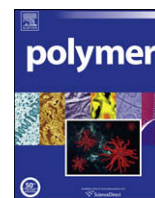


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Feature Article

Retarded anionic polymerization (RAP) of styrene and dienes

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ABSTRACT

The possibilities to achieve a quantitative living-like anionic polymerization of styrene and dienes in the absence of solvent and at elevated temperature and using inexpensive initiating systems were explored to make the anionic polymerization competitive with industrial radical processes and allow the industrial production of anionic polystyrene (PS). It implied at first to control the reactivity and stability of initiating and propagating active species in such unusual operating conditions. To achieve these goals the so-called styrene and butadiene “Retarded Anionic Polymerization” (RAP) have been developed. This review focuses on the description of different bimetallic anionic polymerization systems which are able to approach or fulfill the industrial conditions for styrene and dienes anionic polymerizations.

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1. Introduction

Industrial anionic polymerization was launched in 1938 at IG Farben in Germany with the production of polybutadiene. It was followed about twenty years later by the discovery of the first living anionic polymerization by Szwarc [1,2]. The synthesis of well-defined polymers with precisely controlled molecular architecture allowing the preparation of nano-structured materials could then start. Nowadays a significant amount of rubbers and thermoplastic elastomers (TPE) are prepared by living-type anionic polymerization of styrene and dienes. They found applications in various domains including tires, adhesives, asphalt, thickeners, lubricants, textile, floor, footwear, toys, packaging, cosmetics, paper, etc.

A living polymerization is a reaction without transfer and termination reactions that can proceed up to complete monomer conversion. In addition, when initiation is quantitative and fast compared to the propagation reaction, polymers with precisely controlled chain length and narrow molar mass distribution can be obtained. In the case of an industrial styrene polymerization this would permit to avoid any specific washing or degassing steps, which are necessary in the radical process to remove residual monomer and low molar mass oligomers. Since head-to-head defects along the chains are absent, anionic polystyrene would exhibit also a better thermal stability than radical one. Therefore, production of anionic polystyrene (PS) would be of interest if the

conditions required to control the polymerization could be adapted to the market and be able to compete economically with industrial radical processes. The use of organic solvents and of expensive alkyllithium initiators, as well as the relatively low reaction temperatures required, was some important limitation to overcome. The possibilities to achieve a quantitative living-like anionic polymerization of styrene in the absence of solvent and at elevated temperature, using inexpensive initiating systems, were the main targets identified to tremendously decrease the cost of the anionic process. This implied at first to control the reactivity and stability of initiating and propagating active species in such unusual operating conditions.

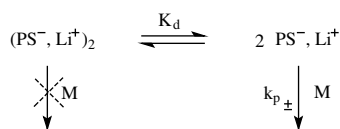
To achieve these goals we have developed the so-called styrene and butadiene “Retarded Anionic Polymerization” (RAP), in which the conditions for reducing the global reactivity of the active species in highly concentrated media (up to bulk conditions) and at high temperature (>100 °C), much above the glass transition of PS to reduce the viscosity were established. This review focuses on the description of several bimetallic anionic polymerization systems which are able to approach or fulfill the industrial conditions for styrene and dienes anionic polymerizations.

It has been shown a long time ago that the substitution of alkali metal counter-ions by alkaline-earth ones may lead to a significant decrease of the styrene and dienes overall polymerization rates in THF [3–8]. This was explained by the much lower ionic dissociation constants of these derivatives compared to the alkali metal ones and by a propagation reaction proceeding mainly through free ions [4–7]. However, in low polar media the

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situation is different, the reaction is governed by ion pairs and the polymerization rates are in the same order of magnitude as lithium initiators [8]. Despite the predominant presence of aggregated polystyryllithium (PSLi) that are almost inactive (Scheme 1) in low polar media, the reactivity of the minute amount of ion pairs is too high to allow working at elevated temperature and in concentrated monomer conditions.



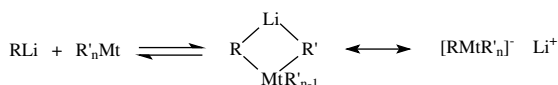
Scheme 1. Active and dormant species in the styrene anionic polymerization in low polar media.

Styrene polymerization initiated by *sec*-butyl lithium (*s*-BuLi) in bulk shows a fast increase in the polymerization rate with time, amplified by incomplete heat-removal, which results in a run-away reaction. For example, at 80 °C, the inside reactor temperature was found to increase as high as 250 °C in a few seconds despite external temperature regulation. Ill-defined polystyrenes exhibiting broad molar mass distributions ranging from oligomers to high polymers and characterized by terminal conjugated unsaturations were obtained.

The influence of a broad series of additives on the reactivity of PSLi species has been reported in the literature. Among these derivatives several have been shown to reduce the reactivity of carbanionic species. Although addition of pluri-amines has been described to decrease the styrene polymerization rate under specific concentration conditions [9–11], the most efficient systems are those based on organometallic additives. The later can be classified into two main groups that show respectively moderate and strong retardation effects:

- alkali salts: alkoxide [12,13], amide [14,15];
- metal alkyls: diethylzinc [16,17], triethylaluminum [16,18], dialkylmagnesium [19,20].

The polarity of the carbon–metal bond, which relies on the electronegativity of the atoms, is a determining parameter for the formation of active species and for their reactivity, however other factors have also to be considered. Organometallic derivatives based on Li, Be, Mg, B and Al metals are known to form homo-complexes in which each molecule is bonded to the others via electron deficient bonds. Mixing derivatives of two of these metals generates the corresponding heterocomplexes, Scheme 2, called “ate” complexes when one metal derivative is alkaline [21,22]. The more commonly used complexes are lithium magnesiate Mg:Li and lithium aluminate Al:Li but systems based on copper, zinc, sodium or potassium derivatives are also of interest and belongs to this family [23].

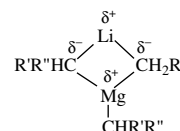


Scheme 2.

We will focus this paper on systems based on the association of alkyl, alkoxide and hydride derivatives of Mg, Al and Zn to alkyl-lithium and alkali metal hydrides, which yield the most interesting initiating systems for the RAP of styrene and dienes.

2. Dialkylmagnesium/alkyllithium systems

The influence of dialkylmagnesium additives on styrene and butadiene polymerizations initiated by alkyllithium ($0 < [\text{Mg}]/[\text{Li}] < 1$) has been investigated at first by Hsieh and Wang [19]. At 50 °C in cyclohexane, they showed that *n,s*-dibutylmagnesium (*n,s*-Bu₂Mg) is inactive alone, but can contribute to the formation of new polymer chains when combined with an alkyllithium in 1:1 *n,s*-Bu₂Mg/*s*-BuLi complex (Scheme 3). Based on the polystyrene molar masses, an initiation efficiency corresponding to the formation of 0.7 PS chain per *n,s*-Bu₂Mg, in addition to the one formed by *s*-BuLi, was observed in cyclohexane at 50 °C. Addition of *n,s*-Bu₂Mg to *s*-BuLi was found also to lower styrene and butadiene polymerization rates by a factor of 2–3 when increasing the ratio $[\text{Mg}]/[\text{Li}]$ from 0 to 0.8.



Scheme 3. Ate complex formation between dialkylmagnesium and alkyllithium.

A similar system based on the combination of *n*-BuLi or *n*-BuNa with *n,s*-Bu₂Mg at ratio $r = [\text{Mg}]/[\text{Mt}] = 1$ in benzene was investigated by Fetters and co-workers [20] for both the polymerization of styrene and isoprene. The PS molar masses were consistent with the formation of one PS chain per BuLi or BuNa and one per *n,s*-Bu₂Mg species. The same system gave polyisoprene with experimental molar masses three times lower than the theoretical ones calculated on the basis of an initiation only by the alkali metal derivative, suggesting again the participation of *n,s*-Bu₂Mg to chain formation, either by direct initiation or through reversible transfer during the propagation.

