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Initiation of Styrene Retarded Anionic Polymerization Using the Combination of Lithium Alkoxides with Organometallic Compounds

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ABSTRACT: The possibility to initiate styrene retarded anionic polymerization in hydrocarbon solvents from bimetallic systems based on lithium alkoxide and metal−alkyl derivatives like trialkylaluminum or dialkylmagnesium was investigated. The combination of the two organometallic compounds, individually inactive, affords an active initiating system which can be an alternative to alkyllithium initiators. Activation involves a ligand exchange inside the bimetallic complex, thus in situ forming an alkyllithium compound complexed with a new alkoxymetal−alkyl derivative. The kinetics and extent of the ligand exchange process are highly dependent on the nature of both the ligand and the metal, magnesium alkyls being much more efficient than aluminum ones. The influence of the nature of both the lithium alkoxide and the metal−alkyl derivatives on the initiation efficiency and retardation of styrene polymerization was studied.

Introduction

We have recently described the use of a series of bimetallic systems as initiators for the retarded anionic polymerization of styrene,[1−4] a workup procedure which allows to control styrene bulk polymerization in conditions close to the industrial radical process. Among these systems, some are based on the combination of polystyryllithium with magnesium[3] or aluminum[4] alkyl alkoxides. The formation of strong bimetallic heterocomplexes in which the reactivity of the polystyryl species is drastically reduced—almost no polymerization at room temperature—appears to be the key step of the retardation process. Ligand exchanges between the two metals in the complex were also postulated. Metal-to-metal ligand exchange reactions between alkyllithium compounds and heavier alkali metal alkoxides have been described for a long time. They are known as a practical route for the preparation of various alkyl−metal compounds of the heavier alkali metals.[5] These bimetallic combinations have also been reported as specific initiating systems for vinyl monomer polymerization and copolymerization.[6−8]

Lithium alkoxide derivatives (LiOR), dialkylmagnesium[9] (R_2Mg), and trialkylaluminum (R_3Al) compounds are inactive alone for initiation of styrene and butadiene anionic polymerization, even at high temperature. However, butadiene anionic polymerization can be initiated in hexane by combinations of *n*- and *sec*-Bu_2Mg and potassium *tert*-butoxide.[10] The authors surmised that alkylpotassium formed through ligand exchange is the true initiator, with the dialkylmagnesium compound serving merely to alkylate potassium. Examples found in the patent literature[11] also describe the polymerization of conjugated dienes in hexane with an initiating system comprising a trialkylaluminum and an alkali metal alkoxide; this system yields polybutadiene chains with the same microstructure as those synthesized from alkyllithium initiators in hydrocarbons.

Various combinations between lithium alkoxides and dialkylmagnesium or trialkylaluminum have been investigated as potential alternatives to the alkyllithium/organometallic systems for the initiation of the retarded anionic polymerization of styrene at high temperature. The main results and conclusions are presented in this paper.

Experimental Section

Materials. *sec*-Butyllithium (*sec*-BuLi; 1.3 M in cyclohexane from SAFC, France), *n*,*sec*-dibutylmagnesium (*n*,*sec*-Bu_2Mg; 1.0 M in heptane from SAFC, France), *n*-butyl,*n*-octylmagnesium (*n*-Bu,*n*-OctMg; 75% butyl group; 20% in heptane from WITCO, Germany), and triisobutylaluminum (*i*-Bu_3Al, 1.0 M solution in toluene from SAFC, France) were used as received. 2,6-Di-*tert*-butyl-*p*-cresol (BHT, 99% powder from SAFC, France) was dried and degassed under vacuum. 2-Propanol (99% from SAFC, France) and 4-nonylphenol (98% from SAFC, France) were degassed over magnesium and distilled before use. Cyclohexane (99% from SAFC, France) was degassed over freshly crushed CaH_2, stored over polystyryllithium oligomers, and distilled before use. Styrene (99% from SAFC, France) was degassed over freshly crushed CaH_2, stored over *n*,*sec*-Bu_2Mg, and distilled before use.

Synthesis of Lithium Alkoxide (or Phenoxide). The two derivatives were prepared by reaction of polystyryllithium with the corresponding alcohols or phenol.

In a typical example, polystyryllithium seeds (PSLi, $\overline{DP_n} = 5$) were prepared at 20 °C under argon in a glass flask equipped with PTFE stopcocks and a UV−vis cell by addition of a *sec*-BuLi solution in hexane (0.90 mL, 1.3 L mol^{-1}, 1.2×10^{-3} mol) to 5 equiv of styrene in cyclohexane (150 mL). After titration of the PSLi concentration by UV−vis spectroscopy, 2-propanol in dry cyclohexane (12 mL, 0.10 L mol^{-1}, 1.2×10^{-3} mol) was added to deactivate the PSLi seeds, yielding the expected lithium alkoxide and inert polystyrene chains. The reaction was followed up to the stoichiometry by monitoring the disappearance of the UV−vis PSLi band at 326 nm.

