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Sodium hydride as a new initiator for the retarded anionic polymerization (RAP) of styrene

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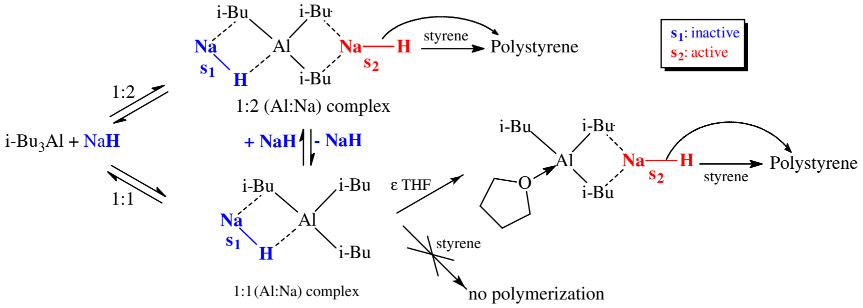
Abstract



Trialkylaluminum and sodium hydride form hydrocarbon soluble heterocomplexes which were used as initiating systems for the retarded anionic polymerization of styrene in hydrocarbon media at high temperature and in concentrated monomer, corresponding to conditions close to those used in industry for styrene radical polymerization. To be active towards styrene polymerization in hydrocarbons, these systems require the presence of a slight excess of metal hydride with respect to AlR_3 ($[Al]/[Na] < 1$), whereas for ratios $[Al]/[Na] \geq 1$ only the initiation step takes place. However, in these last conditions the addition of a few equivalents of a polar additive, such as tetrahydrofuran, allows the polymerization to proceed. Polymerizations initiated by AlR_3/NaH systems are characterized by initiation efficiency not far from one (>0.7) with respect to sodium hydride and by the presence of an important induction period, corresponding to first styrene insertion into M_t—H bonds. This behavior can be explained by the fact that most of the M_t—H bonds have to convert into M_t—styryl bonds before the propagation can start a particular situation which enables the control of the polymerization. The structure of the initiating and propagating sites, inside the bimetallic complexes, and the elementary reaction mechanisms are discussed to the light of experimental data.

Keywords: Anionic polymerization; Styrene; Sodium hydride

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1. Introduction

Since 1995, a strong effort has been directed at the development of new initiator combinations in order to adapt the anionic process to a commodity polystyrene market. Within the retarded anionic polymerization (RAP) concept, MgR_2/RLi combinations were the first systems able to insure the control of anionic styrene polymerization under acceptable industrial conditions [1–3]. Improving the performance and lowering the cost of these first initiating systems led to the growth of a second generation of RAP systems based on AlR_3/BuLi combinations [4,5]. In this article, we report a new initiator generation obtained by the combination of R_3Al with alkali metal hydride and more particularly with sodium hydride. Alkali metal hydrides are readily available and stable for a long period under inert atmosphere. They represent an important class of metal derivatives, which found numerous applications as reducing agent in organic synthesis. However, due to their low solubility in most organic solvents and quite strong M_t–H bonding, the use of alkali metal hydride as polymerization initiator has been extremely limited so far. One work related to the use of potassium hydride and di-*sec*-butylmagnesium describes the preparation of low molecular weight polybutadiene in hexane in the presence of *N*,*N*,*N*,*N*-tetradimethylenediamine [6,7]. More recently, Czech researchers have shown that sodium dihydrido-bis-(2methoxyethoxo)-aluminate ($NaAlH_2(OCH_2CH_2OCH_3)_2$), a commercially available reduction agent soluble in toluene, is able to polymerize diene monomers [8]. Indeed, it is known from Ziegler et al. [9] and Brown et al. [10] pioneering works that alkali metal hydrides can be solubilized through the formation of bimetallic complexes in particular with R_3Al [9], R_3B [10], R_2Zn [11] or R_2Mg [12] derivatives, even in non-polar solvents. The tendency towards formation of heterocomplexes increases with the ionic radius of the alkali metal but the reverse is observed for the solubility of the complexes [13]. The nature of the non-polar solvent also has a strong influence on the solubility parameters and while $KMg(s\text{-}C_4H_9)_2H$ is soluble in benzene, it precipitates in cyclohexane [12]. We have recently shown that lithium hydride generated *in situ* by hydrogenolysis of polystyryllithium either when used alone or in combination with an organometallic derivative is an active initiator for styrene polymerization at 100 °C [14]. This paper focuses on the possibility to associate the readily available sodium hydride with triisobutylaluminum to initiate the controlled styrene anionic polymerization at high temperature.

