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Effect of aluminum derivatives in the retarded styrene anionic polymerization

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Abstract

This paper reports on the influence of various aluminum derivatives, i.e. trialkyl aluminum, diisobutylaluminum hydride and diethylaluminum alkoxides, on the anionic polymerization of styrene in hydrocarbons at high temperature. The importance of the structure of the aluminum additives and of the ratio [Al]/[Li] on both the formation of 'ate' complexes, the retardation effect and the reactivity profile of the polymerization are investigated by UV–visible spectroscopy and polymerization studies. The presence of bulky alkyl groups and/or alkoxide ligands onto aluminum allows the retarded polymerization to proceed for [Al]/[Li] ratios higher than one. Some of these systems offers a broad polymerization window in which the rate of polymerization is strongly reduced and remains almost constant over a large range of [Al]/[Li] ratios. While for trialkylaluminum and diethylaluminum alkoxide the number of PS chains formed can be related directly to the initial amount of lithium initiator, for diisobutyl aluminum hydride and diisobutylpolystyryl aluminum, the hydride and polystyryl groups act as second chain carrier, thus yielding the formation of up to two polymer chains per 'ate' complex.

Keywords: Anionic polymerization; Polystyrene; Aluminum derivatives

1. Introduction

Retarded anionic polymerization is an attractive way to achieve the controlled polymerization of styrene in bulk and at high temperature. It is based on the addition of an organometallic compound, like dialkylmagnesium [1–3], zinc or boron derivatives [4] or triisobutylaluminum [5], to alkyllithium or polystyryllithium (PSLi), which forms 'ate' complexes with the propagating ends [6,7]. They act as regulator and reducer of the intrinsic reactivity of the carbanionic species and allow to control the anionic polymerization in bulk at high temperature. In the case of triisobutylaluminum (i-Bu_3Al or TIBAL) a strong retardation effect is observed in styrene and butadiene polymerizations initiated by lithium derivatives at ratios $r=[Al]/[Li]$ ranging from 0.85 to 0.95, whereas at $r=1$ a total extinction of the polymerization activity occurs. In this narrow reactivity window the stability of the propagating species is drastically improved, thus allowing a living-like bulk polymerization of styrene at temperature above 100 °C. However, because of the sharp decrease of the reactivity between $r=0.85$ and 0.95, reproduction of the retarding effect over several runs is a challenge.

The use of trialkylaluminum and alkylaluminum alkoxide or phenoxide as additives in the anionic polymerization of polar monomers such as methacrylates [8–11], *tert*-butylacrylate [12], acrylonitrile [13,14] has been already reported. These systems yield in a strong decrease of the reactivity of the propagating species, which allow a better control of the polymerization. However, with polar monomers and in contrast to PSLi:i-Bu_3Al/styrene systems, the aluminum derivatives should be added in excess with respect to the propagating species to yield a significant deceleration effect.

The present study was implemented with the aims to optimize the operational reactivity window in the high temperature retarded anionic polymerization of styrene and increase the number of PS chains formed per PSLi/aluminum derivatives, by changing the structure and the nature of the ligands.

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2. Experimental

2.1. Materials

Cyclohexane (99.5% from SAFC, France) and toluene (99.5% from SAFC, France) were degassed over freshly crushed CaH_2, stored over polystyryllithium and distilled before use. Styrene (99% from SAFC, France) was degassed over freshly crushed CaH_2, stored over *n*,*s*-dibutylmagnesium and distilled before use. *s*-Butyllithium (1.3 M in cyclohexane from SAFC, France), triethylaluminum (Et_3Al; 1.0 M in hexanes from SAFC, France), trihexylaluminum (*n*-Hex_3Al; 97% from Witco, Germany), diisobutylaluminum hydride (*i*-Bu_2AlH; 1.0 M in cyclohexane from SAFC, France) and diethylaluminum ethoxide (Et_2AlOEt; 1.6 M in toluene from SAFC, France) were used as received. Diethylaluminum-*sec*-butoxide (Et_2AlOs-Bu), or -*tert*-butoxide (Et_2AlOt-Bu) were synthesized in toluene at room temperature by the reaction of triethylaluminum with the corresponding alcohols. Diethyl-*sec*-butylaluminum (Et_2Als-Bu) and diethylpolystyrylaluminum (Et_2AlPS) were prepared by addition of one equivalent of *s*-BuLi or polystyryllithium ($\overline{DP_n} = 5–100$) to a solution of Et_2AlCl. To allow the removal of LiCl formed, final products were filtrated and kept in solution in glass tube under nitrogen.

2.2. UV–visible spectroscopy

The absorption spectra of the polystyryllithium/aluminum derivatives solutions were recorded on a UV–vis spectrometer Varian–Cary 3E using a quartz cell (0.01 cm path-length) attached to the glass reactor; $\varepsilon_{PSLi} = 13{,}000$ mol dm^3 cm^{-1} at 326 nm, $\varepsilon_{styrene} = 450$ mol dm^3 cm^{-1} at 290 nm.

