UV band increases with time whereas the polymerization starts when the shoulder has almost reached its maximal value. Therefore, it may be concluded that after the insertion of one styrene molecule into Li–H bonds, the newly formed styryl species complexed with *i*-$Bu_3Al$ would remain inactive as long as the ratio of [*i*-$Bu_3Al$]/[$HCH_2CHPhLi$] stays higher than 1, in agreement with the inactivity of the system [*i*-$Bu_3Al$]/[PSLi] at ≥ [Al]/[Li] ≥ 1.[9] This process allows almost complete conversion of LiH bonds into H–styryllithium ones, prior to propagation. The latter finally starts as soon as $CH_3CHPhLi$ concentration is greater than *i*-$Bu_3Al$. This two step procedure is further supported by the narrow molar mass distribution of PS chains ($I_p = 1.1$) observed for these systems. Interestingly, this phenomenon enables high reinitiation efficiency of LiH (close to 90–100% of initial PSLi seeds). In the present system with [Al]/[Li] = 0.7, the propagation only starts when more than 70% of the Li–H bonds are converted into H–styryllithium ones.

After complete polymerization, the UV–visible spectrum is similar to that obtained with PSLi seeds complexed with *i*-$Bu_3Al$.[9] The polymerization rate measured after the induction period is close to the one

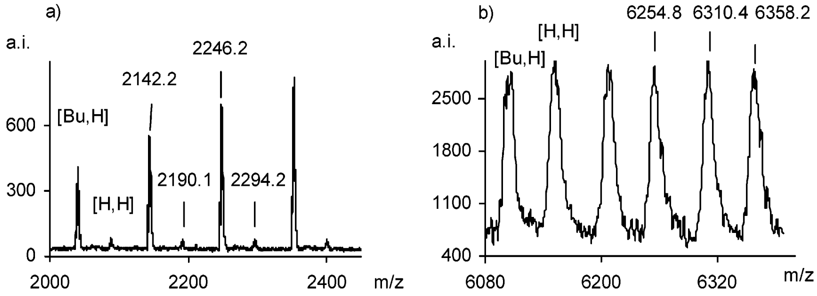
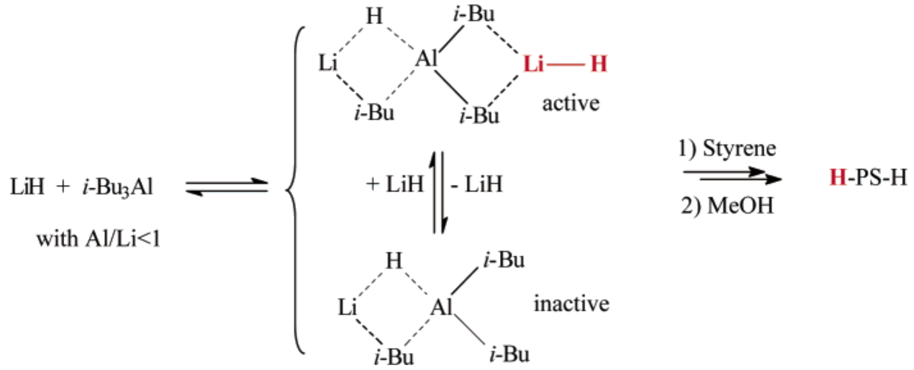


**Figure 6.** Details of the MALDI mass spectrum of polystyrene synthesized from BuMgOBT/LiH (cyclohexane, [Mg]/[Li] = 1.5, 100 °C). Range: (a) 2000–2400 g·mol$^{-1}$ corresponding mainly to hydrogenolyzed Bu–PS–Li seeds; (b) main fraction 6000–6400 g·mol$^{-1}$ formed from LiH–BuMgOBT.

**Scheme 3. Formation of Complexes between Lithium Hydride and Triisobutylaluminum**[a]



[a] The red part in the 1:2 Al:Li complex is where styrene insertion is assumed to take place.