The UV–visible study of the 1:1 PSLi/*n,s*-Bu₂Mg and 1:1 PSNa/*n,s*-Bu₂Mg complexes shows a shift of the absorption maximum of PSLi ($\lambda_{\text{max}} = 335$ nm) and PSNa ($\lambda_{\text{max}} = 332$ nm) species to lower wavelengths ($\lambda_{\text{max}} = 315$ nm). This was interpreted by an increase of the covalent character of the polystyryl ends in the complex and correlated to the observed decrease of reactivity [22]. A similar explanation was proposed by Van Beylen for the system MgBr₂/PSLi in THF in which the reactivity is governed by the amount of MgBr₂ added [24]. Besides the propagation rate decrease observed for these systems, an increase of the stability of polystyryl ends in mixed complexes [23] was noticed. Indeed, the polystyryl living ends concentration only slowly decreases with time, yielding a PS with a terminal double bond, but no further isomerization of the polystyryl end by proton abstraction was noticed, in contrast to what was observed in the polystyryllithium aging process [25–27].

In these first studies only the influence of low proportions of dialkylmagnesium onto alkyl lithium or alkyl sodium ($r = [\text{Mg}]/[\text{Mt}] \leq 1$) was examined. To control styrene and diene anionic polymerizations at higher temperature and high monomer concentration these mixed initiating systems were investigated using higher dialkylmagnesium/alkyllithium ratios.

In these conditions a strong decrease of the reactivity of the active species is observed while the living-like polymerization characteristics are preserved [28–31]. Polymerization kinetics were investigated at first as a function of the initial $[\text{Mg}]/[\text{Mt}]$ ratio at 50 °C in cyclohexane. As shown in Fig. 1, increase of the dialkylmagnesium/alkyllithium ratio results in a strong decrease of the polymerization rate. For example, at 50 °C, the half polymerization time is reduced by a factor 10³ for $r = 4$ [28].

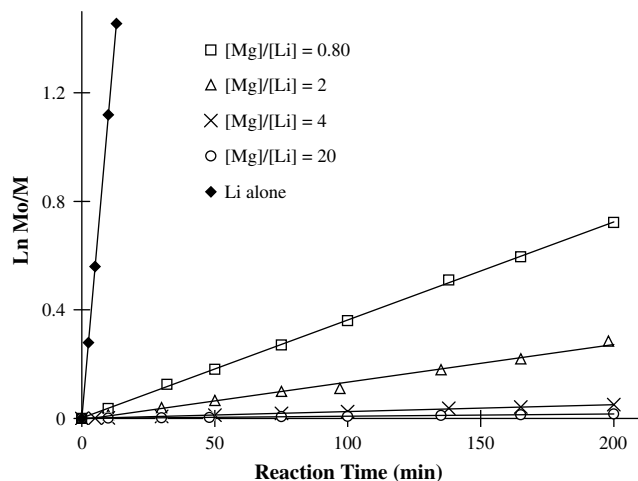


Fig. 1. Influence of $[n,s\text{-Bu}_2\text{Mg}]/[\text{PSLi}]$ ratios on styrene polymerization kinetics ($[\text{PSLi}] = 3\text{--}7 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{styrene}] = 0.3\text{--}0.5 \text{ mol L}^{-1}$; cyclohexane, 50°C).

The influence of $n,s\text{-Bu}_2\text{Mg}$ on the structure of PSLi species was investigated by UV–visible spectroscopy [30]. As shown in Fig. 2a, the addition of $n,s\text{-Bu}_2\text{Mg}$ to PSLi seeds ($r = 0\text{--}1$) leads instantaneously to a shift of the main peak maximum of PSLi species from 326 to 310 nm, indicating a fast complexation. At ratios $[\text{Mg}]/[\text{Li}] < 1$ a fraction of uncomplexed PSLi species is still present (shoulder at 326 nm) in equilibrium with $n,s\text{-Bu}_2\text{Mg}:\text{PSLi}$ heterocomplexes with a stoichiometry of 1:1 (band at 310 nm) and likely 1:2 (Mg:Li) (shoulder at 350 nm). The relative concentration and intrinsic reactivity of each species and in particular of the

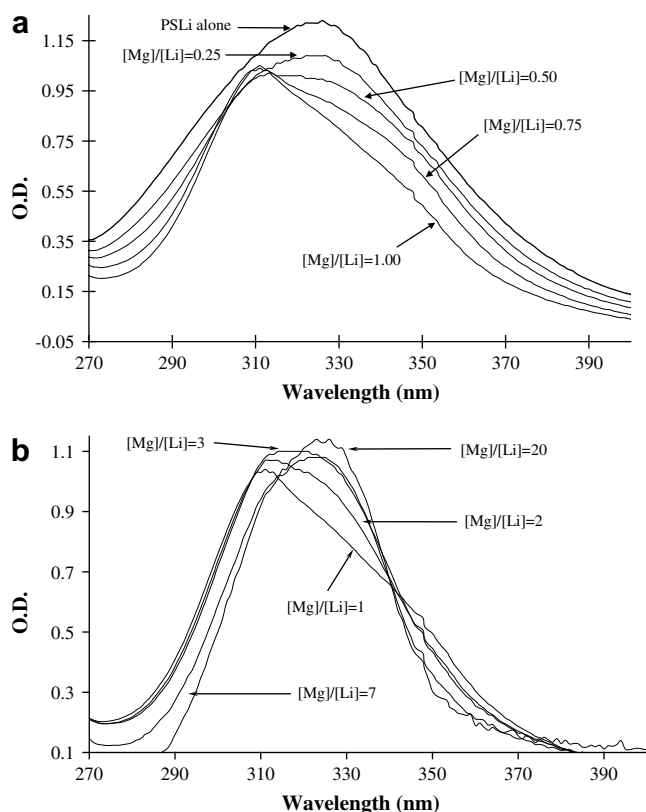
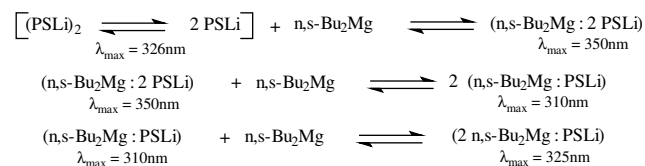


Fig. 2. Influence of increasing amounts of $n,s\text{-Bu}_2\text{Mg}$ on the PSLi UV–visible spectrum (cyclohexane, $T = 25^\circ\text{C}$); (a) $[\text{Mg}]/[\text{Li}] \leq 1$ (b) $[\text{Mg}]/[\text{Li}] \geq 1$.

uncomplexed remaining PSLi species contribute to the observed overall reactivity observed in the $[\text{Mg}]/[\text{Li}] < 1$ range. At $r = 1$ the bands attributed to free PSLi and to the 1:2 complex have almost completely vanished suggesting that their amount is very low compared to the 1:1 complex. At $r > 1$ a new band located at 325 nm starts to increase and then becomes predominant (Fig. 2b), suggesting the conversion of the 1:1 complex into a complex with a higher $n,s\text{-Bu}_2\text{Mg}$ stoichiometry, most likely a 2:1 (Mg:Li) complex. The formation process of the different $[n,s\text{-Bu}_2\text{Mg}]/[\text{PSLi}]$ complexes are summarized in Scheme 4.



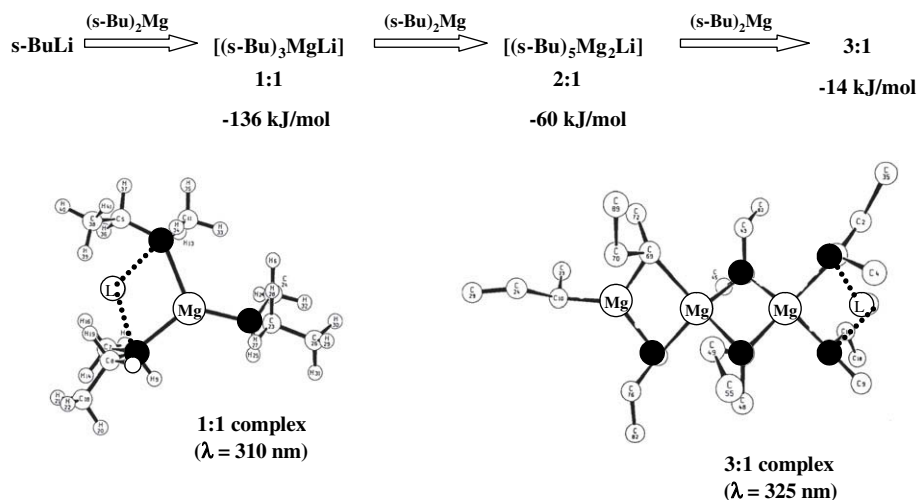
Scheme 4. Formation of $[n,s\text{-Bu}_2\text{Mg}]/[\text{PSLi}]$ complexes with different stoichiometry.