2.3. Polymerizations

They were carried out under dry nitrogen in cyclohexane at 100 °C in glass flasks equipped with a quartz cell and fitted with PTFE stopcocks. Polystyryllithium seeds ($\overline{DP_n} = 5–100$, $[PSLi] = 3.1–8.5 \times 10^{-3}$ M) were used as polymerization initiators. They were prepared by addition of styrene to *s*-BuLi in cyclohexane under nitrogen at 25 °C. A known amount of aluminum derivative was then added to the polystyryllithium seeds solution to obtain the desired ratio [Al]/[Li]. After styrene addition, the polymerization was monitored by following the monomer consumption by UV–visible spectrometry ($\lambda = 290$ nm).

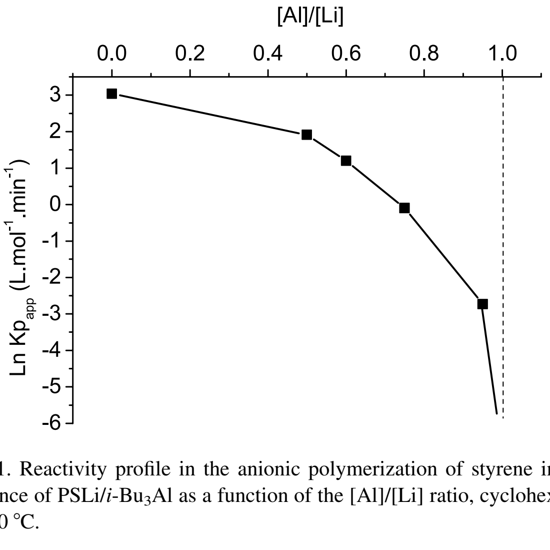


Fig. 1. Reactivity profile in the anionic polymerization of styrene in the presence of PSLi/*i*-Bu_3Al as a function of the [Al]/[Li] ratio, cyclohexane, $T = 50$ °C.

2.4. Polymer characterization

The average molar masses and molar mass distribution of the polystyrenes were determined by size exclusion chromatography (SEC) on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU, refractive index/UV detectors and 4 TSK Gel columns (HXLG 2000, 3000, 4000 and 5000) calibrated with polystyrene standards.

The MALDI-MS (matrix assisted laser desorption ionization mass spectrometry) measurements were performed on a BIFLEX III instrument (Bruker Daltonik GmbH, Bremen). The polymers and the matrix dithranol (1,8,9-trihydroxyanthracen) were dissolved in THF at concentrations of 10 and 20 g/l, respectively. Then the polymer and matrix solutions were mixed in a 1:1 ratio (i.e. 20 µl each). As cationizing agent, 5 vol% (2 µl) of AgTFA (silver trifluoroacetic acid 0.02 molar in THF) is added and this mixture then spotted on the sample holder.

3. Results and discussion

As previously described [5], triisobutylaluminum, used as an additive in the styrene anionic polymerization initiated by lithium derivatives in hydrocarbon media or in bulk, leads to a strong reduction of the reactivity of propagating active species. The rate decrease depends on the ratio [Al]/[Li] and no polymerization is observed for ratios equal or higher than one. This limit corresponds to the quantitative formation of an inactive 1:1 complex (*i*-Bu_3Al:PSLi). At ratio [Al]/[Li] slightly lower than one, the strong decrease in polymerization rate is explained by the formation of a weakly active 1:2 (Al:Li) complex. Fast dynamic equilibrium between the 1:2 and 1:1 complexes results in the formation of a constant number of polystyrene chains through fast exchange reactions. The corresponding polymerisation reactivity profile observed at 50 °C, Fig. 1, also suggests a low equilibrium constant for the formation of the 1:2 (Al:Li) complex from the 1:1 complex and a second PSLi specie: this allows the presence of active PSLi species, non-complexed with *i*-Bu_3Al, likely up to ratio [Al]/[Li] of 0.7–0.8 and, therefore, limit the polymerization reactivity window for high temperature to the range $0.8 < [Al]/[Li] < 1$ [5]. The qualitative evolution of the proportion of the different species present at various [Al]/[Li] ratios is shown in Scheme 1.

In order to enlarge the working reactivity window for styrene high temperature anionic polymerization, the influence on the retardation process of the structure and nature of ligands of the aluminum compounds used as additives to PSLi was investigated.

