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Retarded styrene anionic polymerization. 8. Influence of dialkylphenoxyaluminum on the reactivity of polystyryllithium species

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Abstract

This paper discusses the influence of dialkylphenoxyaluminum additives on the retardation of styrene polymerization initiated by alkyllithium. Data are compared with results obtained with trialkylaluminum. Similar decreases of the propagation rate can be achieved with both types of compounds. Although with R_3Al additives (*i*-Bu_3Al, Et_3Al, Me_3Al), reactivity extinction appears with the formation of inactive 1:1 (Al/Li) mixed complexes, at a ratio of $[Al]/[Li] = 1$, in the presence of diisobutyl-2,6-di-*tert*-butyl-4-methyl-phenoxyaluminum, extinction occurs at a ratio of $[Al]/[Li] = 0.5$. This was correlated to an irreversible ligand exchange between the polystyryllithium and the phenoxyaluminum derivative, as proved by the formation of the corresponding lithium phenoxide, prior to formation of a 1:1 complex. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

BHT (2,6-di-*tert*-butyl-*p*-cresol) or similar hindered phenols are generally present in styrene monomer as stabilizers against spontaneous radical polymerization. Styrene purification is therefore required prior to any radical or anionic polymerization process. In previous studies on retarded anionic polymerization, it was shown that the use of inactive organometallic compounds (dialkylmagnesium [1] or trialkylaluminum [2]) in combination with alkyllithium is an effective solution to control the reactivity in the anionic polymerization of styrene in bulk and at high temperature. Considering the hypothesis that reaction of BHT with such organometallic additives could yield an alkylphenoxymetallic compound able to control the styrene anionic polymerization, BHT could be valuably used and the cost of its elimination suppressed. Indeed, it was already known that alkylaluminum with bulky phenoxy substituents can be used as *t*-BuLi additive in order to polymerize MMA, in toluene, in a living way, at room or even at slightly elevated temperatures [3]. Their effect is even more favorable than simple trialkylaluminum on low-temperature MMA anionic polymerizations [4,5] since these derivatives lead to a strong decrease of MMA polymerization rate as well as to a modification of the tacticity of the polymer chains.

In this paper, the influence of diisobutyl-2,6-di-*tert*-butyl-4-methylphenoxyaluminum (*i*-Bu_2AlOBT) on the retardation of styrene anionic polymerization initiated with alkyllithium species was extensively studied. The behavior of *i*-Bu_2AlOBT/polystyryllithium (PSLi) system is compared to previously studied R_3Al/PSLi systems and a mechanism is proposed to explain the reactivity extinction at a ratio of $[Al]/[Li] = 0.5$.

2. Experimental

2.1. Materials

s-Butyllithium (1.3 M in cyclohexane from SAFC, Saint-Quentin Fallavier, France), triisobutylaluminum (*i*-Bu_3Al, 1.0 M solution in toluene from SAFC), 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 oligostyryllithium and distilled before use. Styrene (99%

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from SAFC) was degassed over freshly crushed CaH_2, stored over *n*-butyl-*s*-butylmagnesium and distilled just before use.

2.2. Synthesis of diisobutyl-2,6-di-tert-butyl-4-methylphenoxyaluminum (i-Bu_2AlOBT)

i-Bu_2AlOBT was prepared by reacting triisobutylaluminum (*i*-Bu_3Al) with BHT. Typically, BHT (0.226 g, 1.0×10^{-3} mol) was placed in a graduated burette fitted with PTFE stopcocks and degassed under vacuum at 50 °C before adding 40 ml of dry cyclohexane. Then, an equivalent molar amount of *i*-Bu_3Al solution, 1.0 M in toluene (0.208 g, 1.05×10^{-3} mol), was added by syringe under argon flow. The mixture was let to react completely at room temperature to yield finally a homogenous solution of *i*-Bu_2AlOBT.

2.3. Synthesis of lithium 2,6-di-tert-butyl-4-methylphenoxide (LiOBT)

BHT (0.438 g, 2.0×10^{-3} mol) was placed in a graduated burette fitted with PTFE stopcocks and degassed under vacuum at 50 °C before adding 75 ml of dry cyclohexane. Then, an equivalent molar amount of *sec*-BuLi, 1.3 M in cyclohexane (0.125 g, 1.95×10^{-3} mol), was added by syringe under argon flow at 25 °C.