At ratios higher than 2, heterocomplexes of higher stoichiometry can possibly form but as suggested by the very little change observed on the UV–visible spectra the new incoming $n,s\text{-Bu}_2\text{Mg}$ molecules are too distant to affect significantly the electron density on the polystyryl moiety.

Ab-initio calculations also support the formation of a 1:1 $n,s\text{-Bu}_2\text{Mg}:\text{s-BuLi}$ complex (Scheme 5) as well as, for r higher than one, the formation of higher complexes through alkyl–Mg bond association, as in the case of dialkylmagnesium homocomplexes.[30] However, the stabilization energy becomes significantly weaker for complexes of stoichiometry higher than 2:1 (Mg:Li).

As shown in Fig. 3, the propagation rate decreases strongly when increasing r to finally reach a plateau at $r > 2\text{--}3$, which corresponds to an almost constant polymerization rate, k_{Papp} , up to the highest ratio examined, $n,s\text{-Bu}_2\text{Mg}/s\text{-BuLi} = 20$. In the case of a polymerization governed by remaining “free” PSLi species dissociating from the ate complex we should observe a continuous decrease of the propagation rate, up to final extinction, with increasing the Mg/Li ratio. These results therefore support that styrene polymerization proceeds into the mixed Mg:Li complexes as illustrated in Scheme 6. A 200-fold decrease of k_{Papp} is observed between $r = 0$ ($s\text{-BuLi}$ alone) and $r > 3$. A less pronounced retardation effect is observed with magnesium derivatives possessing two primary alkyls, such as $n\text{-Bu},n\text{-OctMg}$, Fig. 3. This is in line with UV–visible spectroscopy which shows some significant differences between the two dibutylmagnesium. As for $n,s\text{-Bu}_2\text{Mg}$, addition of $n\text{-Bu},n\text{-OctMg}$ to $s\text{-BuLi}$ in ratios ranging from 0 to 1 results in a hypsochromic shift of the PSLi band to 309 nm, Fig. 4, in agreement with the formation of a 1:1 mixed complex, and to a peak shoulder at 335 nm that can be attributed to a 1:2 (Mg:Li) complex. Further addition of $n\text{-Bu},n\text{-OctMg}$ does not affect significantly the band location, suggesting that complexes of higher stoichiometry do not significantly form, while the persistence of the peak shoulder at 335 nm at $r > 1$ suggests that the 1:2 (Mg:Li) complex is still present. Similar behavior was observed with $n\text{-Bu},n\text{-EtMg}$ and $(n\text{-Hex})_2\text{Mg}$, stressing the distinct role of primary and secondary alkyls towards heterocomplex formation.

The nature of the alkyl groups attached to magnesium plays also an important role in the observed efficiency of the initiating systems [30,31]. This is illustrated in Fig. 5 for styrene polymerization performed in the presence of different dialkylmagnesium compounds at 100°C in cyclohexane and for r ranging approximately from 1 to 10. For polymerizations initiated with the $n\text{-Bu},n\text{-OctMg}/\text{PSLi}$ system the number of PS chains formed closely corresponds to the initial amount of Li species present. In contrast with



Scheme 5.

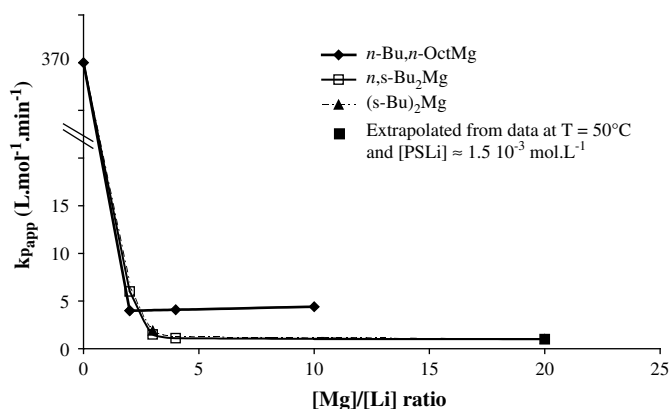
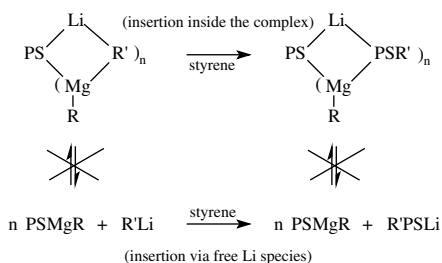


Fig. 3. Influence of $[\text{Mg}]/[\text{Li}]$ ratio on the apparent polymerization rate: effect of primary and secondary alkyl groups in $n,s\text{-Bu}_2\text{Mg}$, $(s\text{-Bu})_2\text{Mg}$ and $n\text{-Bu},n\text{-OctMg}$ ($T = 100^\circ\text{C}$, cyclohexane, $[\text{PSLi}] \approx 5 \times 10^{-3} \text{ mol L}^{-1}$).

$n,s\text{-Bu}_2\text{Mg}$, in addition to one PS chain formed for each $s\text{-BuLi}$, another chain is generated per dialkylmagnesium molecule, whatever the ratio $[\text{Mg}]/[\text{Li}]$ be used. Finally with $(s\text{-Bu})_2\text{Mg}$, the number of chains formed for each dialkylmagnesium is close to 2 at low r values and then decreases to about 1 for $r = 10$. The contribution of alkyl groups attached to magnesium was further confirmed by MALDI-TOF spectrometry, using combinations of magnesium and lithium alkyls with R groups of different size (butyl and hexyl). This allowed us to show the presence of alkyl groups at the PS chain end coming from both the lithium and the magnesium species, with a large preference for secondary alkyls whatever their initial position on lithium or magnesium. As stressed by *ab initio*



Scheme 6.

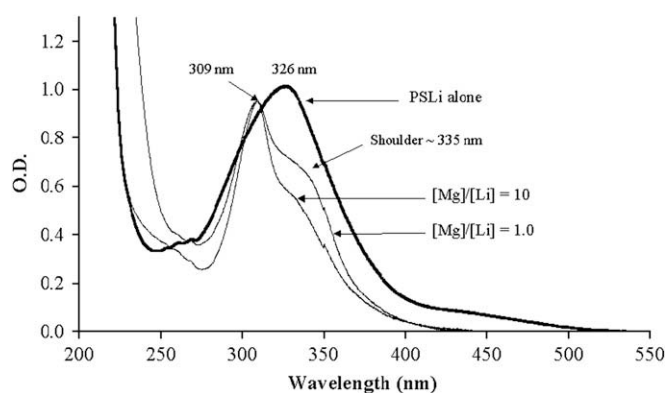


Fig. 4. Influence of increasing amounts of $n\text{-Bu},n\text{-OctMg}$ on PSLi UV-visible spectrum (cyclohexane, $T = 25^\circ\text{C}$).

calculation, it is believed that no direct styrene insertion takes place into R–Mg bonds and therefore that R_2Mg species in the mixed complexes are not a real initiator (Scheme 7). It is believed that reversible ligand exchanges between lithium and neighboring magnesium species, involving alkyl groups and then PS chains, take place inside the mixed complexes. This process, favored in the case

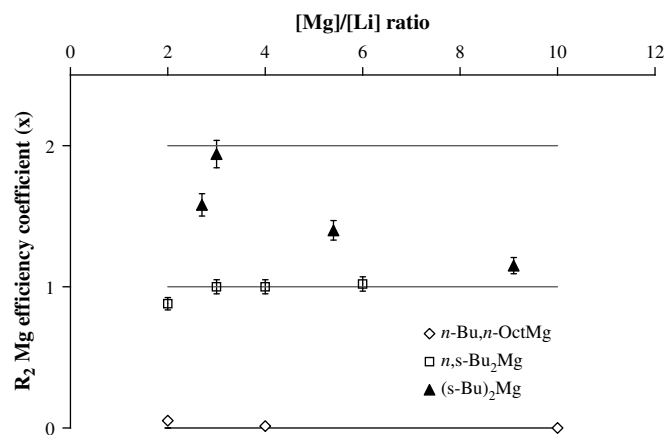
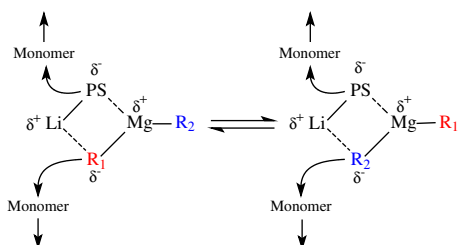
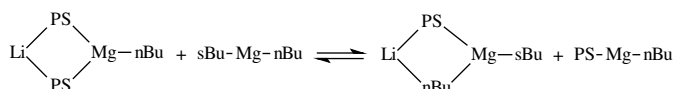


Fig. 5. Influence of $[\text{Mg}]/[\text{Li}]$ ratio on the efficiency factor of dialkylmagnesium (x) ($T = 100^\circ\text{C}$, cyclohexane; $\bar{M}_n(\text{SEC}) = [\text{S}]/([\text{Li}] + x[\text{Mg}])$).