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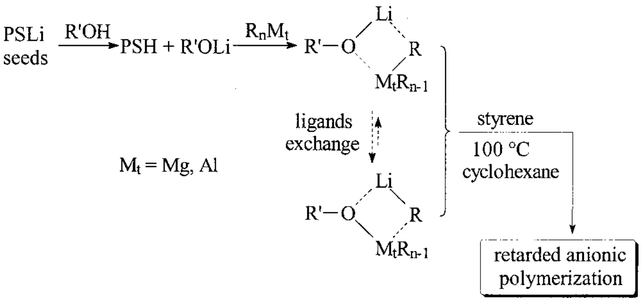
Scheme 1



Polymerization. Polymerizations were carried out under vacuum or dry nitrogen in cyclohexane at 100 °C in glass flasks equipped with a quartz cell and fitted with PTFE stopcocks. In a typical experiment a known amount of *n*-Bu,*n*-OctMg (3.25 mL in cyclohexane; [Mg] = 0.2 L mol^{-1}, 6.5 × 10^{-4} mol) was added to the lithium isopropoxide solution (30 mL, 7.2 × 10^{-3} L mol^{-1}, 2.2 × 10^{-4} mol) in order to obtain a [Mg]/[Li] ratio of 3. After addition of styrene (1.6 mL, 1.4 × 10^{-2} mol), the system was thermostated at 100 °C, and the polymer conversion was measured by following the decrease of the monomer concentration by UV−vis spectrometry. After complete monomer conversion (5 h) the polymerization was stopped by adding methanol previously degassed under vacuum. Polymer yield 1.4 g; $\bar{M}_n$ = 13 000 g mol^{-1}; $\bar{M}_w/\bar{M}_n$ = 1.2.

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: ϵ_{PSLi} = 13 000 L mol^{-1} cm^{-1} at 326 nm; $\epsilon_{styrene}$ = 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 four TSK gel columns: HXLG 2000, 3000, 4000, and 5000 with respectively 250, 1500, 10^4, and 10^6 Å pore size and bead size of 5 μm. Calibration was performed with polystyrene standards.

The MALDI-MS measurements were performed on a BIFLEX III instrument (Brüker Daltonik GmbH) in reflection mode using a dithranol matrix in THF and silver trifluoroacetate as cationizing agent. Spectra were recorded in the positive-ion mode using the reflectron mode and with an accelerating voltage of 20 kV. Polymer samples were dissolved in THF at 10 mg/mL. The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of THF and the solution of cationization agent by dissolving NaI in MeOH. The solutions were combined in a 10:1:1 volume ratio of matrix to polymer to cationization agent. One to two microliters of the obtained solution was deposited onto the sample target and air-dried.

Results and Discussion

A series of lithium alkoxide and phenoxide compounds (LiOR′) as well as lithium hydroxide were prepared in situ by deactivation of PSLi seeds with the corresponding R′OH derivatives. The concentrations of LiOR′ formed was estimated from the OD decrease of the PSLi absorption band at 326 nm. The addition of LiOR′ onto *n*,*sec*-Bu$_2$Mg, *n*-Bu,*n*-OctMg, or *i*-Bu$_3$Al in cyclohexane yields soluble systems that were investigated as potential initiators for styrene retarded anionic polymerization. The general procedure used is summarized in Scheme 1. The behavior of these bimetallic systems was compared to that of the corresponding initiators based on PSLi seeds complexed with alkylalkoxymagnesium[3] or dialkylalkoxyaluminum,[4] i.e., RMgOR′/PSLi and R$_2$AlOR′/PSLi.

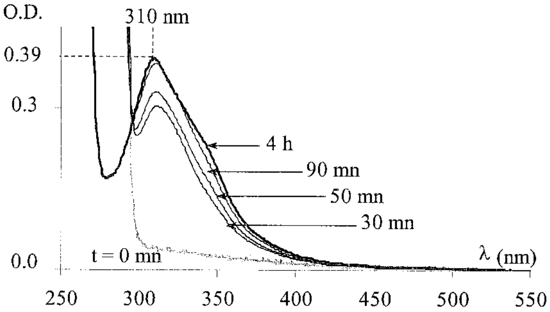


Figure 1. UV−vis spectra of the *n*-Bu,*n*-OctMg/LiOiPr system in cyclohexane in the presence of styrene; [Mg]/[Li] = 3, [LiOiPr]$_0$ = 6.2 × 10^{-3} mol L^{-1}, [styrene]$_0$ = 0.39 mol L^{-1}. Polymerization time at 1000 °C: (a) 0; (b) 30 min; (c) 50 min; (d) 90 min; (e) 4 h, corresponding to end of polymerization.