2. Experimental part

2.1. Materials

Triisobutylaluminum (i-Bu_3Al, 1.0 M solution in toluene from SAFC, Saint-Quentin Fallavier, France) was used as-received. Toluene was degassed over freshly crushed CaH_2, stored over polystyryllithium and distilled before use. Styrene (99%, from SAFC) was degassed over freshly crushed CaH_2, stored over *n-sec*-dibutylmagnesium and distilled before use. THF was distilled over sodium benzophenone, stored over a sodium mirror and redistilled before use. Sodium hydride (95 wt%, powder or 60 wt% dispersion in mineral oil, from SAFC) was stored under argon atmosphere in a glove box.

2.2. Preparation of NaH/*i*-Bu_3Al system

NaH/i-Bu_3Al solutions were prepared by reaction of sodium hydride with triisobutylaluminum in toluene. Typically, either pure NaH (0.096 g, 4×10^{-3} mol) or NaH in 60% dispersion in mineral oil (0.160 g, 4×10^{-3} mol), stored in a glove box, was placed in a glass flask fitted with PTFE stopcocks and degassed under vacuum before adding 50 mL of dry toluene. Then, a known amount of i-Bu_3Al solution (1.0 M in toluene) was added with a syringe under argon flow to reach the appropriate ratio of [Al]/[Na]. The final solution was let under vigorous stirring at 50 °C, until NaH was completely ($[Al]/[Na] \geq 1$) or partially ($[Al]/[Na] < 1$) solubilized, in general for about 3 h.

2.3. Polymerization

Polymerizations were carried out under argon in toluene at 100 °C in glass flasks equipped with a quartz U.V. cell and fitted with PTFE stopcocks. i-Bu_3Al/NaH solutions were added with a syringe under argon flow to dry toluene. After styrene addition, the polymer conversion was measured by following the monomer consumption by UV–vis spectrometry. All polymerization were stopped by adding methanol previously degassed under vacuum. The monomer concentration was maintained in the range 0.4–0.5 mol L^{-1}.

Typically, in a 50 mL glass reactor equipped with a magnetic stirrer previously flamed under vacuum, 35 mL toluene was introduced under vacuum through glass connectors. Then, 1.41 mL of i-Bu_3Al/NaH (ratio $[Al]/[Na] = 0.8$) solution in toluene ($[Na] = 0.15$ mol L^{-1}, 2.12×10^{-4} mol) was added by a syringe under argon atmosphere. Finally, 2.0 mL of styrene (1.75×10^{-2} mol), stored in a graduated tube, was added to the reactor. The system was maintained under stirring in the thermostated bath at 100 °C until complete conversion. The reaction was stopped by adding 0.5 mL of degassed methanol. The polymer was precipitated into ethanol and dried. Yield of recovered PS: 1.818 g; conversion: 100%; experimental $\overline{M}_n$: 9300 g mol^{-1}, PDI: 1.2.

2.4. Analytical techniques

UV–vis absorption spectra were recorded on a 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.

The average molar masses and polydispersity of the polystyrene samples were measured by size exclusion chromatography (SEC) in tetrahydrofuran at 20 °C. Measurements were performed using a JASCO HPLC-pump type 880-PU, a Varian apparatus equipped with refractive index/UV detection and 4

TSK Gel columns (HXLG 2000, 3000, 4000 and 5000) calibrated with polystyrene standards.

