DOI: 10.1002/masy.200551104

New Perspectives in Living/Controlled Anionic Polymerization

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Summary: Control of the reactivity and selectivity of active species remains a major challenge in the course of living/controlled polymerizations of vinyl and heterocyclic monomers. We have found that alkyl metal derivatives such as dialkylmagnesium or trialkylaluminum derivatives or the corresponding alkoxyakyl metal derivatives, when added to conventional anionic polymerization systems, are very effective mediators for the controlled anionic polymerization of both styrenic and oxirane monomers. When used as additives to alkali metal alkyl initiators (alkyl lithium, alkyl sodium) for the styrene anionic polymerizations, they strongly retard the reactivity of the propagating species and allow controlling the polymerization in very unusual conditions (bulk, very high temperature). On the contrary, when used in combination to the same alkali metal based initiators for the anionic polymerization of ethylene oxide or propylene oxide, these additives can drastically enhance the reactivity and the selectivity of the propagating species allowing a fast living-like polymerization to proceed already at low temperature in hydrocarbon media.

Keywords: retarded anionic polymerization; monomer activated polymerization; styrene; propylene oxide

Introduction

Control of the reactivity and selectivity of active species remains a major challenge in the course of living/controlled polymerizations. Although the first example of living polymerization described by Szwarc, almost 50 years ago, already concerned the anionic polymerization of styrene, there is still much effort to be taken in this domain to broaden the scope of living polymerizations to new initiating systems and to polymerization processes that can be more economically attractive to industry.

For example, the living anionic polymerization technique presents several important advantages in comparison to styrene thermal polymerization presently used in industrial processes. Contrarily to the thermal-free radical-prepared ones, polystyrenes (PSs) obtained by a living type anionic mechanism are expected to be free of residual monomer, thermal dimers, and trimers. Moreover, they should exhibit a higher thermal stability, in particular during the processing step, since defects along the chains such as head-to-head monomer placement are absent. It would also become possible to benefit of the living polymerization characteristics to elaborate polymers and copolymers with sophisticated chain structures such as telechelics, branched polymers, block copolymers, etc.

To make the styrene anionic process economically competitive, it is however necessary to avoid polymerization in solution and therefore find conditions which allow high temperature bulk (or highly concentrated) anionic polymerization.

We have found that some alkyl metal derivatives such as dialkylmagnesium or trialkylaluminum or the corresponding alkoxyakyl metal compounds, introduced

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as additives to conventional anionic polymerization systems, are very effective mediators for the controlled anionic polymerization of various monomers. When used in combination with alkali metal alkyl initiators (alkyl lithium, alkyl sodium) for the styrene and/or dienes anionic polymerization, they strongly retard the reactivity of the propagating species and allow controlling polymerization in very unusual conditions (bulk at very high temperature).

On the contrary, when these initiating systems (i.e., those based on trialkylaluminum) are used for the anionic polymerization of ethylene oxide or propylene oxide (PO), a drastic enhancement of the reactivity and the selectivity toward monomer insertion of the propagating species is observed, allowing a fast living-type ring opening polymerization to proceed at 0 °C in nonpolar solvent. This opens interesting opportunities for the preparation of oxirane-type polymer and their block copolymers.

These findings are illustrated and discussed in this article through the presentation of a series of selected systems covering the anionic polymerization of styrene and PO.

Experimental Part

Materials

s-Butyllithium (1.3 M in cyclohexane from SAFC, France), ether-free *n*,*s*-dibutylmagnesium (*n*,*s*-Bu_2Mg; 1.0 M in heptane from SAFC), and triisobutylaluminum (*i*-Bu_3Al; 1.0 M in cyclohexane from SAFC) were used as received. Cyclohexane (99.5% from SAFC) was degassed over freshly crushed CaH_2, stored over polystyryllithium oligomers, and distilled before use. Styrene (99% from SAFC) was degassed over freshly crushed CaH_2, stored over *n*,*s*-dibutylmagnesium, and distilled before use. PO (99%, Fluka) was purified successively over CaH_2 and dialkylmagnesium or triisobutylaluminum, distilled under vacuum, and stored in glass flasks equipped with PTFE stopcocks until use. *i*-PrONa was synthesized by reaction of *i*-PrOH (99.5% anhydrous, Aldrich) previously dried and distilled over CaH_2 with sodium metal (99.95%, cubes in mineral oil, Aldrich) dispersed in toluene. The mixture was reacted at 50 °C for one night and stored over a small excess of sodium metal. The mixture was also reacted at 25 °C for 1 h and the supernatant liquid recovered by filtration.

Polymerizations

All polymerizations were performed under argon in a glass reactor, previously flamed under vacuum, equipped with a magnetic stirrer, and fitted with PTFE stopcocks.