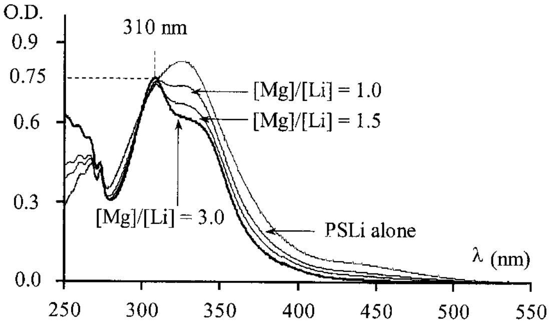


Figure 2. Effect of BuMgOBu increments on the PSLi UV−vis spectrum in cyclohexane at 20 °C. [PSLi] = 6.2 × 10^{-3} mol L^{-1}, $\bar{M}_n$ = 1000 g mol^{-1}.

Initiation of Styrene Anionic Polymerization by Dialkylmagnesium/LiOR′ Systems. Although each component is inactive alone toward initiation of styrene anionic polymerization even at high temperature, the combination of lithium alkoxide with dialkylmagnesium in hydrocarbon media yields active polymerization systems that are very similar to those issued from RMgOR′/RLi associations.[3]

(a) Systems Based on *n*-Bu,*n*-OctMg and LiOR′. Lithium isopropoxide (LiOiPr) is soluble in cyclohexane[12] although it is undecameric. No salt precipitation was observed during its preparation, and the styrene polymerization tests at 100 °C. After monomer addition, the solution containing the *n*-Bu,*n*-OctMg/LiOiPr mixture turned yellow. The evolution of the UV−vis absorption spectrum of the polymerization system, with increasing reaction time, is presented Figure 1; it shows that the intensity of the main absorption band at 310 nm, attributed to the formation of polystyryl species, which increases with time. At 100 °C, most of the corresponding chromophores (75−80%) are formed within 30 min.

As shown in Figure 2, this spectrum is similar to the one obtained for PSLi solutions upon addition of BuMgOBu or *n*-Bu,*n*-OctMg[2] increments; the main PSLi peak of the final spectra ([Mg]/[Li] ≥ 2) are shifted of peak from 326 to 310 nm. There is also a broad shoulder in the range 320−350 nm. These two signals are qualitatively consistent with those formed by initiation of styrene polymerization from *n*-Bu,*n*-OctMg/LiOiPr systems. The lower intensity of the main band in the latter case (about half) is related to a lower concentration in polystyryl species formed.

The initiation efficiency of the *n*,Bu,*n*-OctMg/LiOR systems with respect to the potential formation of R−Li bonds through metal-to-metal ligand exchanges was

Table 1. Polymerization of Styrene at 100 °C in Cyclohexane Initiated with *n*-Bu,*n*-OctMg/PSLi (Series A), BuMgOBu/PSLi (Series B), or *n*-Bu,*n*-OctMg/LiOiPr (Series C)

ref	$[Li]_0$[a] (mol L^{-1})	[Mg]/[Li]	k_{papp}[b] (L mol^{-1} min^{-1})	$\bar{M}_{n,th/Li}$[c] (g mol^{-1})	$\bar{M}_{n,exp}$[d] (g mol^{-1})	I_p[e]	eff[f] (%)
A_1	6.5×10^{-3}	2.0	4.0	4200	3800	1.1	100
A_2	4.9×10^{-3}	4.0	4.1	5700	5400	1.1	100
B	5.8×10^{-3}	4.0	12	10500	9800	1.1	100
C	6.2×10^{-3}	3.0	6.3	6500	13000	1.2	50

[a] $[Li]_0 = [PSLi]_0$ or $[LiOiPr]_0$. [b] $Rp = k_{papp}([Li]_0 \times \text{eff})[S]$. [c] $\bar{M}_n$ calculated from $[Li]_0$. [d] $\bar{M}_n$ measured by SEC. [e] Polydispersity index estimated from SEC. [f] Initiation efficiency = $(\bar{M}_{n,th/Li}/\bar{M}_{n,exp}) \times 100$.