The detection and titration of styrene and ethylbenzene were carried out by vapor phase chromatography on a Varian 3350 apparatus equipped with a flame ionization detector. Each compound was characterized by its specific retention time using references.

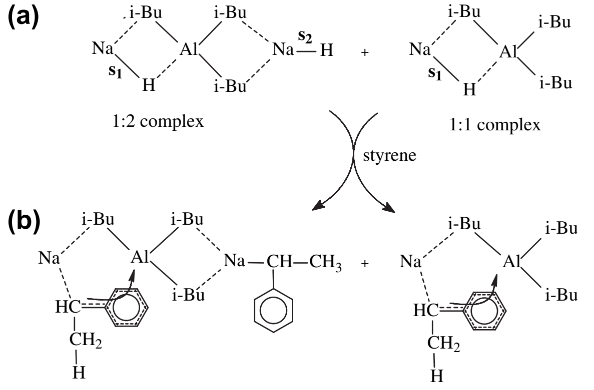
3. Results and discussion

3.1. Study of *i-Bu$_3$Al/NaH* system [15]

One interesting particularity of this bimetallic combination is its solubility in hydrocarbon media allowing a potential use as homogeneous polymerization initiator. Indeed, sodium hydride alone is insoluble in non-polar solvents but can be progressively solubilized by adding trialkylaluminum. At ratios [Al]/[Na] lower than 1, a turbid solution first forms and a complete soluble system is obtained with one equivalent of triisobutylaluminum in agreement with the quantitative formation of a 1:1 complex. At ratios [Al]/[Na] lower than 1, in addition to the partial formation of the soluble 1:1 complex, either the presence of remaining uncomplexed NaH or the formation of insoluble 1:2 [Al]/[Na] complexes can be postulated. Several polymerization results presented in this paper tend to support the formation of 1:2 [Al]/[Na] complexes.

We have shown in a previous paper the possibility to obtain at 100 °C with AlR$_3$/NaH as initiating system polystyrene with controlled high molar mass ($>100\,000$ g mol^{-1}) [16]. For a better understanding of the polymerization mechanism, the influence of *i*-Bu$_3$Al/NaH mixtures of different stoichiometries on the styrene initiation and propagation reactions was investigated in toluene at 100 °C using low monomer concentrations, of about 0.5 mol L^{-1}, allowing UV–vis spectroscopy monitoring. Systems with [Al]/[Na] < 1 are active and initiate the styrene retarded anionic polymerization. Some kinetic data are given in Table 1. On the contrary, in similar conditions, systems containing an equal molar amount or an excess of *i*-Bu$_3$Al ([Al]/[Na] $\geq$ 1) are not able to trigger the styrene polymerization. These results are in close agreement with those reported for *i*-Bu$_3$Al/PSLi systems [4,5], which are also active only for [Al]/[Li] ratios ranging between 0.7 and 1.

The experimental polymer molar masses obtained at ratios 0.7 < [Al]/[Na] < 1 are fitting with the formation of one PS chain by initial sodium hydride molecule and their molar mass distributions are quite narrow ($I_p = 1.1$–1.2). The participation of all the initial NaH at 0.7 < [Al]/[Na] < 1 supports complete de-aggregation of NaH particles, in agreement with the formation of 1:2 [Al]/[Na] complexes in complement to 1:1 complexes (Scheme 1). For ratios lower than 0.7 or when sodium hydride was used alone very low polymerization yields and poor initiation efficiencies were obtained due to heterogeneity and insolubility of the potentially reactive species [16].



Scheme 1. (a) 1:2 and 1:1 heterocomplexes [Al]/[Na] formed in *i*-Bu$_3$Al/NaH systems at [Al]/[Na] < 1; (b) after insertion of one styrene unit into (s$_1$) and (s$_2$) M$_t$–H bonds.