Styrene polymerizations were carried out in cyclohexane or in bulk at temperatures ranging from 50 to 200 °C in glass flasks. Polystyryllithium seeds ($\overline{DP}_n = 5$–100, $[PSLi] = 3.1$–8.5×10^{-3} M) were generally used as polymerization initiators. A known amount of magnesium or aluminum derivative was then added to the seed solution to obtain the suitable ratio [Mt]/[Li]. After styrene addition, the polymerization was followed either by monitoring the monomer consumption by UV-visible spectrometry ($\lambda = 290$ nm) or by taking samples at increasing time.

For PO polymerization, cyclohexane and PO were first introduced followed by the initiator in toluene solution and finally the trialkylaluminum via syringes under argon. After a desired reaction time, HCl/EtOH was added to stop the reaction and the remaining PO and cyclohexane were stripped off under vacuum. Conversions were determined gravimetrically after complete drying of the polymer under vacuum at 50 °C.

Analytical Techniques

Average molar masses and molar masses distribution of PS and polypropylene oxide (PPO) were determined by size exclusion chromatography (SEC) at 20 °C on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU, refractive index/UV detectors and TSK Gel columns calibrated with PS standards.

Results and Discussion

Alkyl Metals as Retarder for Styrene Anionic Polymerization

Styrene polymerization performed in presence of alkyl lithium alone proceeds extremely rapidly at temperatures higher than 50 °C in concentrated media. At 100 °C the heat of polymerization, which is evolved within a very short period of time (less than 1 min), results in a runaway reaction with an increase of the inside reactor temperature up to 350 °C susceptible to yield reactor explosion. As a consequence, low molar mass, ill-defined, yellow colored PS with conjugated unsaturations at the chain end are obtained making the bulk high temperature anionic polymerization of styrene inappropriate for an industrial application.

In order to lower and keep under control the rate of polymerization, the influence of Lewis acids on the reactivity of the propagating species, more particularly alkyl metals, has been investigated.

a) Magnesium Based Systems

The kinetics of styrene polymerization initiated by the system PSLi seeds/*n*,*s*-Bu_2Mg (*n*-butyl, *s*-butyl magnesium) have been investigated in cyclohexane and in bulk at temperatures ranging from 50 to 150 °C.[1–3] As it may be seen in Figure 1, the increase of the *n*,*s*-Bu_2Mg proportion with respect to PSLi, from 0 to 20, is accompanied by a strong decrease of the overall reactivity of the system. Nevertheless, polymerization remains quantitative and the semi-logarithmic plots of the styrene concentration versus time gives straight lines up to high styrene conversions. The corresponding values of $\mathrm{Ln}(R_p/M)$ versus $r = [Mg]/[Li]$ are plotted in Figure 2. As already stressed, a strong and continuous decrease of the styrene polymerization rate is observed in the whole range of *r* (factor 10^3 and 6×10^3 for $r = 4$ and 20, respectively).

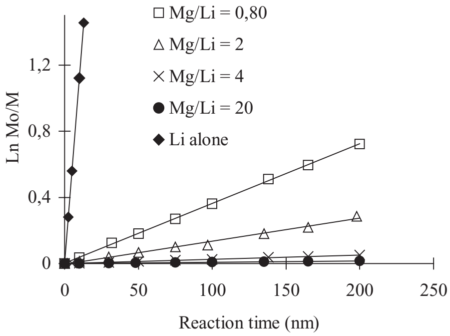


Figure 1.
Influence of the ratio *n*,*s*-Bu_2Mg/PSLi on the kinetics of styrene polymerization; [PSLi] $= 3–8 \times 10^{-3}$ M; [styrene] $= 0.3–0.5$ M; cyclohexane, 50 °C.

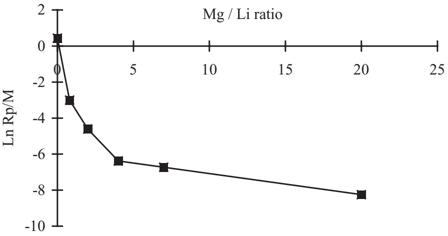


Figure 2.
Influence of the ratio *n*,*s*-Bu_2Mg/PSLi on the styrene propagation rate; [PSLi] $= 3–8 \times 10^{-3}$ M; [styrene] $= 0.3–0.5$ M; cyclohexane, 50 °C.

This strong retardation effect on kinetics can be attributed to the formation of mixed "ate" complexes PSLi/*n*,*s*-Bu_2Mg of various stoichiometry as confirmed by successive shifts of the PSLi absorption band observed by UV-visible spectroscopy.

At different ratios, the $\overline{M}_n$ of PS increases linearly with conversion and distribution remains narrow, in agreement with a living like polymerization process. However, experimental $\overline{M}_n$ does not match the theoretical values calculated assuming initiation only by alkyllithium species. $\overline{M}_n$ decreases continuously while increasing *r* indicating beyond initiation by PSLi needs a second mechanism of chain formation involving the magnesium species which likely act in the ate complex rather as reversible transfer agent than as new initiating site. Almost one chain is formed by Mg species in addition to those from PSLi seeds, Figure 3.