3.1. *Influence of the alkyl groups in tri n-alkylaluminums*

The formation of Al:Li ‘ate’ complexes between polystyryllithium oligomers and triethylaluminium (Et_3Al) or trihexylaluminum (Hex_3Al) was first examined by UV–visible spectroscopy, Figs. 2 and 3. Although Et_3Al is mainly dimeric in hydrocarbons, in contrast to *i*-Bu_3Al, it also forms an heterocomplex with polystyryllithium as indicated by the drastic changes of the UV–visible absorption spectra. Upon addition of Et_3Al a new peak attributed to the aluminate complex develops at about 290 nm. Its formation is completed at a ratio [Al]/[Li] close to one. In contrast, with the more sterically hindered aluminum derivative, Hex_3Al, the formation of the 1:1 aluminate complex requires an excess of at least three times with respect to PSLi to completely suppress the signal of PSLi species at 327 nm. This indicates that the nature/structure of the aluminum alkyl ligands plays a significant role in the formation of mixed complexes, as in the homocomplexation processes of trialkylaluminums [15]. Styrene polymerization using these new aluminate systems was investigated at 50 and 100 °C. Polymerization results are collected in Table 1. The behavior observed with Et_3Al:PSLi is similar to the one previously reported for *i*-Bu_3Al:PSLi [5]: the reactivity sharply decreases when the ratio [Al]/[Li] gets close to one and polymerization is totally inhibited at r equal to one. At $r=0.90$, at 100 °C, the apparent rate constant of propagation is about two orders of magnitude lower than for PSLi alone ($k_{p_{app},\,Et_3Al/PSLi} = 1/96 k_{p_{app},\,PSLi}$). Although significant, this reactivity decrease is about four times less pronounced than with *i*-Bu_3Al/PSLi systems [5]. Both active and ‘dormant’ chains coexist at [Al]/[Li] ratio ranging from 0 to 1 and as already mentioned fast dynamic equilibrium between the 1:2 and 1:1 complexes results in the formation of a constant number of polystyrene chains through fast exchange reactions.

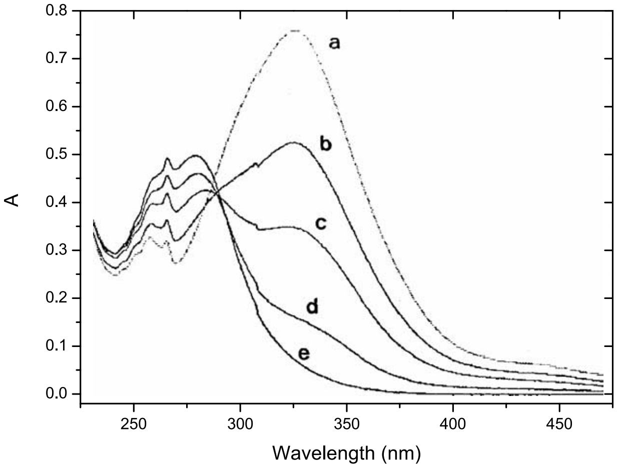


Fig. 2. Influence of increasing amounts of Et_3Al on the PSLi UV–visible spectrum (cyclohexane, $T=25$ °C): (a) PSLi alone, (b) $[Et_3Al]/[PSLi]=0.29$, (c) $[Et_3Al]/[PSLi]=0.58$, (d) $[Et_3Al]/[PSLi]=0.87$, (e) $[Et_3Al]/[PSLi]=1.16$.

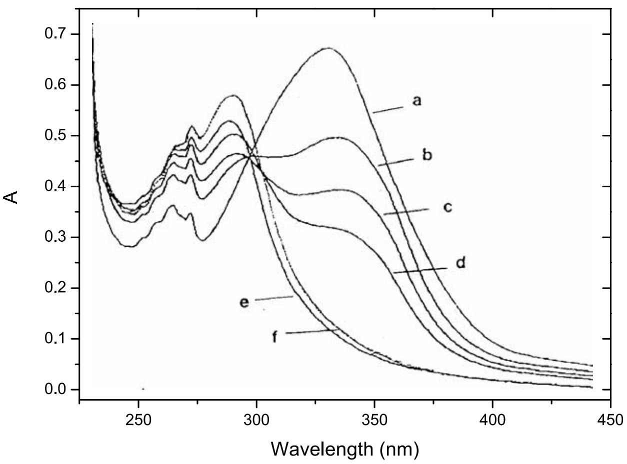
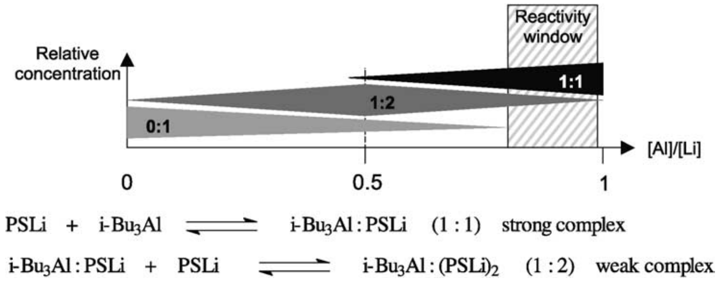


Fig. 3. Influence of increasing amounts of n-Hex_3Al on the PSLi UV–visible spectrum (cyclohexane, $T=25$ °C): (a) PSLi alone, (b) $[n\text{-}Hex_3Al]/[PSLi]=1.0$, (c) $[n\text{-}Hex_3Al]/[PSLi]=1.5$, (d) $[n\text{-}Hex_3Al]/[PSLi]=2.0$, (e) $[n\text{-}Hex_3Al]/[PSLi]=3.0$, (f) $[n\text{-}Hex_3Al]/[PSLi]=6.0$.