2.4. Polymerization

Polymerizations were carried out under vacuum or dry argon in cyclohexane at 100 °C in glass flasks equipped with a quartz cell and fitted with PTFE stopcocks. PSLi seeds ($\overline{DP}_n = 5-20$) used as polymerization initiators were prepared by addition under argon flow of *s*-BuLi to styrene in cyclohexane. After titration of the lithium species by means of UV–visible spectroscopy, a known amount of aluminum derivatives was then added to obtain the convenient [Al]/[Li] ratio ([Al]/[Li] = 0–1.3). After styrene addition, the polymer conversion was measured by following the decrease of the monomer concentration by UV–visible spectrometry.

2.5. 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; $\varepsilon_{PSLi} = 13\,000\ l\ mol^{-1}\ cm^{-1}$ at 326 nm, $\varepsilon_{styrene} = 450\ l\ mol^{-1}\ cm^{-1}$ at 290 nm.

2.6. 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.

3. Results and discussion[1]

The reaction of trialkylaluminum with sterically hindered phenols and especially 2,6-di-*tert*-butyl-4-methylphenol (BHT) were already investigated [6,7]. Whereas the stoichiometric reaction of BHT with Me_3Al or Et_3Al is complicated by the disproportionation of the monophenoxide aluminum into bis(phenoxide) aluminum and starting aluminum trialkyl, it was shown that monomeric *i*-Bu_3Al reacts completely with BHT to give cleanly *i*-Bu_2AlOBT which is a stable non-aggregated liquid [8] at room temperature. The difference between the aluminum derivatives was attributed to the dimeric nature of Me_3Al and Et_3Al whereas *i*-Bu_3Al is monomeric.

3.1. Spectroscopic investigations

3.1.1. Influence of i-Bu_2AlOBT on the polystyryllithium UV–visible spectrum

As shown in Fig. 1, the addition of *i*-Bu_2AlOBT onto PSLi seeds rapidly induces the formation of a new UV absorption band at 290 nm whereas the initial PSLi peak tends to disappear. At a [Al]/[Li] ratio equal to 0.5, only a very small shoulder remains present at 326 nm, suggesting that most of the initial PSLi has been transformed into species absorbing at 290 nm. The intensity of the new peak ($\lambda_{max} = 290$ nm) increases with [Al]/[Li] ratios up to $r = 0.5$ and then remains constant. At the same time, the band of the remaining 'free' PSLi initially located at 326 nm broadens and undergoes a slight bathochromic shift suggesting some possible interaction with the newly formed species. The specific absorption of *i*-Bu_2AlOBT (Fig. 2) has only a slight influence on the PSLi and *i*-Bu_2AlOBT/PSLi absorption bands since it absorbs at low wavelength ($\lambda < 290$ nm) and its molar extinction coefficient is relatively low ($\varepsilon_{i\text{-}Bu_2}$AlOBT ~ 2300 $mol^{-1}\ dm^3\ cm^{-1}$ at 284 nm in cyclohexane).

3.1.2. Nature and stoichiometry of the i-Bu_2AlOBT/PSLi complexes

The percentage of converted PSLi seeds as a function of the [Al]/[Li] ratio was estimated from the relative intensity decrease of the 326 nm band (Fig. 3) upon addition of *i*-Bu_2AlOBT onto PSLi seeds. This determination assumes no absorption of the new *i*-Bu_2AlOBT/

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[1] In this study, the stoichiometry of the mixed complexes between Al and Li derivatives is given in the following order (Al/Li).