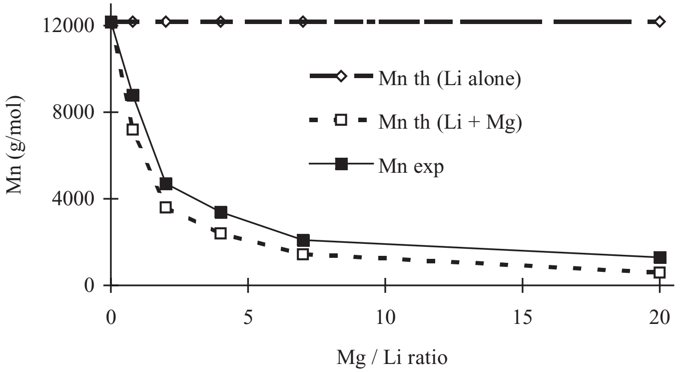


Figure 3.
Influence of the ratio n,s-Bu_2Mg/PSLi on the PS experimental molar masses; polymerization in cyclohexane, at 50 °C.

b) Aluminum Based Systems

As previously described,[4,5] triisobutylaluminum, used as additive in the styrene anionic polymerization, also allows a strong reduction of the reactivity of propagating active species (Figure 4). The rate decrease depends on the ratio [Al]/[Li] but contrarily to magnesium systems no polymerization is observed for ratios equal or higher than one. This limit corresponds to the quantitative formation of an inactive 1:1 complex (i-Bu_3Al:PSLi) whereas at ratio [Al]/[Li] slightly lower than 1 the strong decrease in polymerization rate is explained by the formation of a low activity 1:2 (Al:Li) complex (Scheme 1). Therefore, both active and "dormant" chains coexist at [Al]/[Li] ratio ranging from 0 to 1. However, fast dynamic equilibrium between the 1:2 and 1:1 complexes, through exchange reactions, results in the formation of a constant number of PS chains, close to the initial amount of RLi species.

The polymerization reactivity profile observed (Figure 4) suggests a low equilibrium constant for the formation of the 1:2 (Al:Li) complex from the 1:1 complex and a second PSLi specie, unfortunately this allows at low [Al]/[Li] ratio likely up to $r = 0.7$–0.8, the presence of active PSLi,

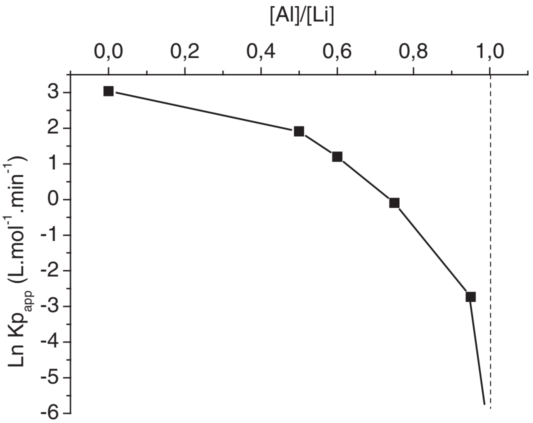
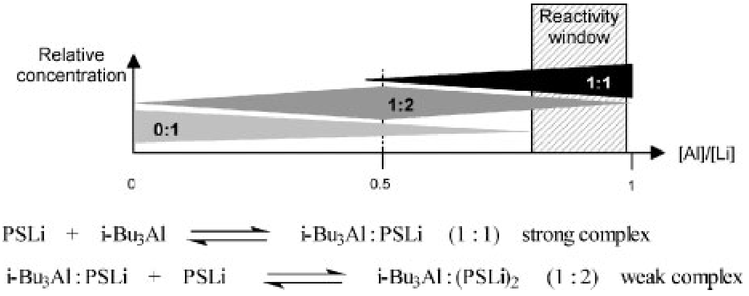


Figure 4.
Reactivity profile in the anionic polymerization of styrene in the presence of PSLi/i-Bu_3Al as a function of the [Al]/[Li] ratio, cyclohexane, $T = 50$ °C.



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

noncomplexed with *i*-Bu_3Al, which strongly contribute to the polymerization reaction. This limits the polymerization reactivity window for high temperature to the range $0.8 < [Al]/[Li] < 1$.

A very similar behavior is observed with Et_3Al. At $r = 0.90$ at 100 °C, the apparent rate constant of propagation is about 2 orders of magnitude lower than for PSLi alone ($k_{p_{app},Et_3Al} = 1/96 k_{p_{app},PSLi}$).