MALDI-TOF analysis of the polystyrene prepared by *i*-Bu$_3$Al/NaH systems indicates that all the PS chains possess an H head-group, in agreement with selective first styrene insertion into H–Na bonds [16]. No insertion into M$_t$–isobutyl group is observed.

Kinetic studies of styrene polymerization, monitored by UV–vis spectroscopy, reveal that propagation starts only after an induction period (Fig. 1). Then, styrene consumption follows a first order kinetic law with an apparent propagation rate constant depending on the [Al]/[Na] ratio (Table 1). During the induction period, the formation of a peak shoulder increasing with time is observed at 300–350 nm (Fig. 2). As already suggested [14] and as it will be shown later on, this shoulder corresponds to CH$_3$CHPhNa species, complexed with *i*-Bu$_3$Al, and formed by first styrene insertion into Na–H bonds. Styrene consumption corresponding to propagation starts when the amount of CH$_3$CHPhNa has reached a plateau corresponding to its maximum concentration. This indicates that the first styrene insertion into M$_t$–H has to be almost completed before propagation can proceed.

Table 1
Polymerization of styrene at 100 °C in toluene with *i*-Bu$_3$Al/NaH system ([S] = 0.5 M, conversion = 100%, time = 8 h)

[Al]/[Na]	[NaH]$_0$ (mol L^{-1})	$k_{p_{app}}$ [a] (L mol^{-1} min^{-1})	$\overline{M}_{n\ th/Na}$ [b] (g mol^{-1})	$\overline{M}_{n\ exp}$ (g mol^{-1})	I_p
0.8	5.2×10^{-3}	0.8[c]	8600	9300	1.2
0.9	1.1×10^{-2}	0.3[c]	4000	3800	1.1
1.0	5.7×10^{-3}	0	–	–	–
1.2	5.6×10^{-3}	0	–	–	–

[a] $R_p = k_{p_{app}}[\mathrm{NaH}]_0[\mathrm{S}]$.
[b] $\overline{M}_n$ calculated from [NaH]$_0$.
[c] Polymerization rate measured after a 2 h induction period.

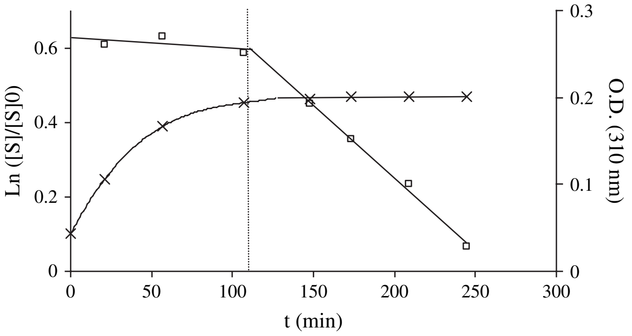


Fig. 1. Polymerization of styrene with i-Bu_3Al/NaH system ([Al]/[Na] = 0.8, toluene, 100 °C). □: Evolution of $\ln([S]/[S]_0)$ with time, [S] = styrene concentration. ×: Evolution of the optical density (O.D.) at 310 nm versus time. $[S]_0 = 0.43\ mol\ L^{-1}$, $[NaH]_0 = 4.5 \times 10^{-3}\ mol\ L^{-1}$.