Scheme 7.

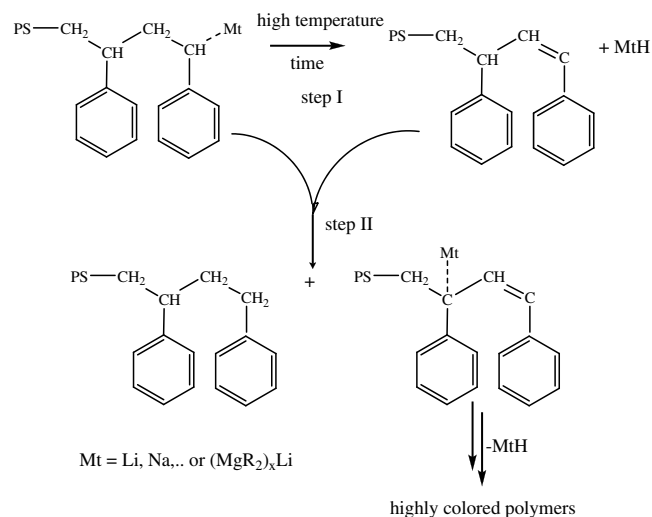


Scheme 8.

of secondary alkyl groups or PS chains attached to magnesium, is equivalent to a reversible transfer reaction and enables the initiation and growth of new PS chains as illustrated in Scheme 7. The large number of PS chains formed with respect to the Li species at high r values indicates that free or oligomeric dialkylmagnesium molecules also contribute to the ligand transfer process with lithium species by entering into the heterocomplexes as illustrated in Scheme 8 for n,s -Bu₂Mg/PSLi systems.

The influence of high temperature on the characteristics of the styrene polymerization has been investigated. At 100 °C in cyclohexane the dialkylmagnesium compounds are still inactive and polymerization is nicely controlled using the combination of R₂Mg with s -BuLi, as demonstrated by the linear increase of the polystyrene molar masses with monomer conversion. This allows the preparation of polystyrene with molar masses up to 150 000 g/mol, see Fig. 6, with relatively narrow distribution (1.1–1.3) whereas the number of PS chains is consistent with the formation of one chain per Li and Mg derivative. For a ratio $[n,s$ -Bu₂Mg]: $[s$ -BuLi] equal to 4 at 100 °C the apparent propagation rate constant is decreased by a factor of 600 as compared to RLi initiated polymerization.

This reactivity decrease is accompanied by a stabilization of the polystyryl ends towards side deactivation processes. The spontaneous deactivation of living ends by metal hydride abstraction, which is the main deactivation process in PSLi systems, step I,



Scheme 9.

Scheme 9, is extremely slow at 100 °C in the case of MgR₂:PSLi systems. Moreover, isomerization of the polystyryl terminus, step II, Scheme 9, is not observed at this temperature. However, at 150 °C in decaline, although polymerization goes very quickly to completion, a rapid evolution of the active polymer solution from yellow to red and brown indicates an isomerization of the living ends (within 30 min) and a colored polystyrene is formed, showing the limits of these dialkylmagnesium/alkyllithium-based bimetallic systems for high temperature styrene anionic polymerization.

Comparable studies carried out with butadiene and isoprene as monomers yield quite similar observations and conclusions. With the n,s -Bu₂Mg/ s -BuLi system a controlled and retarded anionic polymerization of butadiene is obtained ($r = 1$ –4, 40 °C, cyclohexane) with the average formation of one polybutadiene (PBut) chain per lithium and one per magnesium [32]. A detailed study of the PBut microstructure showed an increase of the percentage of 1,2 units with increasing the proportion of magnesium derivatives in the system, see Fig. 7 [32,33]. This microstructure dependence on r is in agreement with a polymerization mechanism involving monomer insertion inside the bimetallic complexes, as already

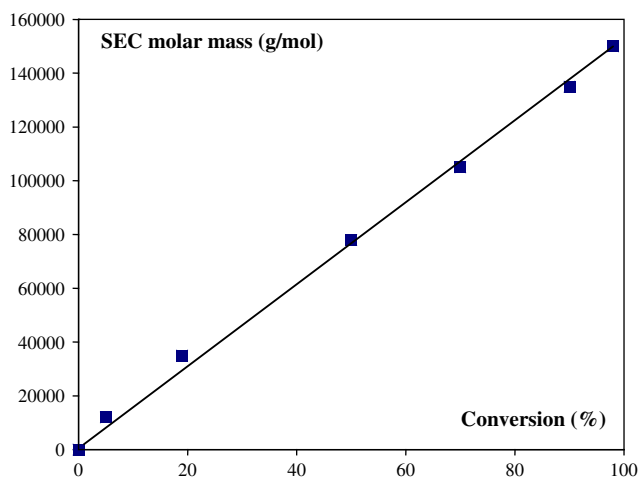


Fig. 6. Evolution of SEC molar masses with conversion for styrene polymerization initiated by n,s -Bu₂Mg/ s -BuLi ($r = 5$) at 100 °C in cyclohexane $[\text{styrene}] = 3.6 \text{ mol l}^{-1}$.

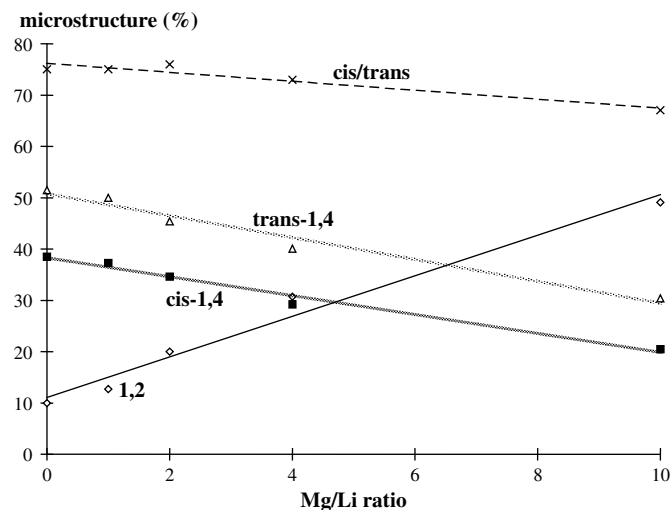
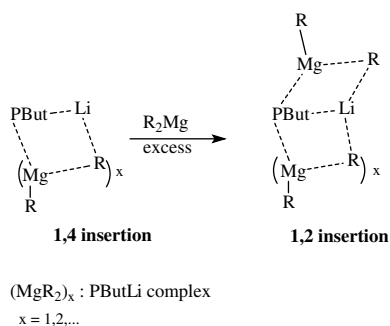
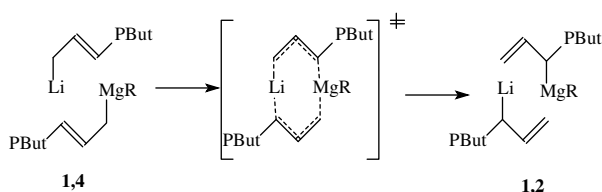


Fig. 7. Influence of $[\text{Mg}]/[\text{Li}]$ ratio on the microstructure of polybutadiene synthesized by n,s -Bu₂Mg/ s -butyl Li, $T = 40$ °C, toluene.



Scheme 10.