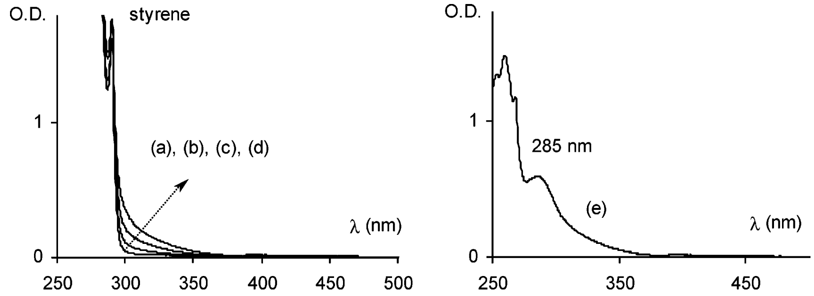


**Figure 7.** Evolution of the UV−visible spectrum of $i$-Bu$_3$Al/LiH system after $H_2$ degassing and addition of styrene (cyclohexane, [Al]/[Li] = 0.7). Reaction time at 100 °C: (a) 0 min; (b) 25 min; (c) 80 min; (d) 210 min; (e) 19 h.

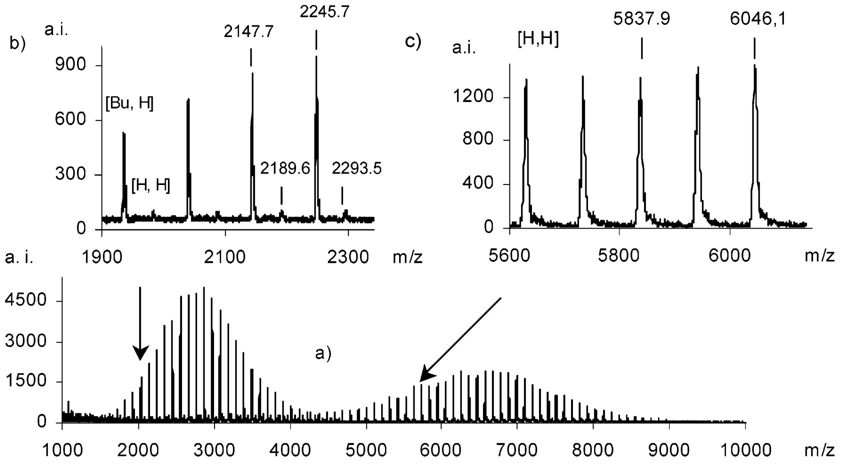


**Figure 8.** MALDI mass spectrum (a) of polystyrene synthesized from $i$-Bu$_3$Al/LiH ([Al]/[Li] = 0.7, cyclohexane, 100 °C). Enlarged part: (b) range 1900−2300 g·mol$^{-1}$; (c) range 5600−6100 g·mol$^{-1}$.

obtained with the system 0.8 $i$-Bu$_3$Al/PSLi. It is likely that a small fraction of insoluble lithium hydride yields a slightly higher apparent [Al]/[Li] ratio than expected from the initial PSLi seeds concentration. The drastic influence of this ratio on the propagation rate was already reported.[9]

All the chains formed by the initiation by LiH associated with $i$-Bu$_3$Al ([Al]/[Li] = 0.7) possess a H-headgroup as confirmed by MALDI−TOF, Figure 8. This is in agreement with the fact that $i$-Bu$_3$Al does not exchange easily its ligands with LiH (and LiR) and does not yield BuLi moieties in the complex as observed with $n$,$sec$-Bu$_2$Mg. Styrene insertion proceeds exclusively into Li−H bonds (Scheme 3).

As for previous systems, in the range 2000−3000 g·mol$^{-1}$, PS chains with a butyl headgroup correspond to the hydrogenolyzed initial Bu−PSLi seeds.

**Initiation Mechanism.** Association of organometallic derivatives such as dialkylmagnesium, alkylalkoxymagnesium and trialkylaluminum with LiH leads to the formation of bimetallic complexes which allows solubilization of LiH in hydrocarbon media. According to the nature of the organometallic derivative and the stoichiometry between the two compounds, monomer insertion takes place in the mixed complexes, see Schemes 1−3. Experimental results suggest that the reaction proceeds in the mixed complex either by insertion into Li−R bonds formed by ligand exchanges within the complex or by direct insertion into complexed Li−H bonds. The balance between the two mechanisms depends on both the capacity of the organometallic derivative to exchange or share its ligands with lithium species and the relative rate of styrene insertion into Li−H and Li−R bonds in the mixed complexes.