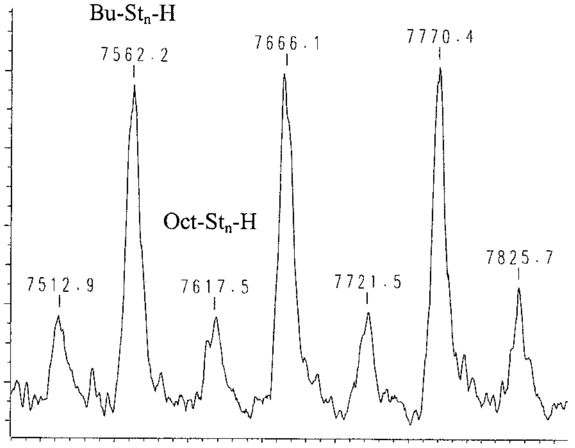


Figure 3. Details of the MALDI mass spectrum of polystyrene (range 7500−7800 g mol^{-1}) synthesized from *n*-Bu,*n*-OctMg/LiOiPr ([Mg]/[Li] = 3, polymerization at 100 °C in cyclohexane).

estimated from the number of polystyrene chains formed. Indeed, *n*-Bu,*n*-OctMg as well as RMgOR′ derivatives cannot co-initiate new chains with lithium species in the present conditions.[2,3] Since conventional transfer processes are negligible, only one chain is expected to form the RLi species generated. Therefore, the efficiency was derived from the PS yield and the chain molar masses. The results gathered in Table 1 for *n*-Bu,*n*-OctMg/LiOiPr ([Mg]/[Li] = 3.0) indicate that about 50% of the initial lithium alkoxide yielded an active alkyllithium chain initiator. This value is consistent with the relative optical densities of the absorption band at 310 nm (0.40 and 0.75) for *n*-Bu,*n*-OctMg/LiOiPr and BuMgOBu/PSLi polymerization systems, respectively. The lower initiation efficiency of the lithium alkoxide systems may result from incomplete ligand exchange, despite the excess of R_2Mg species, and/or from slow initiation of styrene polymerization which involves primary alkyllithium compounds complexed with alkylalkoxymagnesium. However, the polydispersity index of the polymers remains low ($I_p \leq 1.2$).

In the dialkylmagnesium/LiOiPr systems, we believe that initiation of the polymerization takes place in the bimetallic complexes, after ligand exchanges between LiOiPr and *n*-Bu,*n*-OctMg, thus yielding complexed *n*-BuLi and/or *n*-OctLi as active moieties. The MALDI mass spectra of the PS samples show that the chains possess either a butyl or an octyl headgroup (Figure 3). The ratio between the two populations agrees well with the initial fractions of *n*-octyl and *n*-butyl groups (1:3, respectively) present in the commercial *n*-Bu,*n*-OctMg.

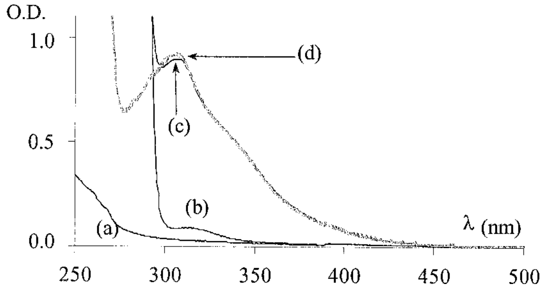


Figure 4. UV−vis spectra of *n*,*sec*-Bu_2Mg/LiOiPr in cyclohexane: (a) [Mg]/[Li] = 2.0, $[LiOiPr]_0 = 7.1 \times 10^{-3}$ mol L^{-1}. Polymerization time at 100 °C: (b) 0; (c) 20 min; (d) 90 min, corresponding to end of polymerization.

The apparent propagation rate constant of styrene determined at 100 °C for *n*-Bu,*n*-OctMg/LiOiPr ([Mg]/[Li] = 3.0) is slightly higher than that measured with the *n*-Bu,*n*-OctMg/PSLi system but still shows a strong retardation effect.[13] As a result of the ligand exchange process, alkylalkoxymagnesium compounds are formed which are less efficient than dialkylmagnesium as retarding agent (see experiment B, Table 1). However, since *n*-Bu,*n*-OctMg can be used in excess and remains in the polymerization medium, the rate increase can be limited.

(b) Systems Based on *n*,*sec*-Bu_2Mg and R′Oli. The reversible exchange of alkyl groups from magnesium to lithium in bimetallic R_2Mg/PSLi complexes proceeds more readily with secondary alkyl groups than with primary ones. Moreover, initiation of styrene polymerization with *sec*-BuLi is much faster than initiation with *n*-butyllithium.[14] Therefore, *n*-Bu,*n*-OctMg was replaced with *n*,*sec*-Bu_2Mg to tentatively increase the initiation efficiency of the R_2Mg/LiOiPr system.