Scheme 11.

proposed for styrene polymerization (Scheme 6), rather than a polymerization into “free” PButLi species dissociated from the heterocomplex. Two mechanisms can be considered to explain the continuous change in microstructure with r ; (i) insertion into different types of heterocomplexes in which lithium is complexed by several alkylmagnesium molecules (Scheme 10) or (ii) isomerization of 1,4 units into 1,2 during ligands exchange between polymer chains carried by two distinct metallic species (Scheme 11).

In conclusion, the use of dialkylmagnesium as additive in the styrene or butadiene anionic polymerization initiated by lithium derivatives in hydrocarbon media yields a strong reduction of the reactivity of propagating active species and an improvement of their stability, thus allowing to control their anionic polymerization at high temperature. The nature of the alkyl groups of the initiating system is essential to determine the number of polymer chains formed, secondary alkyls favoring the formation of a larger number of polymer chains, which therefore decreases the additional cost associated to the use of the relatively expensive dialkylmagnesium compounds.

3. Trialkylboron and dialkylzinc/alkyllithium systems

Trialkylboron (R_3B) and dialkylzinc (R_2Zn) derivatives also tend to form aggregates in apolar solvents [34]. Although R_3B are

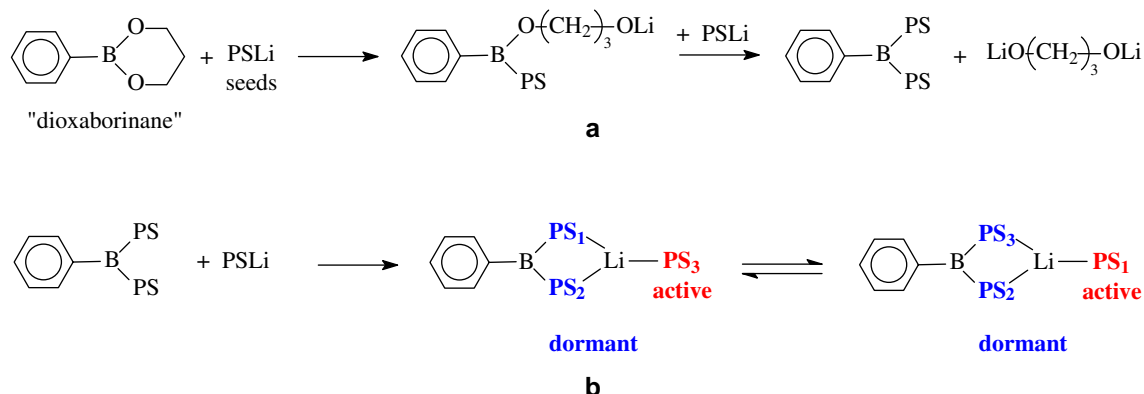
generally monomeric in hydrocarbons, the hydrides (R_2BH) are present as dimers through intermolecular boron–hydrogen bonding. They can also form mixed complexes with alkali metal derivatives [35,36]. Boron derivatives bearing ligands with heteroatoms, such as alkylalkoxyborane, are able to exchange ligands with other metal alkyls through heterocomplex formation followed by a transmetalation reaction, thus yielding trialkylboron species complexed with metal alkoxides [37–39].

Kinetic investigation of the styrene polymerization initiated by *s*-BuLi in the presence of trialkylboron or alkoxyborane, by UV–visible spectroscopy in cyclohexane allowed us to observe the formation of complexes, characterized by an important shift of the PSLi band down to $\lambda = 260$ nm, which induces retardation of the styrene polymerization [40]. For the $Et_3B/PSLi$ system, $[B]/[Li]$ ratios much higher than 1 were necessary to observe a significant decrease of the propagation rate ($k_{papp} = 1/60 k_{papp}(PSLi)$ for $r = 4$ at $100^\circ C$). A similar rate decrease was obtained using an alkoxyborane, i.e. dioxaborinane at a ratio $[B]/[Li] = 0.4$. As shown in Scheme 12a, a transmetalation reaction first takes place between PSLi and borane alkoxy groups, yielding lithium alkoxides and mono-polystyrylborane and di-polystyrylborane that can act as dormant chains. They are re-activated through fast and reversible exchange in the “ate” complex between polystyrylborane and PSLi moieties, thus allowing the growth of all initial polymer chains, Scheme 12b. Total consumption of PSLi in the transmetalation process for ratios $[B-OR]/[PSLi] > 1$ results in the unique presence of polystyrylborane species and a total loss of activity of the system.

The influence of dialkylzinc derivatives towards styrene polymerization initiated by alkyllithium was also investigated. Their effects on PSLi reactivity are much more limited than aluminum derivatives but the polymerization rate still decreases with increasing $[Zn]/[Li]$ ratios. In benzene at $30^\circ C$ the reaction is stopped at a ratio equal to 10. This behavior is also explained by the formation of a 1:1 mixed complex but with a lower equilibrium constant.

An opposite effect was also reported by Hsieh using Et_2Zn/t -BuLi as initiating system for low $[Zn]/[Li]$ ratio [20]. The increase of the styrene polymerization rate upon addition of small amount of diethylzinc was explained by its disaggregating effect onto dimeric lithium species, as confirmed by the viscosity decrease of the PSLi solution.

UV–visible and 1H NMR spectroscopies of diphenylhexyllithium species (DPHLi) in the presence of zinc derivatives in THF were also studied by Waack and Doran [41,42]. A decrease of the characteristic signal of DPHLi ($\lambda_{max} = 496$ nm) was observed with increasing amounts of R_2Zn . At a ratio equal to 15.5 the new signal observed below 400 nm was attributed to the $R_2Zn:DPHLi$



Scheme 12.

complex. This hypsochromic shift can be attributed to an increase of the covalent character of the C–Li bond, which is responsible for the reactivity decrease. NMR analysis allowed to quantify the electronic density on complexed and non-complexed DPPLi and to show fast alkyl exchanges between lithium and zinc derivatives [35,42,43].

Kinetics of styrene polymerization, involving lithium species in the presence of diethylzinc (Et_2Zn) as additive, in cyclohexane at 50 °C, indicate that the apparent polymerization rate constant decreases by half at $[\text{Zn}]/[\text{Li}] = 8$, compared to the system free of additives [40]. This weak retardation effect is explained by the presence of remaining free PSLi species, in relation with the low complexation constant between PSLi and Et_2Zn . The good agreement observed between experimental and theoretical PS molar masses, assuming one chain formed by PSLi seeds, is consistent with a living polymerization process and indicates that alkyl groups of dialkylzinc do not participate in the formation of new PS chains.

4. Trialkylaluminum/alkyllithium systems

Although the mixed initiating systems described so far show a strong retardation effect towards styrene and dienes anionic polymerizations involving lithium species they show some drawbacks in particular the large amount of metal alkyl (MgR_2 , ZnR_2) required to control the polymerization at high temperature and high monomer concentration. In contrast to magnesium, trialkylaluminum compounds are largely used in industry as cocatalyst in Ziegler Natta olefin polymerization and since they form “ate” complexes with alkali metal derivatives they could be good candidates to control the anionic polymerization of styrene and dienes at elevated temperature.

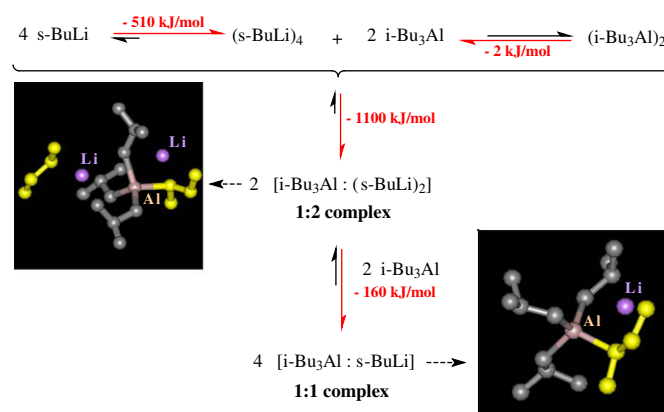
Trialkylaluminum of various structures is readily available and is used already in anionic polymerization in combination with lithium derivatives for the polymerization of polar monomers like (meth)acrylates, vinylpyridine, etc. The complexes formed enable the stabilization of propagating species and reduce the contribution of side reactions [44–50]. Aluminum alkoxides are also used as initiator for lactones polymerization [51,52]. In hydrocarbons they are associated into dimers, trimers or tetramers but the addition of an organometallic derivative (RLi , RNa , ...) allows the formation of mixed complexes as discussed for magnesium derivatives.