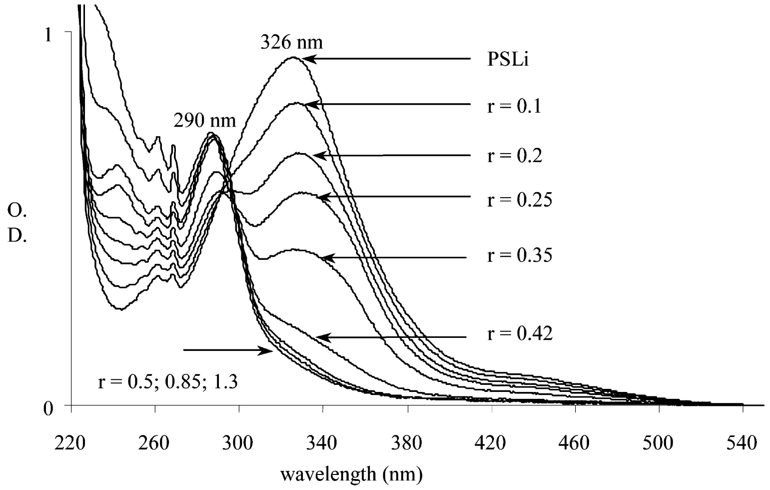


Fig. 1. Influence of i-Bu_2AlOBT increments on the PSLi UV–visible spectrum (cyclohexane, 20 °C, $r = [Al]/[Li]$, $[Li] = 8.4 \times 10^{-3}\ mol\ l^{-1}$).

PSLi species at 326 nm and assigns the remaining peak to the uncomplexed PSLi species.

The experimental values closely fit the curve calculated assuming formation of a 1:2 (Al/Li) mixed complex between PSLi seeds and i-Bu_2AlOBT. No significant deviation from linearity is observed, even for a ratio of [Al]/[Li] close to 0.5, in agreement with a high complexation constant and an almost complete formation of a 1:2 complex at $r = 0.5$. Possible structures for this 1:2 complex are shown in Scheme 1. However, molecular models of i-Bu_2AlOBT show that the steric hindrance of the t-butyl substituents strongly restricts the access to the aluminum for complexation to one side of the molecule [3]. Therefore, the formation of such 1:2 complexes is very unlikely.

A second possibility, based on a ligand exchange between Al and Li atoms prior to formation of a stable 1:1 complex, can be considered to explain the complete disappearance of PSLi absorption band at a ratio of $Al/Li = 0.5$. The trend of organoaluminum compounds to group exchange through redistribution reactions involving an associative mechanism is well known [9,10]. Few examples of ligand exchanges with another metal derivative are described [11–13]. Systems involving t-BuLi and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) were studied by Clegg et al. [14] and it was shown that the reaction yields the corresponding LiOBT.

This process may be described in two steps (Scheme 2).

Step 1. Inside the mixed (1:1) complex which is instantaneously formed between PSLi species and i-Bu_2AlOBT (complex C_1), a ligand exchange between PSLi and Al-OR bonds takes place rapidly so that the absorption band of C_1 complex is not experimentally observed.

A reliable evidence for this process was found in the formation of LiOBT crystals from concentrated solutions of i-Bu_2AlOBT/PSLi in cyclohexane at 100 °C. Indeed, at this temperature, LiOBT, which has a low solubility crystallizes, to yield large crystals. These crystals were isolated and washed with cyclohexane. Their UV–visible spectrum (absorption bands at 241 and 293 nm) is similar to that obtained with LiOBT directly synthesized by reaction between s-BuLi and BHT in cyclohexane (Fig. 4).

It was also checked that the same crystallization process takes place rapidly when this solution is set at 100 °C as confirmed by the decrease of the LiOBT characteristic absorption bands. The solubility limit of LiOBT was estimated to be around $5 \times 10^{-3}\ mol\ l^{-1}$ at 100 °C in cyclohexane.

Step 2. Due to its high dilution and its low molar extinction coefficient ($3900\ mol^{-1}\ dm^3\ cm^{-1}$ at 293 nm in

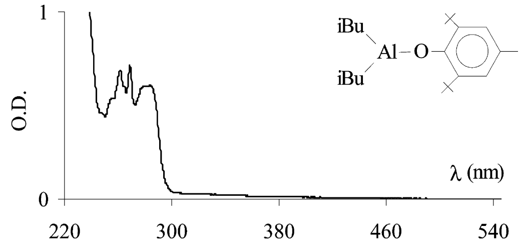


Fig. 2. UV–visible spectrum of i-Bu_2AlOBT (cyclohexane, 20 °C, $[i$-$Bu_2AlOBT] = 2.6 \times 10^{-2}\ mol\ l^{-1}$). The peaks at 261 and 268 nm correspond to signals of toluene used as i-Bu_3Al solvent.