In contrast, for Hex_3Al:PSLi, the polymerization proceeds up to [Al]/[Li] ratio of about three and is completely inhibited at $r \geq 3$. According to UV–visible



Scheme 1. Evolution of the relative proportion of PSLi (0:1) and *i*-Bu_3Al:PSLi (1:2 and 1:1) complexes with the ratio [Al]/[Li].

Table 1
Styrene polymerization initiated by Et_3Al/PSLi and n-Hex_3Al/PSLi at different [Al]/[Li] ratio, cyclohexane, $T=25$, 50 and 100 °C

R_3Al	$[R_3Al]/[PSLi]$	T (°C)	[PSLi] ($\text{mol l}^{-1}\times10^3$)	$R_p/[M]$ ($\text{min}^{-1}\times10^3$)	$k_{p_{app}}$ [a] ($\text{l mol}^{-1}\text{ min}^{-1}$)	$\bar{M}_{n(\text{th})}[Li]_0$ [b]	$\bar{M}_n$(SEC)	I_p
Et_3Al	0	25	3.1	20	6.5	24,000	23,100	1.09
		50	6.2	130	21	10,200	10,900	1.05
		100	–	–	370[c]	–	–	–
	0.85	100	4.9	100	20.5	14,000	17,000	1.16
	0.90	50	6.2	1.1	0.18	7500	7300	1.09
		100	6.2	24	3.87	7500	7300	1.09
	1	100	7.4	0	0	–	–	–
Hex_3Al	2	25	7.6	11	1.45	5200	10,100	1.11
	2.7	50	4.2	0.13	0.031	14,300	24,300	1.05
	3	100	5.3	≈0	≈0	–	–	–

[a] $k_{Papp}=(R_P/M)/[PSLi]$.

[b] $\bar{M}_n$ calculated assuming the formation of one PS chain per Li ($\bar{M}_{n(\text{th})}=\bar{M}_n$ PS seeds + $([S]_0/[Li]_0)M_0$yield).

[c] k_{Papp} value extrapolated from the Arrhenius law ($E_a=50$ kJ/mol, $A=1.83\times10^8$).

spectroscopy (Fig. 3) this can be related to the complexation of PSLi by Hex_3Al likely by formation of an inactive 1:1 aluminate complex. As indicated by the total disappearance of its absorption band at 327 nm, quantitative complexation of PSLi requires about three equivalents of Hex_3Al. For ratios lower than three, free PSLi first and then possibly active 1:2 (Al:Li) complexes are present and govern the polymerization. At 50 °C and for a ratio 2.7, $k_{p_{app},\,n\text{–}Hex_3Al/PSLi}$ is equal to $1/680k_{p_{app},\,PSLi}$.

The experimental PS molar masses obtained with the Et_3Al/PSLi system are in good agreement with theoretical ones calculated from the styrene and PSLi seeds initial concentrations, independently of the r-value. This indicates that all the PSLi species in active or dormant 'ate' complexes (1:2 and 1:1) contribute to the polymerization, and that Et_3Al does not act as a new chain generator. In contrast, with Hex_3Al/PSLi systems, the higher experimental molar masses observed compared to theoretical values indicate only a partial initiation and suggest that some of the Li species are inactive in the presence of large excess of trihexylaluminum.

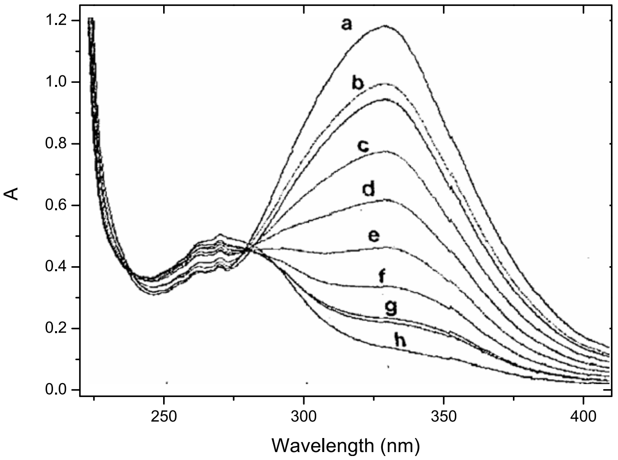


Fig. 4. Influence of increasing amounts of i-Bu_2AlH on the PSLi UV–visible spectrum (cyclohexane, $T=25$ °C): (a) PSLi alone, (b) $[i\text{-}Bu_2AlH]/[PSLi]=0.11$, (c) $[i\text{-}Bu_2AlH]/[PSLi]=0.22$, (d) $[i\text{-}Bu_2AlH]/[PSLi]=0.3$, (e) $[i\text{-}Bu_2AlH]/[PSLi]=0.44$, (f) $[i\text{-}Bu_2AlH]/[PSLi]=0.55$, (g) $[i\text{-}Bu_2AlH]/[PSLi]=0.66$, (h) $[i\text{-}Bu_2AlH]/[PSLi]=0.77$.