**Table 3. Polymerization of Styrene Initiated by PSLi in the Presence of Various Organometallic Additives under $H_2$ Atmosphere ($P$ = 1.2 bar, 70 °C, Cyclohexane, $[PSLi]_0 = (7 -7.5) \times 10^{-3}$ mol·L$^{-1}$)**

| additive | [Mt]/[Li] | $\bar{M}_{n,theor}$[a] (g·mol$^{-1}$) | $\bar{M}_{n,expt}$[b] (g·mol$^{-1}$) | $I_p$[c] | A−PS−H[d] |
|---|---|---|---|---|---|
| *i*-Bu$_3$Al | 0.7 | 7300 | 6600 | 1.15 | Bu−PS−H and H−PS−H |
| BuMgOBT | 3.0 | 7200 | 5700 | 1.2 | Bu−PS−H and H−PS−H |
| BuMgOBT | 1.0 | 12 100 | 9600 | 1.15 | Bu−PS−H and H−PS−H |
| *n,sec*-Bu$_2$Mg | 2.0 | 6800 | 7100 | 1.15 | Bu−PS−H |

[a] $\bar{M}_n$ calculated from $[PSLi]_0$ or $[PSLi + n,sec\text{-}Bu_2Mg]_0$. [b] $\bar{M}_n$ measured by SEC. [c] Polydispersity index estimated from SEC. [d] Polystyrene chain-ends characterized by MALDI−TOF mass spectroscopy.

**Table 4. Termination Rate and Half-life Time ($t_{1/2}$) of Active Centers at 50 °C in Cyclohexane Solution under $H_2$ Atmosphere**

| | [Mg]/[Li] | P (bar) | $[H_2]$[a] (mol·L$^{-1}$) | $R_t$/[RLi] (min$^{-1}$) | $k_{tapp}$ (L·mol$^{-1}$·min$^{-1}$) | $t_{1/2}$ |
|---|---|---|---|---|---|---|
| PSLi | 0 | 1.1 | $5.5 \times 10^{-3}$ | | | ∼40 min |
| BuMgOBT/PSLi | 2 | 1.1 | $5.5 \times 10^{-3}$ | $3.4 \times 10^{-4}$ | 0.062 | 34 h |
| BuMgOBT/PSLi | 2 | 50 | 0.24 | $1.5 \times 10^{-2}$ [b] | 0.062[b] | ∼50 min[b] |

[a] See ref 6. [b] Estimated assuming $R_t = k_{t,app}[RLi][H_2]$ and experimental $k_{t,app}$ of line 2.

**$H_2$ as Chain Transfer Agent for Styrene Anionic Polymerization.** Most of the data on chain transfer reactions in anionic polymerization of vinyl monomers (styrene, butadiene, isoprene) deals with toluene[10] used as solvent. However, Quirk recently investigated more efficient chain transfer agents such as 1,1-diphenylpropane in the living anionic polymerization of styrene initiated by alkyllithium.[11] Indeed the use of an efficient, nontoxic, and costless transfer agent is worthy for the large scale development of anionic polymerization since it may significantly reduce the initiator cost.

As shown in previous sections, $H_2$ is able to deactivate PSLi chains and the LiH formed as well as its bimetallic complexes are able to reinitiate styrene anionic polymerization. Therefore, the possibility to use hydrogen as a transfer agent in vinyl aromatic polymerizations was further investigated.

A series of styrene polymerizations was carried out in cyclohexane, under $H_2$ atmosphere ($P$ = 1.2 bar), at 70 °C, using PSLi seeds associated with various organometallic additives, including $R_2Mg$, RMgOR, and $R_3Al$ derivatives. Results are collected in Table 3.

With *i*-Bu$_3$Al and BuMgOBT, the experimental values of $\bar{M}_n$ are slightly lower than the theoretical ones calculated assuming no transfer process. Two different populations of polymers are formed as confirmed by MALDI−TOF. The first one centered in the range 2000−3000 g·mol$^{-1}$ corresponds to PS chains with a H headgroup; the second population with a butyl headgroup is largely predominant and corresponds to PS chains initiated by initial Bu−PSLi seeds. No significant effect due to the presence of hydrogen on the polymer molar mass distribution is observed, indicating a low contribution of the transfer process in our conditions.

As indicated earlier, for the *n,sec*-Bu$_2$Mg/PSLi system ([Mg]/Li] = 2.0) the absence of chain transfer worsens the situation. This likely results from the ability of $R_2Mg$ derivatives to easily exchange its secondary alkyl group with lithium hydride, therefore reforming Bu−Li initiating species and Bu−Mg−H, as already been discussed.