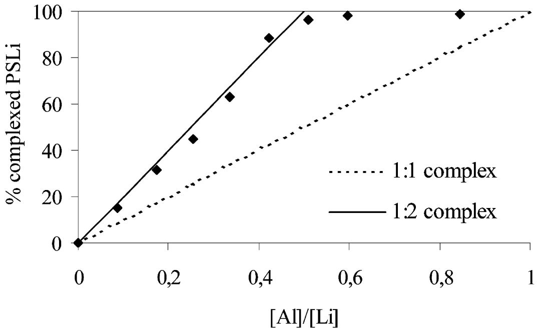
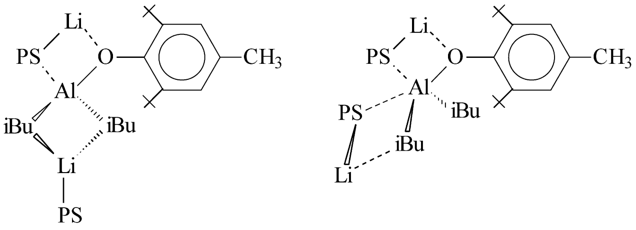


Fig. 3. Percentage of converted PSLi as a function of the [Al]/[Li] ratio (◆). $[PSLi]_0 = 8.4 \times 10^{-3}\ mol\ l^{-1}$.



Scheme 1. (1:2) complexes between PSLi and i-Bu_2AlOBT. Some possible structures.

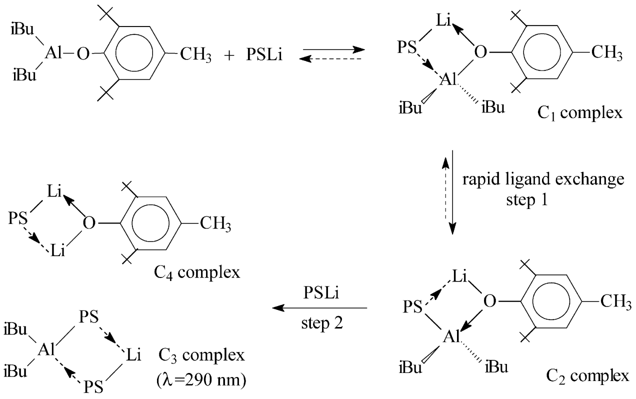
cyclohexane at 20 °C), the formation of LiOBT has little influence on the UV–visible spectrum of PSLi species (complexed and uncomplexed). Although the LiOBT band at 293 nm is superposed to the band at 290 nm, the latter can be attributed mainly to new PSLi chromophores.

In direct relation to the formation of LiOBT, ligand exchanges yield conversely i-Bu_2AlPS. The new aluminum derivative is able to competitively complex with a new PSLi species to form a 1:1 i-Bu_2AlPS/PSLi complex. Therefore, the disappearance of the uncomplexed PSLi absorption band at 326 nm corresponds to twice the amount of added i-Bu_2AlOBT derivative. Trialkylaluminum compounds associated to PSLi usually give $(1{:}1)_n$ complexes [2]: for triisobutylaluminum, the 1:1 complex shows an absorption band located at 290 nm.

Different situations can be considered depending on the [Al]/[Li] ratio.

3.1.3. For [Al]/[Li] ≤ 0.5

Assuming the reaction pathway given in Scheme 2 for [Al]/[Li] ≤ 0.5, the formation of complexes C_3 and C_4 must take place. The direct complexation of PSLi with LiOBT (complex C_4) leads to a bathochromic shift of the PSLi band from 326 to 335 nm which is evidently observed in Fig. 1. This is further demonstrated by direct addition of BHT increments on PSLi (Fig. 5). On the contrary, C_3 complexes yield an hypsochromic shift which is associated to the band located at 290 nm (Fig. 1). UV spectra confirmed the preferential complexation of PSLi with i-Bu_2AlPS which is quantitatively formed at [Al]/[Li] = 0.5. C_4 complex is only formed when PSLi is in excess with respect to i-Bu_2AlPS.



Scheme 2. Ligand exchange process between PSLi species and i-Bu_2AlOBT ([Al]/[Li] ≤ 0.5).

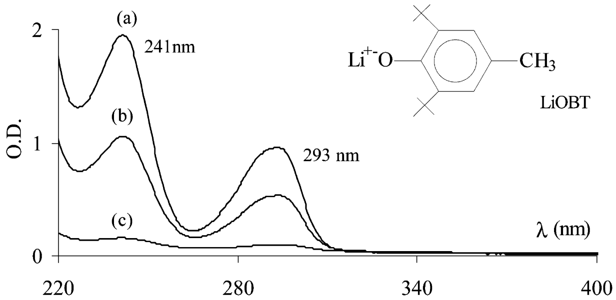


Fig. 4. UV–visible spectra of LiOBT (cyclohexane, [LiOBT] = 0.026 mol l^{-1}). (a) 20 °C; (b) After 45 min at 100 °C; (c) After 16 h at 100 °C.