These results confirm that the reactivity window is effectively controlled by the rate of formation of heterocomplexes between PSLi ends and the trialkylaluminum derivatives.

3.2. Diisobutyl aluminum hydride

The UV–visible absorption spectra of PSLi seeds after addition of i-Bu_2AlH increments are shown Fig. 4. The evolution of the PSLi absorption bands is comparable to the one observed with trialkylaluminum except that the absorption signal maximum of the new complex is slightly shifted to a lower wavelength (≈275 nm), suggesting an interaction of PSLi with the hydride group of aluminum in the complex. The residual shoulder of PSLi seeds, still present at ratio $[Al]/[Li]=0.66$, vanishes from $r=0.8$. In term of polymerization, Table 2, a drastic reduction of the styrene propagation rate is observed at $r=0.66$ ratio whereas total extinction of the activity is observed at 0.80, in agreement with the formation of strong aluminate complexes.

Data reported so far for retarded styrene polymerization with trialkylaluminum/RLi systems were consistent with the unique contribution of RLi species and the absence of any input of the trialkylaluminum derivatives in the formation of additional PS chains. In contrast, with the i-Bu_2AlH system experimental molar masses are about half than theoretically calculated from the PSLi seeds concentration, suggesting the occurrence of a second chain generation process. The latter could be formed by elimination of a dead PS chain with an unsaturated terminus and lithium hydride (LiH), which could then reinitiate the growth of a new PS chain. Initiation of the retarded styrene polymerization at 100 °C by in situ formed LiH has already been described [16], however, the absence of unsaturated termini on the PS

Table 2
Styrene polymerization initiated by i-Bu_2AlH/PSLi, $Et_2Al$$s$-Bu/PSLi and Et_2AlPS/PSLi systems at different [Al]/[Li] ratio, cyclohexane, $T=100$ °C

$[R_2AlR']$	$[R_2AlR']/[PSLi]$	[PSLi] ($mol\ l^{-1} \times 10^3$)	$R_p/[M]$ ($min^{-1} \times 10^3$)	$k_{p_{app}}$ [a] ($L\ mol^{-1}\ min^{-1}$)	$\bar{M}_{n(th)}$ [b]	$\bar{M}_n$(SEC)	I_p
i-Bu_2AlH	0	–	–	370[c]	–	–	–
	0.68	7.7	2.3	0.30	5800	2600	1.09
	0.70	5.3	1.1	0.21	7700	2300	1.12
	0.80	8.3	0	0	–	–	–
	∞	0	0	0	–	–	–
Et_2Als-Bu	0.85	6.4	3.8	0.59	5600	5400	1.08
	0.90	5.4	0.34	0.063	5100	5100	1.10
Et_2AlPS	0.90	4.8	2.77	0.58	5800	3500	1.06

[a] $k_{Papp}=(R_P/M)/[PSLi]$.
[b] $\bar{M}_n$ calculated assuming the formation of one PS chain per Li ($\bar{M}_{n(th)}=\bar{M}_n$ PS seeds + $([S]_0/[Li]_0)M_0$yield).
[c] See footnote Table 1.

oligomers, as checked by proton NMR, as well as the absence of such transfer process in the corresponding R_3Al/PSLi systems is not consistent with this mechanism. Reversible chain transfer to diisobutylaluminium hydride through ligand exchanges between aluminum and lithium in the i-Bu_2AlH/PSLi complex, Scheme 2, or direct monomer insertion into the i-Bu_2Al–H bond by hydroalumination [17] and polymerization into the Al–C_{sec} bond, Scheme 3, could be postulated.

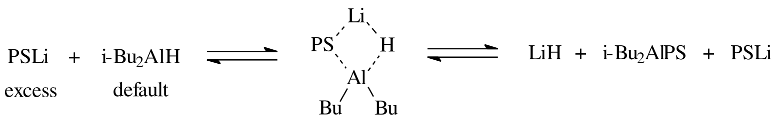
To check this second hypothesis, complementary experiments were implemented using higher molar mass PSLi seeds, see Table 3, to differentiate chains growing from PSLi seeds in the i-Bu_2AlH/PSLi complexes ($r=0.75$) from those formed by hydride initiation or transfer. As shown by Maldi-Tof, Fig. 5, a polymer with a bimodal distribution is formed. The difference between the two PS populations corresponds to the molar mass of the PSLi seeds; the higher fraction with a butyl end-group coming from the PSLi seeds whereas the lower molar mass population possesses an H terminus. These results are in agreement with the growth of PS chains, at the same rate, from the PSLi seeds and the hydride of i-Bu_2AlH in the 'ate' complexes. However, we cannot definitely conclude whether the new chains formed grow directly onto the aluminum center in the complex or result from a reversible chain exchange between the lithium and the aluminum center. This exchange is believed to be rapid with respect to propagation since narrow molar mass distributions are obtained. The bimodal distribution observed corresponds to initiation from species of quite different molar masses (metal hydride and PSLi seeds) from which the chains grow at the same rate due to the exchange process.