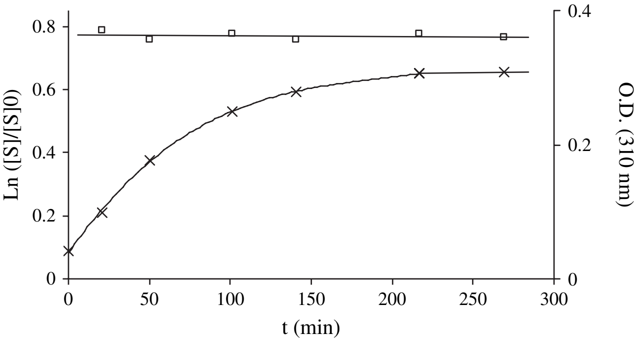


Fig. 3. Polymerization of styrene with i-Bu_3Al/NaH system ([Al]/[Na] = 1.2, toluene, 100 °C). □: Evolution of ln $([S]/[S]_0)$ with time, [S] = styrene concentration. ×: Evolution of the optical density (O.D.) at 310 nm versus time. $[S]_0 = 0.41\ mol\ L^{-1}$, $[NaH]_0 = 5.7 \times 10^{-3}\ mol\ L^{-1}$.

The formation of a similar peak shoulder is also observed at ratio [Al]/[Na] ≥ 1 despite these systems were found inactive towards styrene propagation in the present conditions. This is illustrated in Fig. 3 for a ratio [Al]/[Na] = 1.2. To confirm that a first styrene insertion readily takes place during the induction period, the system i-Bu_3Al/NaH ([Al]/[Na] = 1.2) was reacted for 4 h at 100 °C with about 4 styrene equivalents. After deactivation by methanol, the resulting solution was analyzed by vapor phase chromatography and SEC. Data confirm the formation of ethylbenzene (EB) in agreement with one single styrene insertion into M_t–H bonds and the absence of any PS oligomer. The amount of EB formed ($[S]_0 = 0.26\ mol\ L^{-1}$, 4 h, 100 °C), corresponds approximately to 80% conversion of the initial Na–H bonds into styryl–Na species. This shows that i-Bu_3Al/NaH systems with ratios below and above the 1:1 stoichiometry behave quite similarly with respect to the first styrene insertion into H–M_t bonds. However, the situation becomes drastically different for further monomer insertion into styryl–M_t bonds since only i-Bu_3Al/NaH systems having ratios [Al]/[Na] < 1 are active in the conditions of this study for propagation.

These results suggest that either the initiation and propagation reactions proceed on different types of active sites or a modification of the complex structure takes place after the first monomer unit insertion. Arest-Yakubovich [17,18] proposed that bridged structures involving di- (s_1) or tri- (s_2) coordinated sodium atoms can be present in alkylsodium trialkylaluminum complexes (Scheme 1a). Depending on the [Al]/[Na] stoichiometry, complexes of different compositions are formed in which s_1 and s_2 or only s_1 structures are present. Accordingly, it may be anticipated that initiation can proceed both in s_1 and s_2 sites (Scheme 1) whereas the propagation is restricted only to s_2 sites (Scheme 2).

At ratios [Al]/[Na] ≥ 1, only 1:1 complexes (and possibly 2:1 [Al]/[Na] complexes) are present. In these systems Na–H is believed to be involved only in s_1 structures. This implies that styrylsodium units, produced by M_t–H initiation, can form also in s_1 sites while propagation cannot proceed since no s_2 sites are present. On the contrary at ratios [Al]/[Na] < 1, both 1:1 and 1:2 [Al]/[Na] complexes with s_2 sites active for the propagation are present (Scheme 2). Following this assumption that s_2 are the only active sites for propagation, the induction period observed with [i-Bu_3Al]/[NaH] < 1 suggests that styrylsodium species once formed are preferentially complexed with i-Bu_3Al and converted into inactive s_1 sites. This allows almost all NaH present in s_2 sites to be progressively transformed into styrylsodium units without propagation. When all the possibilities of creating s_1 sites (one per