3.1.4. For 0.5 < [Al]/[Li] ≤ 1.0

For [Al]/[Li] > 0.5, the UV–visible spectrum of PSLi chromophores does not evolve anymore upon addition of i-Bu_2AlOBT increments and remains similar to the one observed at a ratio of [Al]/[Li] = 0.5. i-Bu_2AlOBT likely interacts with LiOBT to form a new i-Bu_2AlOBT/LiOBT complex but does not modify the i-Bu_2AlPS/PSLi complex (no modification of the intensity of the 290 nm band). This supports strong interactions between PSLi and i-Bu_2AlPS in the complex.

The same modifications of the UV–visible spectrum were observed by addition of increasing amounts of PSLi onto a solution of i-Bu_2AlOBT. Therefore, even if the 1:1 complex between i-Bu_2AlPS and PSLi is not 'preformed', it corresponds to the final evolution of the system. This result confirms that the species are involved in equilibrated and reversible reactions.

3.2. Polymerization kinetics

3.2.1. i-Bu$_2$AlOBT/PSLi system

The influence of i-Bu_2AlOBT as retarding agent in

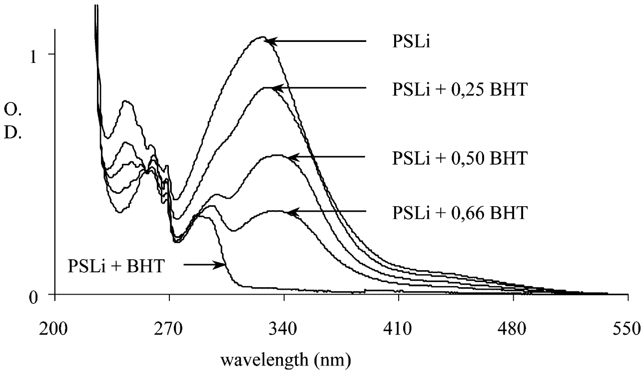


Fig. 5. Influence of BHT increments on the PSLi UV–visible absorption spectrum: in situ formation of LiOBT/PSLi complexes (cyclohexane, 20 °C, [Li] = 8.2 × 10^{-3} mol l^{-1}).

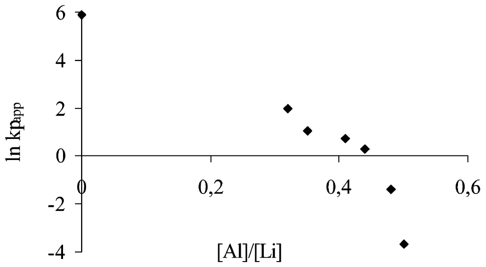


Fig. 6. Variation of the apparent propagation rate constant with the ratio of *i*-Bu_2AlOBT to PSLi (T = 100 °C, cyclohexane). $R_p = k_{p_{app}}$[PSLi][S].

anionic styrene polymerization initiated with PSLi seeds was investigated in cyclohexane at 100 °C (Fig. 6). Styrene apparent propagation rate constants, at various [Al]/[Li] ratios, have been determined for a set of experiments performed at approximately constant initial monomer and PSLi seed concentration. Data obtained in solution are indicated in Table 1. Results show that the addition of *i*-Bu_2AlOBT results in a strong reduction of the styrene polymerization rate for the ratios close to [Al]/[Li] = 0.5. At the ratios higher than 0.5, no polymerization activity is detected anymore.

3.2.2. PSLi/LiOBT system

Since LiOBT is formed by ligand exchange between PSLi and *i*-Bu_2AlOBT, it may contribute to the retarding effect of this system. The influence of LiOBT on styrene polymerization initiated with PSLi was first investigated. Indeed, it was already reported that the propagation rate (R_p) of styrene anionic polymerization initiated with alkyllithium slightly decreases in the presence of increasing amount of lithium alkoxide [15,16] ([*t*-BuOLi]/[*s*-BuLi] = 2, cyclohexane, 30 °C, R_p/2). Similar experiments were carried out replacing the lithium alkoxide by LiOBT. Results gathered in Table 2 indicate a much stronger retarding effect.