In order to check the efficiency towards styrene insertion of such dialkylaluminum-styryl centers in aluminate complexes, Et_2AlPS was prepared and used as additive to PSLi to form an Et_2AlPS/PSLi complex which was used as polymerization initiator. In the range $r=0.8$–0.9, corresponding to a strong retardation of styrene polymerization, the observed polymer molar masses are in agreement with both the participation of PS chains attached to lithium and to aluminum (Tables 2 and 3). This is again in agreement with an active role of dialkylAl–H and dialkylAl–PS bonds as growing center and more likely with a reversible transfer of the active chain from Li to Al centers during the retarded styrene polymerization since there is no direct evidence for the growth of new chains directly from Al–H bond. It is worthy to note that for low ratios ($r \leq 0.7$) no new PS chain starting with hydrogen is observed. Polymerization is rapid and certainly faster than the monomer insertion step into the Al–H bond. No reversible exchange occurs at such condition.

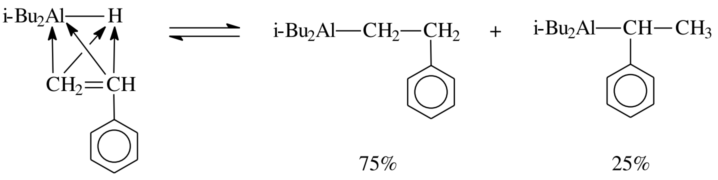
In order to check if these results could be generalized to trialkylaluminum derivatives possessing at least a secondary alkyl group, a similar experiment was performed using $Et_2Al$$s$-Bu prepared by reaction of s-BuLi onto Et_2AlCl. Strong retardation of the polymerization is again observed at ratios lower than one, however, in this case, the polymer molar masses are consistent with the unique contribution of the lithium centers, Table 2. These results indicate that the nature and structure of the groups on the aluminium derivatives are determining for an active contribution of aluminum centers to the formation of PS chains in aluminate complexes initiated styrene polymerization.

3.3. Dialkylaluminum alkoxides

Finally, the influence of several diethylaluminum alkoxide additives, ethoxide (Et_2AlOEt), sec-butoxide



Scheme 2.



Scheme 3.

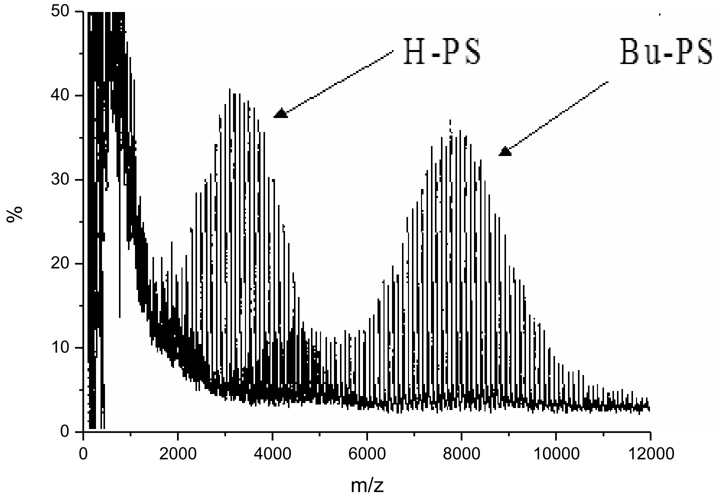


Fig. 5. MALDI mass spectrum of polystyrene oligomers synthesized from [*i*-Bu_2AlH]/[PSLi] = 0.75 (PSLi seeds = 4900 g/mol).

(Et_2AlOs-Bu), and *tert*-butoxide (Et_2AlOt-Bu), has been investigated to broaden the scope of reactivity in aluminum derivatives/PSLi retarded systems. Changes in the UV–visible spectrum of PSLi in the presence of different diethylaluminum alkoxides confirm the formation of 'ate' complexes (Fig. 6) and the strong influence of the nature and bulkiness of the alkoxide group on the reactivity rate. Total disappearance of the PSLi peak is observed at $r = 1$–1.5 for Et_2AlOEt (Fig. 6(a)), 2.5–3 for Et_2AlOs-Bu (Fig. 6(b)) whereas the PSLi band is still observed at $r = 3$ for Et_2AlOt-Bu (Fig. 6(c)).