Although no chromophoric species are present in the complexes initially formed between *n*,*sec*-Bu_2Mg and LiOiPr, an absorption band with a maximum located at 310 nm rapidly forms on the UV−vis spectra upon styrene addition at 100 °C (Figure 4). It most likely corresponds to both BuMgOiPr:PSLi and PSMgBu chromophores since *n*,*sec*-Bu_2Mg was used in excess relative to LiOiPr. Indeed, as indicated by the observed polystyrene molar masses (Table 2), *n*,*sec*-Bu_2Mg is still able to co-initiate new chains with RLi even in the presence of RMgOR′ derivatives. A mechanism is proposed in Scheme 2.

The increase of the polystyryl chromophores' band intensity with time shows that their formation is faster with *n*,*sec*-Bu_2Mg/LiOiPr than with *n*-Bu,*n*-OctMg/LiOiPr. As illustrated in Figure 4, almost all the polystyryl species are formed (>95%) within 20 min at 100 °C. There is no further evolution of the UV−vis spectra, except the decrease in the styrene band (λ = 290 nm), corresponding to its polymerization.

The higher optical density of the 310 nm polystyryl band compared to the one formed with *n*-Bu,*n*-OctMg/LiOiPr (Figure 1) suggests a more efficient initiation. This could be attributed both to a more complete isopropoxide−*sec*-butyl ligand exchange and a faster styrene addition into ^{s}Bu−Li bonds.

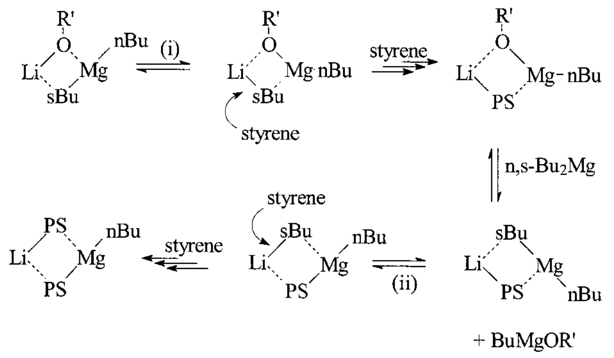
The efficiency of the ligand exchange between LiOiPr and *n*,*sec*-Bu_2Mg (Scheme 2, i) to yield within the complex BuMgOiPr and BuLi moieties is difficult to evaluate since several types of alkyl ligand transfer may occur in this system. Indeed, even if the conversion of LiOR′ into BuLi is incomplete, the remaining *n*,*sec*-Bu_2Mg can exchange its *sec*-butyl group with the com-

Table 2. Polymerization of Styrene in Cyclohexane at 100 °C Initiated with *n,sec*-Bu$_2$Mg/PSLi (Series D), *n,sec*-Bu$_2$Mg/BuMgOBT/PSLi (2:1:1, Series E), or *n,sec*-Bu$_2$Mg/LiOR′ (Series F)

ref	ROH	[Mg]/[Li]	$[Li]_0$[a] (mol L^{-1})	k_{papp}[b] (L mol^{-1} min^{-1})	$\bar{M}_{n,th/Li+Mg}$[c] (g mol^{-1})	$\bar{M}_{n,th/Mg}$[d] (g mol^{-1})	$\bar{M}_{n,exp}$[e] (g mol^{-1})
D_1		2.0	4.8×10^{-3}	6.0	4600		5000
D_2		3.0	6.2×10^{-3}	1.9	3500		3500
D_3		4.0	4.9×10^{-3}	1.1	3100		3100
E_1		3.0	8.5×10^{-3}	0.8	3200		3300
F_1	2-propanol	2.0	7.1×10^{-3}	7.9		6100	6400
F_2	BHT	2.0	7.0×10^{-3}	2.2		5400	6700
F_3	BHT	3.0	5.7×10^{-3}	1.4		3500	3600
F_4	nonylphenol	3.0	5.3×10^{-3}	1.1		3600	4400
F_5	H_2O	5.0	5.3×10^{-3}			2000	3400

[a] $[Li]_0 = [PSLi]_0$ or $[LiOR']_0$. [b] $Rp = k_{papp}[Li]_0[S]$. [c] $\bar{M}_n$ calculated from [PSLi + *n,sec*-Bu$_2$Mg]$_0$. [d] $\bar{M}_n$ calculated from [*n,sec*-Bu$_2$Mg]$_0$. [e] $\bar{M}_n$ measured by SEC.

Scheme 2



plexed polystyryllithium species formed and thus generate new polystyrene chains[2] (Scheme 2, ii). For clarity, ternary *n,sec*-Bu$_2$Mg:BuMgOiPr:PSLi complexes are not represented in the scheme although they are likely to be present in the reaction medium.