3.2.3. Decrease of the polymerization rate in the i-Bu₂AlOBT/PSLi system

1:1 complexes between RLi and R_3Al are known to be inactive as initiator of styrene anionic polymerization [2,17,18]. Therefore, it can be assumed that propagation proceeds either from remaining free PSLi or C_4 complexes, depending on the [Al]/[Li] ratio. A rapid exchange between uncomplexed or PSLi in C_4 complex with species in C_3 complex yields an homogenous growth of all the chains. Since the effective active species corresponds to PSLi not associated with *i*-Bu_2AlPS in 1:1 complex, their concentration is equal to $[PSLi]_e = [PSLi]_0 - 2 \times [i\text{-}Bu_2AlOBT]$. However, apparent propagation rate constants calculated according to this hypothesis do not give a satisfying agreement with experimental results (Table 3). The sole effect of LiOBT on PSLi reactivity cannot explain the drastic decrease of the polymerization rates measured in the *i*-Bu_2AlOBT/PSLi system.

In the range [0–0.33], PSLi species, which are in excess with respect to both *i*-Bu_2AlPS and LiOBT, are likely responsible for the high polymerization rate observed. For ratios in the range [0.33–0.5], the decrease of the propagation rate not only results from the complexation between PSLi and LiOBT. As in the case of *i*-Bu_3Al, 1:2 complexes between PSLi and *i*-Bu_2AlPS (Scheme 3) of low reactivity might also be involved.

For ratios ≥0.5 or higher, all PSLi is assumed to be trapped in the inactive 1:1 complex formed with *i*-Bu_2AlPS. There is neither remaining free PSLi nor PSLi/LiOBT or $(1{:}n)_{n>1}$ (Al/Li) complexes to insure the polymerization. As a consequence, the system is inactive.

Table 1
Polymerization of styrene with *i*-Bu_2AlOBT/PSLi at 100 °C in cyclohexane, initiated by PSLi seeds ($\overline{DP}_n \sim 8$)

[Al]/[Li]	[PSLi]^{a} (mol l^{-1})	$k_{p_{app}}$^{b} (l mol^{-1} min^{-1})	$\bar{M}_{n\ th/Li}$^{c} (g mol^{-1})	$\bar{M}_{n\ exp}$^{d} (g mol^{-1})	I_p^{e}
0	–	370^{f}	–	–	–
0.28	6.7×10^{-3}	–^{g}	5700	900^{h} 6600	1.2
0.32	6.3×10^{-3}	7.1	6200	700^{h} 7000	1.1
0.35	6.0×10^{-3}	2.8	6000	800^{h} 7300	1.2
0.41	4.2×10^{-3}	2.0	7600	10 700	1.1
0.44	4.9×10^{-3}	1.3	6200	6600	1.1
0.48	4.9×10^{-3}	0.24	5900	4700	1.3
0.50	4.55×10^{-3}	0.03	4300	3900	1.2
0.56	4.2×10^{-3}	0	6300	–	–

[a] PSLi concentration after complete ligand exchange with *i*-Bu_2AlOBT. $[PSLi] = [PSLi]_0 - [i\text{-}Bu_2AlOBT]$.

[b] $R_p = k_{p_{app}}$[PSLi][S].

[c] $\bar{M}_n$ calculated from PSLi seeds initial concentration $[PSLi]_0$.

[d] $\bar{M}_n$ measured by SEC.

[e] Polydispersity index estimated from SEC of the main peak in case of bimodal distribution.

[f] Extrapolated from Arrhenius law (E_a = 51.5 kJ mol^{-1}, A = $6.0 \times 10^{+9}$).

[g] For ratios lower than 0.3, polymerization rates are very high at 100 °C and could not be accurately measured by the UV–visible technique.

[h] Bimodal distribution.