The polymerization results obtained with Et_2AlOEt/PSLi are given in Table 4. The retardation effect is even stronger than for trialkylaluminum systems. In contrast to previous systems, for $r = [Al]/[Li]$ of about 1.1 ($k_{P_{app},\ Et2AlOEt} = 1/265 k_{P_{app},\ PSLi}$), the retardation reaches a plateau and remains almost constant over a domain of [Al]/[Li] ratios ranging from about 1.1 to 5 (Fig. 7). In this broad domain, the reactivity decreases only by a factor of less than three. The observed PS molar masses are consistent with the formation of one PS chain per PSLi seed chain, whereas their molar mass distribution remains very narrow (1.1). Polymerization experiments performed in absence of any PSLi initiator confirm that the contribution of a radical process in the polymer formation is negligible at this temperature. In contrast to previous trialkylaluminum:PSLi systems, these results are in agreement with the formation of an active diethylaluminum ethoxide:PSLi complex for ratios higher than one, which is able to polymerize styrene at 100 °C, and permits to greatly enlarge the reactivity window.

The Et_2AlOs-Bu/PSLi behaves relatively similarly as the

Table 3
Molar mass of polystyrenes obtained initiated by *i*-Bu_2AlH/PSLi and Et_2AlPS/PSLi systems at different [Al]/[Li] ratios, cyclohexane, $T = 100$ °C

[R_2AlR']	[R_2AlR']/[PSLi]	$\bar{M}_n$ PSLi seeds	$\bar{M}_{n(th)}$[Li][a]	$\bar{M}_{n(th)}$ $[Al]_0 + [Li]_0$	$\bar{M}_n$(SEC)	I_p
i-Bu_2AlH	0.75	4900	9800	2800[b]	3000	1.10
				7300[c]	7300	1.08
Et_2AlPS[d]	0.80	10,000	15,800	3900[b]	3800	1.09
				13,200[c]	14,000	1.06
	0.90	10,000	17,200	4500[b]	4700	1.07
				13,800[c]	13,600	1.06

[a] $\bar{M}_n$ calculated assuming the formation of one PS chain per Li ($\bar{M}_{n(th)} = \bar{M}_n$ PS seeds + $([S]_0/[Li]_0)M_0$yield).

[b] Assuming hydride initiation.

[c] Assuming initiation from PSLi seeds.

[d] Et_2AlPS: $\bar{M}_n(PS) = 700$ g/mol.

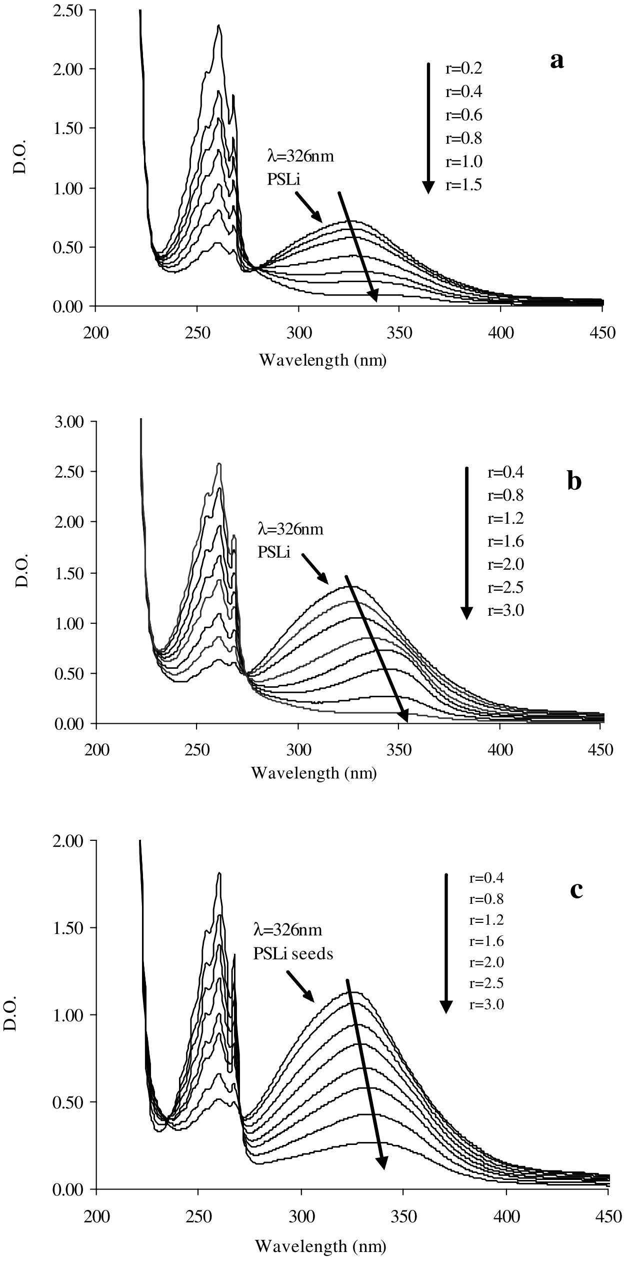


Fig. 6. Influence of increasing amounts of Et_2AlOEt (a), Et_2AlOs-Bu (b) and Et_2AlOt-Bu (c) addition on the PSLi UV–visible spectrum at 20 °C in cyclohexane, $r=[Al]/[Li]$.

ethoxy complex, however, higher proportions of the aluminum derivatives with respect to PSLi are necessary to reach the reactivity plateau ($r>3.5$–4). This could be due to the presence of uncomplexed PSLi in the system, which contributes strongly to the observed reactivity. For Et_2AlOt-Bu/PSLi a very fast and uncontrolled styrene polymerization is observed in these conditions. This can be explained by the larger size of the ligand which does not favour the complexation between the two species yielding to a high proportion of uncomplexed PSLi chains, even in presence of a three-fold excess of Et_2AlOt-Bu.