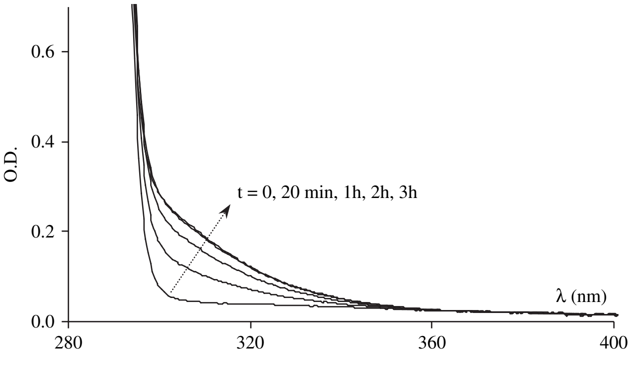
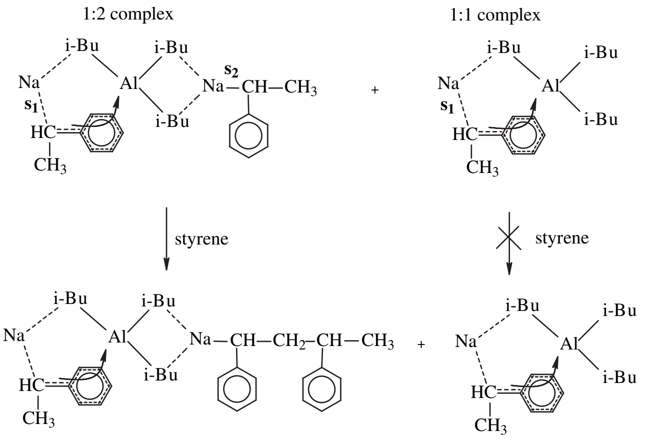
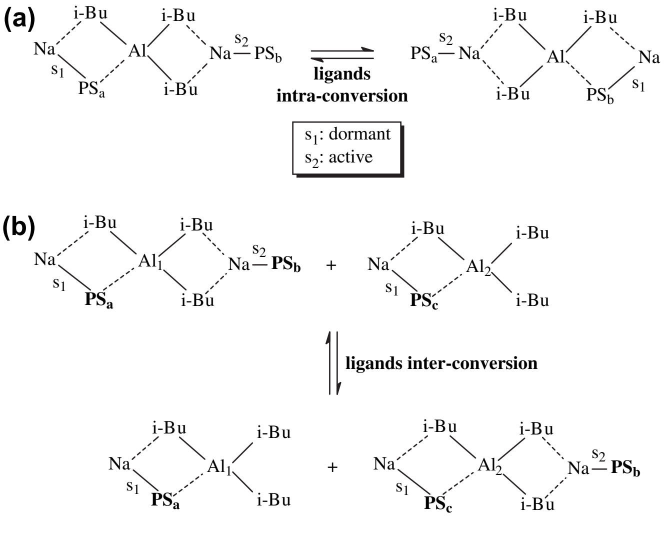


Fig. 2. Variation with time of the UV–vis spectrum of i-Bu_3Al/NaH system after styrene addition, in toluene at 100 °C. Same conditions as in Fig. 1.



Scheme 2. Propagation step in i-Bu_3Al/NaH systems ([Al]/[Na] < 1).



Scheme 3. Intra- (a) and intermolecular (b) complexes exchanges of PS chains between dormant (s_1) and active (s_2) sites.

i-Bu_3Al molecule) are completed, the new styrylsodium species formed are involved in s_2 type structures, which are able to propagate. For the ratio [Al]/[Na] = 0.8 examined, we found that approximately 80% of the initial H—Na bonds were converted into styryl—Na ones. This value corresponds nicely with the total number of s_1 sites available (one per 1:1 and one per 1:2 complexes). At this stage new styrylsodium species formed can only complex with *i*-Bu_3Al according to s_2 mode and thus propagation can start.

Beside this mechanism, the observed simultaneous growth of PS chains from all styryl—Na bonds implies fast intra- and intermolecular exchanges between PS chains located on s_1 (dormant) and on s_2 (active) sites (Scheme 3a and b). As a consequence of these reversible exchanges, the initiation efficiency is high yielding almost the formation of one polystyrene chain per NaH molecule, while the molar mass distribution remains relatively narrow ($I_p = 1.2$), despite the slow initiation step.