Table 2
Polymerization of styrene with PSLi/LiOBT in cyclohexane solution

[LiOBT]/[PSLi]	[PSLi] (mol l^{-1})	T (°C)	$k_{p_{app}}$ [a] (l mol^{-1} min^{-1})	$\bar{M}_{n\ th/Li}$ [b] (g mol^{-1})	$\bar{M}_{n\ exp}$ [c] (g mol^{-1})	I_p [d]
0	–	50	28[e]	–	–	–
2	2.25×10^{-3}	50	0.49	22 000	29 000	1.0
0	–	100	370[e]	–	–	–
2	2.25×10^{-3}	100	9.3	22 000	30 000	1.0

[a] $R_p = k_{p_{app}}[\text{PSLi}][\text{S}]$.
[b] $\bar{M}_n$ calculated from PSLi concentration.
[c] $\bar{M}_n$ measured by SEC.
[d] Polymolecularity index from SEC.
[e] Extrapolated from Arrhenius law ($E_a = 51.5$ kJ mol^{-1}, A $= 6.0 \times 10^{+9}$).

Table 3
Influence of LiOBT as retarding agent; apparent styrene propagation rate constants determined at various PSLi/LiOBT ratio (cyclohexane, 100 °C)

[Al]/[Li]	[PSLi]$_e$ (mol l^{-1})	[LiOBT]/[PSLi]$_e$	$k^{th}_{p_{app}}$ [a] (l mol^{-1} min^{-1})	$k^{exp\ b}_{p_{app}}$ (l mol^{-1} min^{-1})
0.32	3.4×10^{-3}	0.9	–	13
0.35	2.8×10^{-3}	1.2	≥ 9.3	6.2
0.41	1.35×10^{-3}	2.3	~ 9.3	6.4
0.44	1.0×10^{-3}	3.7	–	6.2
0.48	4.3×10^{-4}	12	–	2.7

[a] $R_p = k_{p_{app}}[\text{PSLi}][\text{S}]$.
[b] $R_p = k_{p_{app}}[\text{PSLi}]_e[\text{S}]$.

Table 4
Polymerization of styrene with i-Bu$_2$AlOBT/PSLi (100 °C, cyclohexane, [PSLi]$_0 = 9.2 \times 10^{-3}$ mol l^{-1})

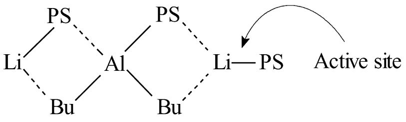
[Al]/[Li]	$\bar{M}_{n\ seeds}$ (g mol^{-1})	$\bar{M}_{n\ th/Li}$ [a] (g mol^{-1})	$\bar{M}_{n\ th/0.7Li}$ [b] (g mol^{-1})	$\bar{M}_{n\ exp}$ [c] (g mol^{-1})	
0.3	2300	8700	11 400	2600	12 200

[a] $\bar{M}_n$ calculated from PSLi initial concentration.
[b] $\bar{M}_n$ calculated assuming that only 70% of the initial PSLi participates to the propagation.
[c] $\bar{M}_n$ measured by SEC.

3.3. Polystyrene molar masses

For ratios [Al]/[Li] in the range [0–0.4], two peaks are present on the SEC chromatogram. One peak corresponds to polystyrene chains with the same molar masses as the initial PSLi seeds ($\overline{\text{DP}}_n \sim 8$). These chains were transferred during the ligand exchange process onto the organoaluminum compound thus yielding i-Bu$_2$AlPS. It was anticipated that these PS chains do not participate to the polymerization.

In order to verify this hypothesis, an experiment was carried out with PSLi seeds of higher molar masses ($\overline{\text{DP}}_n \sim 23$). The corresponding results are given in Table 4 and Fig. 7 for a ratio of [Al]/[Li] equal to 0.3. One of the two peaks observed on the SEC chromatogram still corresponds to initial PSLi seeds (i). The second peak (ii) corresponds to polystyrene chains that have grown during the reaction. As expected, for [Al]/[Li] = 0.3, the experimental molar masses are in agreement with calculated ones, assuming from the ligand exchange mechanism that only 70% of the initial PSLi can participate to the propagation. This is quantitatively consistent with the transfer of one



Scheme 3. Active and inactive complexed PSLi species in i-Bu$_2$AlPS/PSLi: 1/2 complexes ([Al]/[Li] ≤ 1).

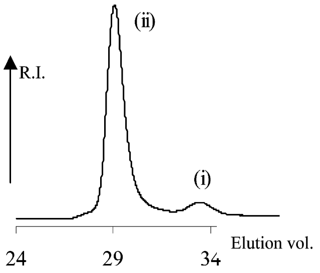


Fig. 7. SEC trace of sample described in Table 4.

polystyrene chain from initial PSLi seeds per organoaluminum compound i-Bu$_2$AlOBT, yielding i-Bu$_2$AlPS.