Thus, the PS experimental molar masses with *n,sec*-Bu$_2$Mg should correspond to one PS chain formed per Mg atom, even if the alkoxy–alkyl ligand exchange is not complete.

$$\bar{M}_{n,th} = [S]/([\text{initially formed BuLi}] + [n,sec\text{-Bu}_2\text{Mg in excess}]) = [S]/[\text{initial } n,sec\text{-Bu}_2\text{Mg}]$$

This was verified at various [Mg]/[Li] ratio with the *n,sec*-Bu$_2$Mg/LiOiPr systems. For the ratio [Mg]/[Li] = 2, approximately half of the chains may result from the formation of alkyllithium moieties through the alkoxy–alkyl ligand exchanges. Another half can then form through the reversible ligand exchange between polystyryllithium and *n,sec*-Bu$_2$Mg.

The other lithium alkoxides behave similarly (see Table 2).

The apparent propagation rate constants are given in Table 2. They were calculated assuming complete alkoxy–alkyl ligand, i.e., $[RLi]_0 = [LiOR']_0$. At the same [Mg]/[Li] ratio, the propagation rate measured with the *n,sec*-Bu$_2$Mg/LiOiPr system (Table 2, experiment F_1) is slightly higher than that obtained with *n,sec*-Bu$_2$Mg/PSLi (Table 2, experiment D_1). This result can again be explained by the formation of alkylalkoxymagnesium derivatives which are less efficient retarding agents than *n,sec*-Bu$_2$Mg (see for example for a ratio Mg/Li of 4 Table 1, experiment B with BuMgOBu and Table 2, experiment D_3 with *n,sec*-Bu$_2$Mg).

Influence of the Nature of the OR′ Group. The influence of the nature of the alkoxy group on both the initiation efficiency and the retardation of styrene polymerization was further investigated; lithium phenoxide and lithium hydroxide derivatives were used in place of lithium isopropoxide.

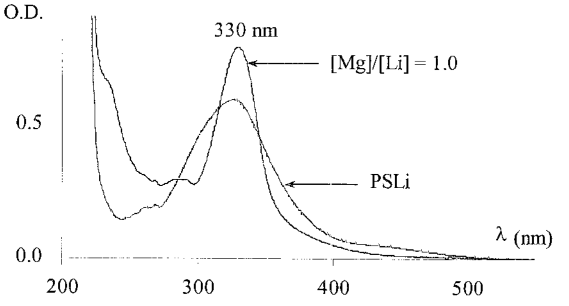


Figure 5. Effect of the addition of BuMgOBT on the PSLi UV–vis spectrum[3] (cyclohexane, 20 °C, [PSLi] = 5.5×10^{-3} mol L^{-1}).

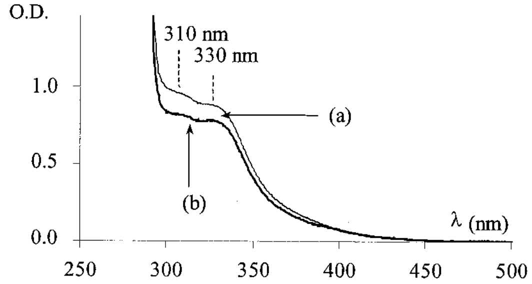


Figure 6. UV–vis spectra of *n,sec*-Bu$_2$Mg/LiOBT ([Mg]/[Li] = 3.0) (a) and *n,sec*-Bu$_2$Mg/BuMgOBT/PSLi (2:1:1) (b) after 90 min at 100 °C in the presence of styrene. [Li] = 5.5×10^{-3} mol L^{-1}, [styrene] = 0.58 mol L^{-1}.

(a) Lithium 2,6-Di-*tert*-butyl-4-methylphenoxide (LiOBT). The complexation of PSLi species by 2,6-di-*tert*-butyl-4-methylphenoxybutylmagnesium (BuMgOBT) yields a 1:1 complex with a well-defined absorption band at 330 nm (see Figure 5). Similar heterocomplexes should also form through ligand exchanges when starting from LiOBT and *n,sec*-Bu$_2$Mg.

The absorption spectra of *n,sec*-Bu$_2$Mg/LiOBT ([Mg]/[Li] = 3) and the corresponding *n,sec*-Bu$_2$Mg/BuMgOBT/PSLi (2:1:1) system recorded after 1.5 h reaction at 100 °C with styrene are presented Figure 6. Both spectra are very similar, indicating that the ligand exchange between *n,sec*-Bu$_2$Mg and LiOBT takes place to a large extent. In addition to the 330 nm band, the shoulder at 310 nm can be attributed to the formation of PSMgBu species as already discussed. A hypothetical structure for this complex and assignment of the UV–vis band are proposed in Scheme 3.