Further investigations were carried out to determine which step of the transfer process is rate determining in the BuMgOBT/PSLi system. The deactivation of active species by $H_2$ was followed by UV−visible spectroscopy monitoring the optical density decrease of the active centers located at 330 nm at 50 °C. The initial termination rate was then estimated at 50 °C assuming a first-order kinetics ($R_t = k_{tapp}[RLi][H_2]$) with $[H_2]$ roughly constant in the reaction medium during the initial stage of the deactivation process. The results gathered in Table 4 show a strong decrease of the hydrogenolysis rate constant compared to that observed with PSLi alone, suggesting that the formation of bimetallic complexes yields a strong decrease of the reactivity of poly(styryllithium) species. Although the propagation rate is also drastically reduced, the rate of formation of lithium hydride in the reaction medium remains too low to yield efficient chain transfer. To shift the reaction toward the formation of lithium hydride, much higher $H_2$ pressures are required in order to increase its instantaneous concentration in the reaction medium; see Table 4, line 3. Experiments could not be attempted under these conditions.

## Conclusions

Lithium hydride, as long as it remains soluble, is a potential initiator of styrene anionic polymerization, at least at 100 °C, even in nonpolar solvent. The efficiency of this initiator is improved by complexation with organometallic derivatives which first ensure its solubility and then reduce the styrene propagation rate. When *n,sec*-Bu$_2$Mg is used as additive, Li−H bonds are not the real initiating sites, the polymerization proceeding after a ligand exchange between the two metal atoms.

At high temperature, $H_2$ acts as a chain transfer agent in styrene anionic polymerization. However, to be efficient, its concentration in the medium should be high in order to shift the equilibrium toward the formation of metal hydride. This requires high hydrogen working pressures.

This study also affords some support for the reactivity, at least at high temperature, of aged systems containing isomerized $PSM_t$ species as suggested by some authors.[12] This reactivity likely results from the metal hydride which is also generated by $PSM_t$ thermal deactivation.

The possibility to use directly “commercial” metal hydrides to initiate styrene retarded anionic polymerization will be presented in a following paper.

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## References and Notes

(1) Ménoret, S.; Fontanille, M.; Deffieux, A.; Desbois, P. *Macromol. Chem. Phys.* **2002**, *203*, 1155.

(2) (a) Ashby, E. C.; Nohding, A. *J. Org. Chem.* **1980**, *45*, 1041: (b) Klusener, P.; Brandsma, L.; Verkruijsse, H. D.; Scheleyer, P. v. R.; Pi, R. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 465: (c) Pi, R.; Friedl, T.; Scheleyer, P. v. R.; Klusener, P.; Brandsma, L. *J. Org. Chem.* **1987**, *52*, 4299.

(3) (a) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 982. (b) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

(4) Williams, J. L. R.; Laakso, T. M.; Dulmage, W. J. *J. Org. Chem.* **1957**, *23*, 638.

(5) Needles, H. L. *J. Polym. Sci., Part A-1* **1969**, *7*, 1437.

(6) Kertes, A. S. *Solubility Data Series*; Pergamon Press: Oxford, England, 1981; Vol. 5/6, pp 25.

(7) (a) Kern, W. J.; Anderson, J. N.; Adams, H. E.; Bouton, T. C.; Bethea, T. W. *J. Appl. Polym. Sci.* **1972**, *16*, 3123. (b) Viola, G. T.; Bortolotti, M.; Zazzetta, A. *J. Polym. Sci., Part A, Polym. Chem.* **1996**, *34*, 13.

(8) Ménoret, S.; Carlotti, S.; Fontanille, M.; Deffieux, A.; Desbois, P.; Schade, C.; Schrepp, W.; Warzelhan, V. *Makromol. Chem. Phys.* **2001**, *202*, 3219.

(9) Desbois, P.; Fontanille, M.; Deffieux, A.; Warzelhan, V.; Schade, C. *Macromol. Symp.* **2000**, *157*, 151.

(10) Arest-Yakubovich, A. A.; Litvinenko, G. I. *Prog. Polym. Sci.* **1996**, *21*, 335.

(11) Quirk, R. P.; Li, J. *Macromol. Symp.* **1996**, *107*, 199.

(12) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133.

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