This behavior is drastically modified for [Al]/[Li] ratios close to 0.5. As the polymerization rate strongly decreases, results of Table 1 suggest that the PS-Al bonds also take part to the propagation. Indeed, the molar masses of the main SEC peak becomes closer to the theoretical molar masses calculated assuming one chain formed per initial alkyllithium species, whereas the SEC peak at low molar masses attributed to i-Bu$_2$AlPS tends to disappear. As already described with Et$_2$AlPS derivatives [19] formed by reaction of Et$_2$AlCl with PSLi, the participation of Al-PS bonds is observed only if the overall reactivity is strongly decreased. Indeed, the exchange of PS chain between Al and Li atoms is a slow process.

4. Conclusion

Aluminum derivatives like diisobutyl-2,6-di-*tert*-butyl-4-methylphenoxyaluminum (i-Bu$_2$AlOBT) resulting from the reaction of trialkylaluminum with hindered phenol are powerful retarding agent for anionic styrene polymerization initiated by alkyllithium species. Inside mixed 1:1 complexes, ligand exchange between the two metals yields the formation of LiOBT and a new trialkylaluminum derivative (i-Bu$_2$AlPS). The latter forms strong complexes with PSLi species. As a consequence, the reactivity extinction occurs at $[\mathrm{Al}]/[\mathrm{Li}] = 0.5$ since at this ratio, all PSLi species are part of an inactive 1:1 complex. Adjustment of the [Al]/[Li] ratio is of utmost importance to control the reactivity.

This behavior is specific for alkylaluminum with a phenoxy substituent but cannot be extended to alkylalkoxyaluminum [20]. This study stresses again that the nature of the substituents anchored to the metals has a drastic influence on the mechanism and extent of retardation in anionic polymerization of styrene. Besides, it affords a reliable evidence for a rapid ligand exchange inside bimetallic (Al/Li) complex. Moreover, it was shown that the presence of LiOBT in alkyllithium solutions yields a strong decrease of the propagation rate, much more pronounced than lithium alkoxides do.

References

[1] Desbois P, Fontanille M, Deffieux A, Warzelhan V, Lätsch S, Schade C. Macromol Chem Phys 1999;200:621.
[2] Desbois P, Fontanille M, Deffieux A, Warzelhan V, Schade C. Macromol Symp 2000;157:151.
[3] Ballard DGH, Bowles RJ, Haddleton DM, Richards SN, Sellens R, Twose DL. Macromolecules 1992;25:5907.
[4] Schlaad H, Müller AHE. Macromol Symp 1996;107:163.
[5] Hatada K, Kitayama T. Polym Int 2000;49:11.
[6] Skowronska-Ptasinska M, Starowieyski KB, Pasynkiewicz S, Carewska M. J Organomet Chem 1978;160:403.
[7] Shreve AP, Mulhaupt R, Fultz W, Calabrese J, Robbins W, Ittel SD. Organometallics 1988;7:409.
[8] Benn R, Jansen E, Lehmkuhl H, Rufinska A, Angermund K, Betz P, Goddard R, Krüger C. J Organomet Chem 1991;411:37.
[9] Hoffmann EC. Bull Soc Chim 1963;1467.
[10] Eisch JJ, Comprehensive organometallic chemistry, vol. 1. Oxford: Pergamon Press; 1982.
[11] Lehmkuhl H. Angew Chem Int Ed 1963;3:107.
[12] Williams KC, Brown TL. J Am Chem Soc 1966;88:4134.
[13] Moedritzer K. Adv Organomet Chem 1968;6:171.
[14] Clegg W, Lamb E, Liddle ST, Snaith R, Wheatley AEH. J Organomet Chem 1999;573:305.
[15] Roovers JEL, Bywater S. Trans Faraday Soc 1966;62:701.
[16] Hsieh HL. J Polym Sci A 1970;8:533.
[17] Welch FJ. J Am Chem Soc 1960;82:6000.
[18] Arest-Yakubovich AA. Macromol Symp 1994;85:279.
[19] Desbois P. Thèse de Doctorat. Université Bordeaux 1, France; 1998.
[20] Menoret SP. Thèse de Doctorat. Université Bordeaux 1, France; 2001.