Welch was the first to investigate the use of $\text{R}_3\text{Al-RLi}$ mixtures in the anionic polymerization of styrene [16,53]. Addition of a Lewis acid such as triisobutylaluminum strongly decreases the polymerization rate until complete extinction of activity at a ratio of $[\text{Al}]/[\text{Li}] = 1$. This was explained by a diminution of the active alkyl-lithium concentration and the formation of an inactive 1:1 mixed complex in equilibrium with uncomplexed species. This is in line with the fact that AlLiR_4 (and NaAlR_4) complexes are inactive for the initiation of styrene and diene polymerizations in hydrocarbon media [16].

Table 1

Aggregation state of $i\text{-Bu}_3\text{Al/PSLi}$ active chain ends for various $[\text{Al}]/[\text{Li}]$ ratios as measured by viscosimetry ($\bar{M}_n(\text{PSLi}) = 5000 \text{ g mol}^{-1}$, cyclohexane, 35 °C).

$[i\text{-Bu}_3\text{Al}]/[\text{PSLi}]$	$(\eta_{\text{living}}/\eta_{\text{deactivated}})^2$	Scheme view
0	1.80	
0.25	1.65	
0.50	1.43	
0.75	1.26	
0.90	1.11	
1	1.05	



Scheme 13.

Using UV–visible spectroscopy Waack and Doran [53] and then Welck [16] have studied systems based on trialkylaluminum associated to diphenylhexyllithium (DPHLi) [16,53]. The hypsochromic shift of the DPHLi band in the complex was attributed to the participation of electrons of the C–Li bond to the formation of a new dative bond of lower energy [16,53].

The formation of a 1:1 Al:Li “ate” complex in AlR_3/PSLi systems in hydrocarbons is supported by viscosimetric measurements [54]. As shown in Table 1, the aggregation number, N , decreases upon addition of the aluminum derivative onto the polystyryllithium solution. $(\text{PSLi})_2$ dimers ($N = 1.80$ at $[\text{Al}]/[\text{Li}] = 0$) are converted into mixed complexes containing only one polystyryl chain ($N = 1.05$ at $[\text{Al}]/[\text{Li}] = 1$).

Ab-initio calculation also confirms preferential formation of mixed complexes, Scheme 13. For $r = [\text{Al}]/[\text{Li}]$ of 0.5, a stable Al:Li (1:2) complex is formed with a stabilization energy of about -1100 kJ/mol . At higher $[\text{Al}]/[\text{Li}]$ ratio, $r > 0.5$ a 1:1 complex is then preferentially formed. The lower stabilization energy (-160 kJ/mol) when going from the 1:2 to the 1:1 complex suggests that both species are present, as long as r does not reach 1 [55].

Addition of alkyl- or alkoxyalkyl-aluminum to PSLi species allows to strongly decrease the reactivity at low ratio of aluminum, $r = [\text{Al}]/[\text{Li}] < 1$, whereas complete extinction of the polymerization is observed at $r = 1$ [56,57]. As shown for the $\text{Et}_3\text{Al:PSLi}$ system, Table 2, at $r = 0.9$ the apparent polymerization rate constant k_{Papp} is decreased by a factor of 100 as compared to PSLi, in cyclohexane at 100 °C. Polystyrene with controlled molar masses corresponding to one chain formed by alkyllithium and narrow dispersity is obtained in these conditions. These results are consistent with the formation of a 1:1 complex inactive

Table 2

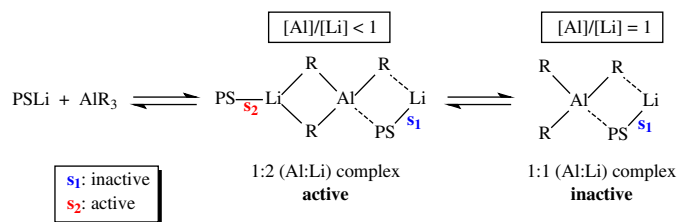
Styrene polymerization initiated by $\text{Et}_3\text{Al/PSLi}$ system in cyclohexane at various $[\text{Al}]/[\text{Li}]$ ratios.

$[\text{Et}_3\text{Al}]/[\text{PSLi}]$	T (°C)	$[\text{PSLi}]$ ($\text{mol L}^{-1} \times 10^3$)	$R_p/[S]$ ($\text{min}^{-1} \times 10^3$)	k_{Papp}^a ($\text{L mol}^{-1} \text{ min}^{-1} \times 10^3$)	$\bar{M}_n(\text{th})$ ($[\text{Li}]_0^b$) (g mol^{-1})	$\bar{M}_n \text{ SEC}$ (g mol^{-1})	I_p
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	100	6.2	24	3.87	7500	7300	1.09
1	100	7.4	0	0	–	–	–

^a $k_{\text{Papp}} = (R_p/[S])/[\text{PSLi}]$.

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

^c k_{Papp} extrapolated from the Arrhenius law ($E_a = 50 \text{ kJ mol}^{-1}$, $A = 1.83 \times 10^{+8}$).



towards styrene polymerization whereas, at ratio lower than 1, once all the PSLi is incorporated into the mixed complexes, the reactivity is tuned by the reactivity and relative concentration of the 1:2 (Al:Li) complex. In contrast to dialkylmagnesium species that yield still active retarded polymerization systems at high r values, up to 20, trialkylaluminum systems should be used at r lower than 1. A second important difference is that trialkylaluminum does not contribute to the formation of new PS chains, their number being determined by the total amount of lithium moieties incorporated in 2:1 or 1:1 complexes. This can be attributed to the higher energy of the metal–alkyl bond in aluminum derivatives than in magnesium ones. As it will be indicated later in this report, an intermediate situation is observed when using dialkylaluminum hydride. In agreement with the work of Arest-Yakubovich [8] two different modes of coordination of PSLi onto trialkylaluminum derivatives, s_1 and s_2 , can be proposed, Scheme 14. The PSLi s_1 site present in 1:1 complex is considered inactive, while the s_2 site generated in 2:1 complex enables monomer insertion. Fast exchanges between 1:1 and 1:2 complexes as well as a rapid inter-conversion of s_1 and s_2 sites would explain the growth of one PSLi chain per initial Li initiator.

The use of low amount of organoaluminum as additive for the retarded styrene polymerization is a strong advantage in terms of cost since, in addition, trialkylaluminum compounds are much cheaper than magnesium ones. Nevertheless, the suitable reactivity window $0.75 < r > 0.95$ was quite narrow, which could be problematic in industry for a good reproducibility of the polymerizations. Dialkylaluminum alkoxides were investigated as Li additives since they revealed a similar retardation effect but over a larger range of r values and for values higher than 1 [57]. The formation of a heterocomplex between polystyryllithium and diethylaluminum *tert*-butoxide, accompanied by a shift of the PSLi absorption band from 326 nm to 260 nm, is illustrated in Fig. 8. r values higher than 3 are required for an almost complete disappearance of the PSLi band while a significant and almost constant

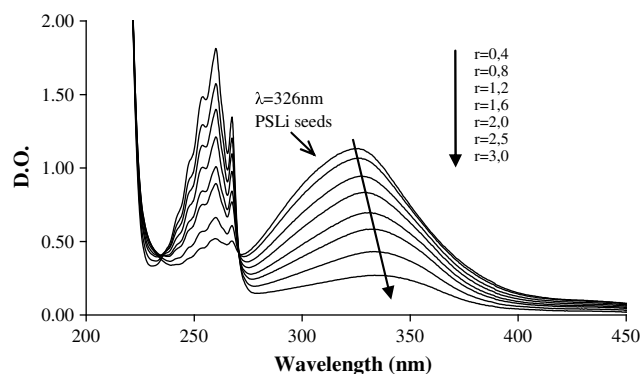


Fig. 8. Influence of increasing amounts of $\text{Et}_2\text{AlO}t\text{-Bu}$ addition on the PSLi UV–visible spectrum (20 °C, cyclohexane, $r = [\text{Al}]/[\text{Li}]$).