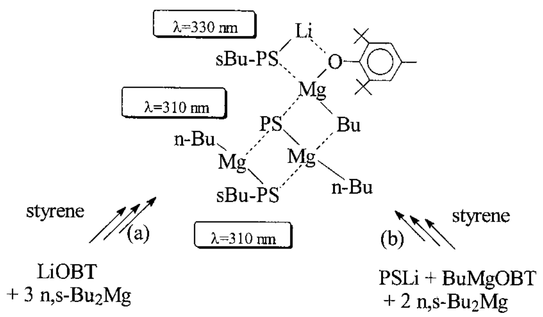
The higher polymerization activity observed with *n,sec*-Bu$_2$Mg/LiOBT is attributed to the fact that polymerization proceeds before complete formation of the final heterocomplex of low reactivity.

Table 3. Polymerization of Styrene at 100 °C in Cyclohexane Initiated with i-$Bu_3Al/PSLi$ (A), $Et_2AlOEt/PSLi$ (B), or i-$Bu_3Al/LiOR'$ (Series C)[i]

ref	ROH	$[Li]_0$[a] (mol L^{-1})	[Al]/[Li]	k_{papp}[b] (L mol^{-1} min^{-1})	$\bar{M}_{n,th/Li}$[c] (g mol^{-1})	$\bar{M}_{n,exp}$[d] (g mol^{-1})	eff[e] (%)	I_p[f]
A		7.4×10^{-3}	0.80	3.6	6400	6800	100	1.1
B		8.2×10^{-3}	0.80	5.7	6200	6600	100	1.7
C_1	2-propanol	8.0×10^{-3}	0.50	6.4	5800	54000	10	1.2
C_2	H_2O[g]	8.6×10^{-3}	0.50	1.75	5000	142000	3.0	2.7
C_3	BHT	6.0×10^{-3}	0.50	~0				
C_4	nonylphenol[h]	6.0×10^{-3}	0.50	0.15	3100	16400	19	1.3

[a] $[Li]_0 = [PSLi]_0$ or $[LiOR']_0$. [b] $R_p = k_{papp}([Li]_0 \times \text{eff})[S]$. [c] $\bar{M}_n$ calculated from $[Li]_0$. [d] $\bar{M}_n$ measured by SEC. [e] Initiation efficiency = $(\bar{M}_{n,th/Li}/\bar{M}_{n,exp}) \times 100$. [f] Polydispersity index estimated from SEC. [g] 85% conversion after 90 h. [h] 53% conversion after 94 h. [i] It was checked that, in similar conditions (cyclohexane, $[styrene]_0 = 0.4$ mol L^{-1}, 100 °C), the contribution of the radical process to the formation of polystyrene is negligible, even after 120 h (monomer conversion < 1%).

Scheme 3



(b) Lithium Hydroxide. Ligand exchange and initiation of styrene anionic polymerization from *n,sec*-$Bu_2Mg/LiOH$ mixtures were also successfully attempted. However, the polymerization was very slow (at 100 °C, 60% conversion after 22 h) and resulted in polymer with very high molar masses. This suggests that the amount of alkyllithium moieties generated by ligand exchange is very low and yields a high [Mg]/[Li] ratio, which is associated with strong retardation. The behavior of this system is also complicated by the possible formation of BuMgOMgBu derivatives.

The experimental polystyrene molar masses are in agreement with an important contribution of *n,sec*-Bu_2Mg to the formation of PS chains (Table 2, F_5). Co-initiation by *n,sec*-Bu_2Mg is the main source of PS chains, but the final ratio R_2Mg/RLi is probably too high to allow the participation of all *n,sec*-Bu_2Mg compounds ($\bar{M}_{n,th/Mg} < \bar{M}_{n,exp} \ll \bar{M}_{n,th/Li}$).

Initiation of Styrene Anionic Polymerization by Systems Based on R_3Al and LiOR′. A similar study was conducted using i-Bu_3Al instead of dialkylmagnesium derivatives as alkyl source. Previous studies have shown that the reactivity of i-$Bu_3Al/PSLi$ systems toward styrene polymerization is highly dependent on the [Al]/[Li] ratio,[1] and systems with ratios $[Al]/[Li] \geq 1$ are totally inactive.[15] i-Bu_3Al and R_2AlOR' derivatives when associated with alkyllithium species are also unable to co-initiate the formation of new chains.[1,4] As a consequence, the efficiency of the alkyl−alkoxy ligand exchange in the $AlR_3/LiOR'$ systems can be directly related to the number of PS chains formed, assuming no conventional transfer reactions. The initiating efficiency was calculated from the PS yield and the chain molar masses. Although styrene polymerization proceeds in agreement with ligand exchanges, polymers of very high molar masses were obtained, indicating low initiation efficiencies (see Table 3).