The drastic difference between initiation and propagation steps could result from a modification of the bridging bond nature in the complexes after a first styrene insertion. Unsymmetrical bridged associations based on electron deficient bondings (very close to three-center, two-electron bonds [19,20]) are likely involved in the case of *i*-Bu_3Al/NaH complexes. It is believed that the benzylic type electronic system of styrylsodium, acting as a two-electron ligand (2e2c), yields different types of bonding with aluminum. As a consequence only styrylsodium species involved in s_2 structures would be able to propagate. This situation is also likely valid in *i*-Bu_3Al/polystyryllithium systems which form inactive 1:1 complexes [4].

3.2. Activation of *i*-Bu_3Al/NaH ([Al]/[Na] $\geq$ 1) by addition of tetrahydrofuran

It is reported in the literature that $R_3Al{:}NaR'$ ([Al]/[Na] > 1) systems, where R′ is an aromatic group, can initiate the anionic polymerization of butadiene [17,18,21]. Indeed, polymerizations were performed in the presence of a polar additive (tetrahydrofuran or dimethyldioxane), which affects the structure of the corresponding heterocomplexes. The influence of such additives on the *i*-Bu_3Al/NaH systems (for [Al]/[Na] $\geq$ 1) towards styrene polymerization was investigated.

In a first series of experiments (Table 2, series A), the initiating systems were prepared in two steps: PSNa species complexed with *i*-Bu_3Al were obtained from styrene polymerization initiated with *i*-Bu_3Al/NaH system ([Al]/[Na] = 0.8). Then, a further amount of *i*-Bu_3Al was added to yield *i*-Bu_3Al/PSNa systems with a ratio [Al]/[Na] of 1.4 and 1.8. In pure hydrocarbon solvents, as previously stated, no polymerization occurs even at 100 °C (Table 2, run A_0). Upon addition of 50 equivalents of THF, the polymerization starts without any induction period and proceeds smoothly, the apparent propagation rate constant being in the range of active *i*-Bu_3Al/NaH system with [Al]/[Na] = 0.8.

In a second set of experiments (series B, Table 2), *i*-Bu_3Al/NaH systems (with 1 < [Al]/[Na] < 2) were directly used as initiating systems in the presence of THF as additive. Styrene anionic polymerization also takes place and goes to completion. At a constant ratio [Al]/[Na], the apparent propagation

Table 2
Polymerization of styrene in toluene at 100 °C with *i*-Bu_3Al/NaH system in the presence of THF as additive (conversion = 100%, time = 8 h)

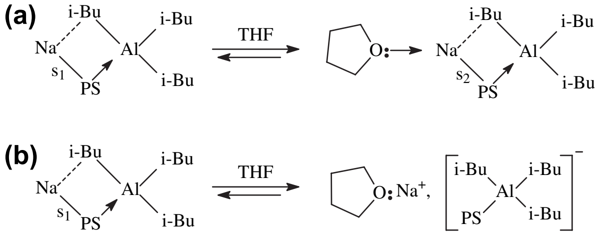
Run[a]	[Al]/[Na]	[THF]/[Na]	$[NaH]_0$ (mol L^{-1})	$k_{p_{app}}$[b] (L mol^{-1} min^{-1})	t_i[c] (min)	$\overline{M}_{n\ th/Na}$[d] (g mol^{-1})	$\overline{M}_{n\ exp}$ (g mol^{-1})	I_p
A_0	1.5	0	5.5×10^{-3}	0	–	7600	–	–
A_1	1.4	50	5.7×10^{-3}	2	0	8000	8400	1.4
A_2	1.5	50	4.1×10^{-3}	1.8	0	10 800	11 500	1.3
A_3	1.8	50	4.0×10^{-3}	1.5	0	10 000	8400	1.3
B_1	1.2	50	4.2×10^{-3}	2.0	60	8300	10 500	1.4
B_2	1.5	50	4.8×10^{-3}	1.3	90	7600	8200	1.4
B_3	1.5	7	6.3×10^{-3}	0.4	120	7600	6500	1.3
B_4	1.8	50	6.7×10^{-3}	0.9	90	6500	5800	1.3

[a] A = two steps preparation of the initiating systems: *i*-Bu_3Al/PSNa ([Al]/[Na] = 0.8) firstly prepared then a further amount of *i*-Bu_3Al was added to yield the desired ratio; B = initiating systems directly used.