Table 3

Styrene polymerization initiated by $\text{Et}_2\text{AlO}t\text{-Bu}$ /PSLi systems for various $[\text{Al}]/[\text{Li}]$ ratios (cyclohexane, $T = 100$ °C).

$[\text{Et}_2\text{AlO}t\text{-Bu}]/[\text{PSLi}]$	$[\text{PSLi}]$ ($\text{mol L}^{-1} \times 10^3$)	$R_p/[S]$ ($\text{min}^{-1} \times 10^3$)	$k_{p,app}$ ^a ($\text{L mol}^{-1} \text{min}^{-1}$)	$\bar{M}_n(\text{th})$ [Li] ₀ ^b (g mol^{-1})	\bar{M}_n SEC (g mol^{-1})	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 $k_{p,app} = (R_p/[S])/[\text{PSLi}]$.

^b \bar{M}_n calculated according to the formation of one PS chain per Li ($\bar{M}_n(\text{th}) = \bar{M}_n^{\text{PSseeds}} + ([S]_0/[\text{Li}]_0) \times M_0 \times \text{yield}$).

^c $k_{p,app}$ extrapolated from the Arrhenius law ($E_a = 50 \text{ kJ mol}^{-1}$, $A = 1.83 \times 10^{+8}$).

retardation effect takes place at 100 °C in cyclohexane for r ranging from 1.1 to about 5, see Table 3.

In the presence of diisobutylaluminum hydride (*i*-Bu₂AlH) as additive for PSLi retarded polymerization the experimental polymer molar masses are two times lower than theoretical ones suggesting the contribution of *i*-Bu₂AlH to PS chain formation [57]. MALDI-TOF analysis clearly shows two series of PS chains, one terminated by a butyl group coming from the *s*-butyllithium and a second one with an α -H attributed to an initiation (or a reversible transfer process) involving the hydride of *i*-Bu₂AlH (Fig. 9).

Diene monomers can be polymerized in a quite similar way using *i*-Bu₃Al:PButLi systems with apparent propagation rate constants directly related to the $[\text{Al}]/[\text{Li}]$ ratio. The microstructure of polydienes is very close to the one obtained with lithium in apolar solvents and the polybutadiene content in 1,4 units is close to 90% [32,33]. This behavior, different from the one observed with magnesium additives, can be explained by the structure of the formed complexes and in particular the quite different $[\text{Mt}]/[\text{Li}]$ ratios ($\text{Mt} = \text{Mg}$ or Al) used for diene retarded polymerization. Indeed, for ratio $[\text{Mg}]/[\text{Li}] < 1$, corresponding to those typically used with trialkylaluminum/PButLi systems, the content in 1,4 butadiene units remains close to PButLi systems. A possible complementary explanation is the absence of chain exchange between trialkylaluminum and PButLi, while 1,4 to 1,2 isomerization may proceed during the transfer of growing chain between lithium and magnesium compounds, Scheme 9.

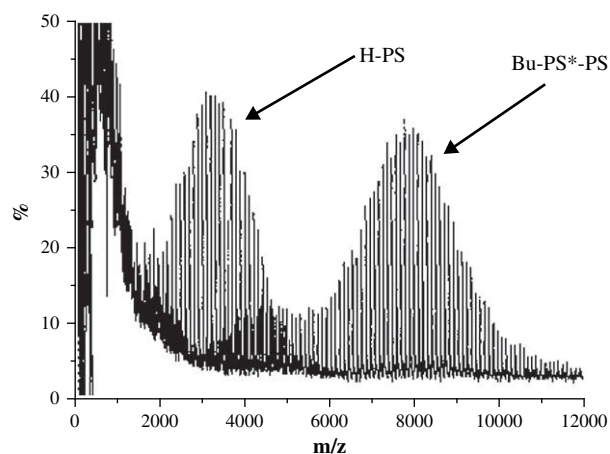


Fig. 9. MALDI-TOF spectrum of polystyrene initiated by *i*-Bu₂AlH:PS^{Li} ($r = 0.75$) (*Bu-PSLi seeds).

5. Aluminum derivatives/alkali metal hydrides systems

Using alkylsodium in the presence of an organoaluminic compound (Sodal system) as initiator, Arest-Yakubovich and co-workers were able to polymerize butadiene in hydrocarbons, up to complete conversion. Thanks to a strong reduction of transfer reactions high molar mass polybutadienes could be obtained [58–61]. The rate of butadiene polymerization was observed to drastically increase with the [Al]/[Na] ratio up to a maximum followed by a decrease until complete extinction. This was explained by the quantitative formation of an inactive mixed complex when increasing trialkylaluminum concentration [18,61–63]. According to Kessler, association of NaR and AlR₃ yields inactive Na⁺[AlR₄][−] complexes in which all the R groups are linked to a negatively charged tetracoordinated aluminum atom facing an isolated sodium cation [64,65]. To obtain active Sodal, it was necessary that a direct bonding remains between one R group of the complex and sodium, for instance by association to trialkylaluminum of an organosodium possessing an aromatic substituent, able to generate a delocalized carbanion [8,59,60].

These data and the increased initiation efficiency observed with the dibutyl aluminum hydride/s-Buli system, as described in the previous section, lead us to explore the use of alkali metal hydrides (Li, Na, K) in place of alkyllithium. These derivatives, readily available and much cheaper than alkyllithium, are commonly used in organic synthesis as reducing agents. However, due to their insolubility in most organic solvents, their use in polymerization remained very limited so far. Very few papers deal with the anionic polymerization of vinylic monomers initiated by metal hydrides. Williams briefly investigated styrene polymerization initiated by sodium hydride (NaH) in hexane at 25 °C [66] and reported very low initiation efficiency. Even after long polymerization times monomer conversion was incomplete. Needles reported the formation of oils of low molar masses using NaH to initiate the styrene polymerization in dimethylsulfoxide [67]. It was proposed that the polymerization proceeded by attack of NaH onto DMSO and addition of the resulting dimethyl anion to styrene, followed by rapid transfer and/or termination.

Several papers indicate that Lewis acids such as R₃Al [68,69], R₃B [70,71], R₂Zn [72] or R₂Mg [73] allow the solubilization of alkali metal hydrides in non-polar solvents by formation of bimetallic complexes, solubility increasing with the size of the alkali metal. Among these systems, the 1:1 complex between NaH and AlH(OCH₂CH₂OCH₃)₂, used mostly as reducing agent, revealed some potentiality in the synthesis of polybutadiene [74]. Polybutadiene oligomers were also prepared with the system KH:n,s-Bu₂Mg in the presence of tetramethyl ethylene diamine (TMEDA) [75,76].

Addition of trialkylaluminum (Et₃Al or *i*-Bu₃Al) to LiH, NaH and KH in hydrocarbons was shown to significantly improve their solubility. For instance, in toluene and in cyclohexane complete solubilization of NaH (2 h at 50 °C) and of KH (2 h at 20 °C) is observed at ratio [R₃Al]/[MtH] = 1. This is in agreement with the formation of 1:1 R₃Al:MtH bimetallic complexes. In contrast, in similar conditions, LiH remained partly insoluble even after several hours at 80 °C.

The performance of R₃Al:MtH systems for styrene retarded polymerization at [Al]:[Mt] ratio ranging from 0.5 to 1 was first investigated at 100 °C in toluene. At *r* = 0.9, the following reactivity order is observed: R₃Al:LiH < R₃Al:NaH ≪ R₃Al:KH.

Best results in terms of efficiency and styrene polymerization control are obtained with sodium hydride at [Al]:[Na] ratios ranging from 0.8 to less than one. In contrast both lithium-based and potassium-based systems exhibit low initiation efficiencies. This is linked in one hand to the heterogeneous character of lithium

Table 4

Polymerization of styrene at 100 °C in toluene with *i*-Bu₃Al/NaH system ([S] = 0.5 M, conversion = 100%, time = 8 h).

[<i>i</i> -Bu ₃ Al]/[NaH]	10 ³ [NaH] (mol L ^{−1})	<i>k</i> _{p,app} ^a (L mol ^{−1} min ^{−1})	\overline{M}_n (th) [Na] ₀ ^b (g mol ^{−1})	\overline{M}_n SEC (g mol ^{−1})	Ip
0	5.1	–	9600	^c	–
0.5	5.2	nd	2600	8900	2.6
0.8	5.2	0.8	8600	9300	1.2
0.9	5.4	0.4	2800	3000	1.2
0.95	2.2	0.2	80 000	104 000	1.2
1.0	5.7	0	–	–	–
1.2	5.6	0	–	–	–

^a *k*_{p,app} = (*R*_p/[S])/[NaH].