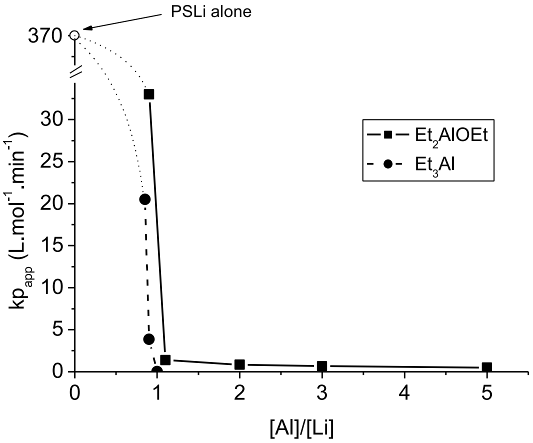


Fig. 7. Variation of $k_{p_{app}}$ with the ratio [Al]/[Li] for PSLi/Et_2AlOEt. For comparisons $k_{p_{app}}$ of PSLi/Et_3Al systems are given at different ratios (cyclohexane, 100 °C).

4. Conclusion

We have shown that aluminum derivatives used as additives to PSLi are good retarding agents for high temperature styrene polymerization. Depending on the nature and structure of the aluminum ligands the retardation effect takes place at [Al]/[Li] ratio, lower or higher than one. This can be related to the ease of formation of aluminate (1:1) complexes and the quantitative complexation of PSLi species by the aluminum derivative. The presence of bulky ligands on the aluminum is not favorable to complex formation and tends to shift the retardation effect to r-values much higher than one. In the case of triethylaluminum and dialkylaluminum hydride, the 1:1 complexes formed are inactive towards styrene polymerization and retardation is governed by the reactivity and the proportion of a 1:2 Al:Li complex. The narrow domain of existence of this 1:2 complex, in absence of any uncomplexed PSLi, determines the reactivity window where retardation is operational.

In contrast, complexes remain active for ratios higher than one and exhibit a very low intrinsic reactivity with dialkylaluminum alkoxides. This results in a quite different reactivity profile with respect to [Al]/[Li] ratios, which can be characterized by two distinct domains. In the first one the reactivity decreases with the consumption of PSLi by the dialkylaluminum alkoxide to form the ‘ate’ complex. In the second one, the reactivity reaches a plateau corresponding to a complex close to the 1:1 stoichiometry and the presence of inactive dialkylaluminum alkoxide in excess. These last initiating systems offer a very broad operational domain for high temperature retarded anionic styrene polymerization.

In most of these polymerization systems, the number of PS chains is determined by the amount of lithium species without any noticeable contribution of the aluminum derivatives to the chain formation. However, when an hydride or styryl group is present in the aluminum derivatives, more than one PS chain per ‘ate’ complex can be produced through either reversible chains exchange

Table 4
Styrene polymerization in the presence of Et_2AlOEt/PSLi seeds at different [Al]/[Li] ratio, cyclohexane, $T = 100$ °C

[Et_2AlOEt]/[PSLi]	[PSLi] (mol L^{-1} × 10^3)	$R_p/[M]$ (min^{-1} × 10^3)	$k_{p_{app}}$ [a] (L mol^{-1} min^{-1})	$\bar{M}_{n(th)}$ [b]	$\bar{M}_n$(SEC)	I_p
0	–	–	370[c]	–	–	–
0.9	6.5	0.21	33	8000	9300	1.16
1.1	6.4	0.009	1.4	6700	7500	1.09
2.0	5.9	0.005	0.9	5500	5900	1.07
3.0	3.7	0.003	0.7	5400	5600	1.03
5.0	5.4	0.0025	0.5	3600	2600	1.03

[a] $k_{Papp} = (R_P/M)/[PSLi]$.

[b] $\bar{M}_n$ calculated assuming the formation of one PS chain per Li ($\bar{M}_{n(th)} = \bar{M}_n$PS seeds + ([S]$_0$/[Li]$_0$) × M_0 × yield).

[c] See footnote Table 1.

between the two metals, which seems more probable, or direct insertion of styrene into aluminum-hydride and then into aluminum–styryl bonds.

Further studies of these aluminum-based retarded polymerization systems are in progress.

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