[b] $R_p = k_{p_{app}}[NaH]_0[S]$.

[c] Induction time.

[d] $\overline{M}_n$ calculated from $[NaH]_0$.



Scheme 4. Influence of THF on an inactive 1:1 complex – sodium complexation.

rate increases with the amount of THF added. However, even in the presence of only 7 THF equivalents with respect to Na, the system is already active. Indeed, the polymerization rate can be controlled either by adjusting the [THF]/[NaH] or the [i-Bu$_3$Al]/[NaH] ratios. Besides, as shown in Table 2, these ternary i-Bu$_3$Al/NaH/THF systems are much less sensitive to [Al]/[Na] variations than binary systems (without THF) at ratios lower than 1. In all these experiments, an induction period which duration depends on the amount of THF added was observed. Note that at $0.7 < [Al]/[Na] < 1$ a reactivity increase is also observed in presence of THF, but since the systems are already active in the absence of additive, the interest of adding THF remains limited in comparison to activation of systems with $[Al]/[Na] > 1$.

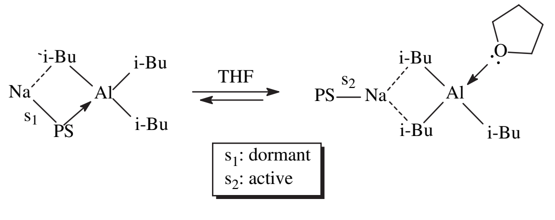
Activation of i-Bu$_3$Al/PSNa systems ($[Al]/[Na] \geq 1$) by THF can be tentatively explained in 2 ways. A first interpretation is based on the preferential solvation of Na by THF yielding either an activation of s_1 sites (Scheme 4a) or the formation of tight ion pairs (Scheme 4b) as proposed for NaAlBu$_4$ [22]. According to these authors, the addition of polar additives could transfer the sodium alkyl group onto aluminum, thus forming an anionic system. However, these first assumptions seem unlikely since in both cases Na complexation by THF would reinforce styryl–Al bonds.

A second hypothesis deals with the competition between the polar additive and PSNa towards i-Bu$_3$Al complexation. As proposed in Scheme 5 the presence of THF could lead to the formation of mixed complexes in which the formation of s_2 active sites is favored.

4. Conclusion

The use of metal hydride in combination with trialkylaluminum derivatives is an important step in the development of new alkyllithium-free and inexpensive systems able to quantitatively initiate the styrene anionic polymerization. Well-controlled polymerization can be achieved at high temperature, up to 150 °C, in hydrocarbons even in highly concentrated monomer conditions. In the present study we have shown that systems in which sodium hydride is in slight excess with respect to trialkylaluminum yield the formation of about one PS chain per initial NaH molecule. On the contrary, 1:1 AlR$_3$:NaH complexes and systems with Al/Na stoichiometry >1 yield only insertion of one styrene unit into the H–Na bond but are unable to ensure the propagation. However, in the presence of THF as additive, it is possible to get active polymerization systems even at AlR$_3$:NaH ratio significantly higher than 1. These results can be interpreted by the contribution of 2 distinct coordination sites in 1:1 and 1:2 heterocomplexes.

These initiating systems allow the first economically attractive anionic polymerization for the industrial polymerization of styrene with approximately the same cost as the radical route.



Scheme 5. Influence of THF on an inactive 1:1 complex – aluminum complexation.

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