^b \overline{M}_n calculated according to the formation of one PS chain per Na.

^c Low conversion and multimodal distribution.

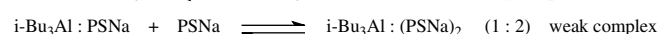
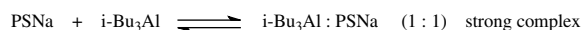
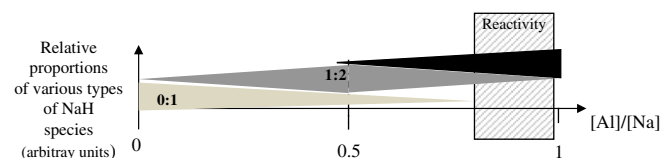
complexes and on the other hand to a too fast propagation rate with the soluble potassium complex.

As observed with R₃Al:RLi initiators, R₃Al:NaH systems are useful initiators for styrene RAP at ratios 0.8 < [Al]/[Na] < 1, Table 4, whereas at stoichiometry equal or higher than one (*r* > 1) they became again inactive [77,78]. This upper limit could be displaced by adding tetrahydrofuran (THF) as second additive. In this case reactivity could be tuned by adjusting both *r* and/or the amount of THF. MALDI-TOF analysis shows that all the polystyrene chains formed possess an H head-group in agreement with hydride initiation. No chain corresponding to Metal-alkyl bond initiation is observed [79].

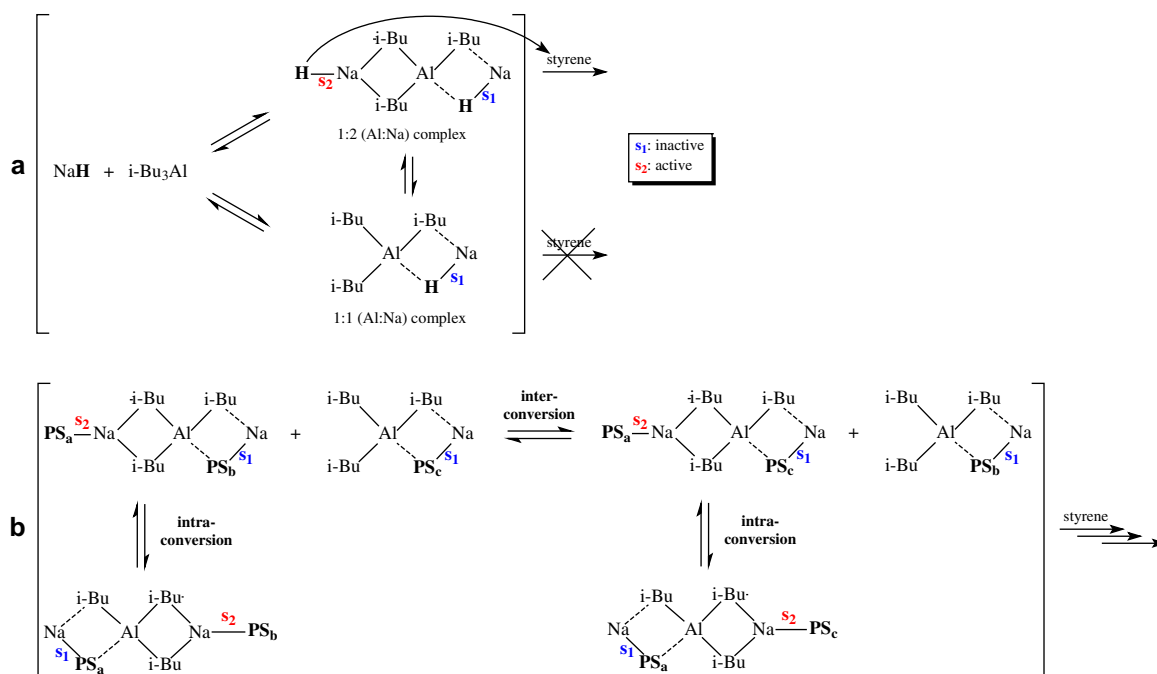
In bulk styrene at 100 °C an almost linear increase of polystyrene molar masses, with narrow dispersity with conversion was observed. The presence of a small fraction (<10%) of polymer of higher molar mass attributed to concurrent radical polymerization was also noticed [77].

Some aluminate systems are also effective for butadiene and isoprene polymerizations although polymerization rates are very slow. However, the addition of metal alkoxide as third component was shown to significantly enhance the polymerization rate at high temperature, rendering these reactions more attractive [79]. In contrast to isoprene polymerization in which transfer to monomer is predominant, polybutadiene with well-controlled molar mass and a relatively high 1,4-units content (70%) can be prepared at 80 °C in cyclohexane using the KH/*i*-Bu₃Al system in the presence of 0.2–1 equiv of potassium *tert*-amyloxide.

This shows that properly designed aluminate complexes of alkali metal hydrides allow a good control of the high temperature anionic polymerization of styrene and butadiene. The nature and proportion of the different complexes formed as a function of the Al/Na ratio are illustrated in Scheme 15 in the case of styrene polymerization. In the optimal reactivity window (0.8 < *r* < 1) both 1:2 and 1:1 [R₃Al]:[NaH] complexes are present. A dynamic equilibrium between the two complexes, via fast ligand



Scheme 15.



Scheme 16.

exchanges, would explain the formation in these conditions of a polymer chain by NaH molecule introduced, although the 1:1 complex is inactive. As illustrated already in Scheme 14 for PSLi, di- (s_1) and tri- (s_2) coordinated sodium atoms are present in 1:2 complex whereas only di- (s_1) coordinated sodium atoms can form in 1:1 complex, Scheme 16. It was proposed that styrene propagation proceeds onto s_2 sites of 1:2 complexes while s_1 sites in 1:1 and 1:2 complexes are dormant. As discussed above, the latter can be transformed into s_2 through ligands rearrangements within the 1:2 complex (intra-conversion) or exchange reactions between 1:1 and 1:2 complexes (inter-conversion), allowing almost all of the NaH molecules to initiate the growth of PS chains.

6. Conclusion

The technology of “living” anionic polymerization has been used for almost 20 years at BASF to produce styrene–butadiene block copolymers like Styrolux® and lately Styroflex®. Attempts to transfer the anionic process to general purpose polystyrene (GPPS) and high impact polystyrene (HIPS) productions were impeded by excessively high reaction rate that necessitated the use of dilute reaction conditions, in contrast to the commercial radical process. The key to commercial success of anionic polystyrene (A-PS) required reducing the reactivity of the active species in order to produce it in bulk conditions. To that aim, the Retarded Anionic Polymerization (RAP), which allows styrene polymerization to 100% conversion under similar reaction conditions as the radical polymerization has been developed. It is based on the use of new low cost anionic initiating systems (BuLi-free) based on sodium hydride and trialkylaluminum, which allow reactivity control over broad temperature and concentration ranges, even up to bulk conditions. Today, BASF has succeeded in operating continuous retarded anionic polymerization for HIPS production (named A-HIPS) on a pilot plant scale (200 t/year) and has developed an A-HIPS injection molding and

extrusion grade process with a property profile similar to the radical process but free of residual styrene and with a much lower content in styrene oligomers. Thanks to the proprietary initiator and reactor design technology, specific investment for a grass route plant is similar to the radical process but includes in situ rubber production. This new technology leads to an interesting reduction of variable costs. The implementation of this process into an existing radical plant set up (drop in process), without the necessity of major investments is a further opportunity for a rapid commercial production of A-HIPS. The gate for further innovative products provided by retarded anionic polymerization is opened.

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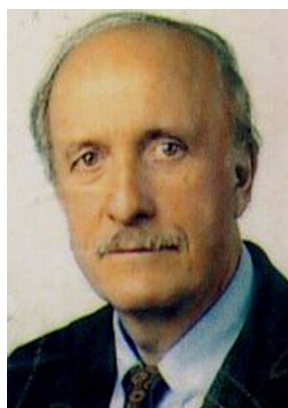
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