For the LiOiPr/i-Bu_3Al system ([Al]/[Li] = 0.5) at 100 °C, only 10% of LiOiPr is converted into alkyllithium initiating species. This corresponds to a ratio [Al]/[PSLi] = 5. Since 1:1 ($^iBu_3Al$:PSLi) complexes are reported to be inactive, this result supports complexation of the remaining LiOiPr with i-Bu_3Al.

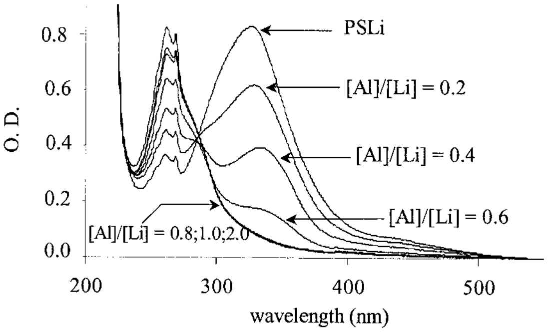


Figure 7. Effect of Et_2AlOEt increments on the PSLi UV−vis spectrum in cyclohexane at 20 °C. $[PSLi] = 8.1 \times 10^{-3}$ mol L^{-1}; $\bar{M}_n = 1000$ g mol^{-1}.

The UV−vis technique yields only a little information about the nature and the concentration of formed polystyryl species. Indeed, the absorption bands of polystyryl in heterocomplexes are located at low wavelengths and superimpose the styrene and polystyrene absorption peaks, as already observed with $PSLi/R_3Al$[1] and $PSLi/R_2AlOR'$ (Figure 7) systems.

Because of charge delocalization on the phenol aromatic ring and in connection with the pK_a values of phenol and alcohol, the ligand exchange should be slower for lithium phenoxide than for lithium alkoxide. In the LiOR′ series examined, the highest initiation efficiency observed yet is in the presence of lithium nonylphenoxide (Table 3, C_4). This can be tentatively explained by the extremely low reactivity of the $^iBu_3Al$/lithium nonylphenoxide system for styrene polymerization, thus allowing the exchange reaction to proceed over a much longer time.

Besides, the inactivity of the i-Bu_3Al/LiOBT system is consistent with previous observations concerning the use of diisobutyl-2,6-di-*tert*-butyl-4-methylphenoxyaluminum (i-Bu_2AlOBT) in association with PSLi seeds.[4] In this system, a completely reversed ligand exchange takes place, yielding i-Bu_2AlPS and LiOBT moieties. The transfer of the −OBT group from lithium to $^iBu_3Al$ and thus formation of alkyllithium moieties are therefore very unlikely.

Finally, as already considered for the corresponding magnesium system, the very low efficiency of the ligand exchange between LiOH and i-Bu_3Al likely results from LiOH insolubility. Moreover, LiOH may also react with the formed RLi species to yield inactive Li_2O salt.

Comparison of $R_2Mg/LiOR$ and $R_3Al/LiOR$ systems (*n*-Bu,*n*-OctMg/LiOiPr, [Mg]/[Li] = 3 and i-Bu_3Al/LiOiPr, [Al]/[Li] = 0.5), which exhibit very close reactivity, shows that 50% and 10% of the lithium alkoxide, respectively, is involved in the initiation of the polymerization and yields a polystyrene chain. As indicated by the relative metal−alkyl bond lengths[16] ($d_{C-Mg} = 2.19$ Å and $d_{C-Al} = 1.97$ Å), alkyl groups are more strongly linked to aluminum than to magnesium. As a consequence, the ligand exchange between *i*-Bu_3Al and LiOR′ is more difficult, yielding lower initiation efficiencies.

Conclusions

The combination of lithium alkoxide or phenoxide with dialkylmagnesium or trialkylaluminum affords an alternative way to the direct use of alkyllithium derivatives to initiate styrene anionic polymerization. The activation mechanism proceeds through an alkoxy−alkyl ligand exchange between the two metal derivatives. This process is highly improved by the presence of secondary alkyl groups attached to the magnesium atom. Some of these systems are highly efficient for retarded polymerization conditions. The generation of new initiating systems from lithium salts associated with dialkylmagnesium is not restricted to LiOR′ systems. Further studies based on these metal-to-metal ligand exchanges are in progress.

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