In contrast, for Hex_3Al:PSLi, the polymerization proceeds up to [Al]/[Li] ratio of about 3. According to UV visible spectroscopy this corresponds to the quantitative complexation of PSLi, and likely the unique formation of the inactive 1:1 aluminate complex. These observations confirm that in aluminum-based systems the reactivity window is effectively controlled by the rate of formation of heterocomplexes between free PSLi ends and the trialkylaluminum derivatives.

With the aim to broaden the scope of reactivity in aluminum derivatives/PSLi systems, the influence of several diethylaluminum alkoxide additives, ethoxide (Et_2AlOEt), *sec*-butoxide (Et_2AlO*s*-Bu), and *tert*-butoxide (Et_2AlO*t*-Bu), has been also investigated.[6] The retardation effect is even stronger than for trialkylaluminum systems. However, in contrast to previous systems, the retardation reaches a plateau and remains almost constant over a domain of [Al]/[Li] ratios ranging from about 1.1 to 5 (Figure 5), in this broad domain the reactivity decreases only by a factor of less than 3. The observed PS molar masses are also consistent with the formation of one PS chain per PSLi seed; whereas their molar mass distribution remains narrow (1.1). These results indicate that 1:1 dialkylaluminum alkoxide:PSLi complexes are active for the polymerization of styrene at 100 °C, thus enlarging greatly the reactivity window in contrast to trialkylaluminum systems.

Trialkylaluminum as Activator of Propylene Oxide Polymerization

Improvement of PO polymerization and the ways to control its living character is still the object of important research efforts since PPO found important applications, both as functional oligomers and as high molar mass elastomer. Indeed, despite significant progress, the anionic PO polymerization still suffers from several important drawbacks due to the high basicity of propagating species generated by alkali metal alkoxides or hydroxides initiators, and proton abstraction from the PO methyl group takes place yielding a transfer reaction to monomer.[7] This side process results in the exclusive formation of PPO oligomers, a large fraction of which possesses a terminal allylic unsaturation.

Controlled PO polymerization has been achieved one decade ago with aluminum porphyrin initiators.[8] Very recently, the possibility to substitute porphyrin initiators, very difficult to remove from PPO, by simpler systems based on the association of ammonium salts with a bulky bisphenoxy aluminum electrophile was proposed.[9] However, up to now, only the synthesis of PPO oligomers with molar

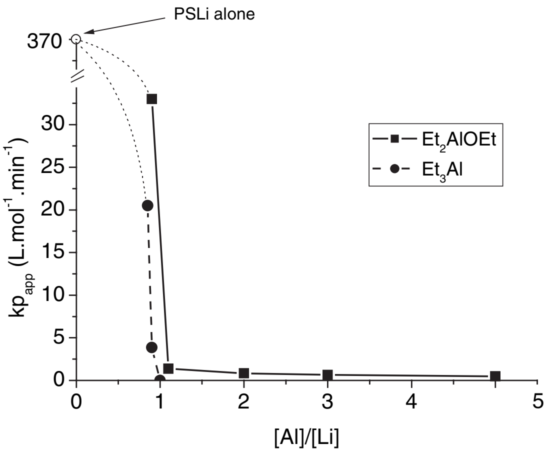


Figure 5.
Variation of $k_{p_{app}}$ with the ratio [Al]/[Li] for PSLi/Et_2AlOEt. For comparisons $k_{p_{app}}$ of PSLi/Et_3Al systems are given at different ratios (cyclohexane, 100 °C).

masses of less than 5 000 g · mol^{-1} was reported for this last system. We have found that simple trialkylaluminum compounds used as additives to conventional alkali metal alkoxide initiators strongly activate the oxirane polymerization.[10,11]

Whereas PO does not polymerize in cyclohexane in the presence of Na *tert*-amyloxide, the polymerization readily occurs in the presence of triisobutylaluminum in hydrocarbon media between −30 and 20 °C, Table 1.

Indeed, polymerization proceeds only when the molar ratio $r = [i\text{-}Bu_3Al]/[i\text{-}PrONa]$ is higher than 1. At $r > 1$, the higher the fraction of trialkylaluminum, the faster the polymerization, in agreement with an important activating effect of the "free" trialkylaluminum derivative. Moreover at 0 °C, in the whole molar mass range examined, the experimental PPO molar masses are close to theoretical values calculated assuming the formation of one polymer chain per *i*-PrONa. Molar mass distributions are narrow although a slight broadening can be noticed for PPO of molar masses higher than 10 000 g · mol^{-1}. This suggests a living-like character for the PO polymerization or at least a significant decrease of the contribution of the monomer transfer process, which is observed with alkali metal based initiators.

These results are consistent with a strong activation of the polymerization by R_3Al

Table 1.
PO polymerization initiated by *i*-PrONa (I) in the presence of triisobutylaluminum in cyclohexane.

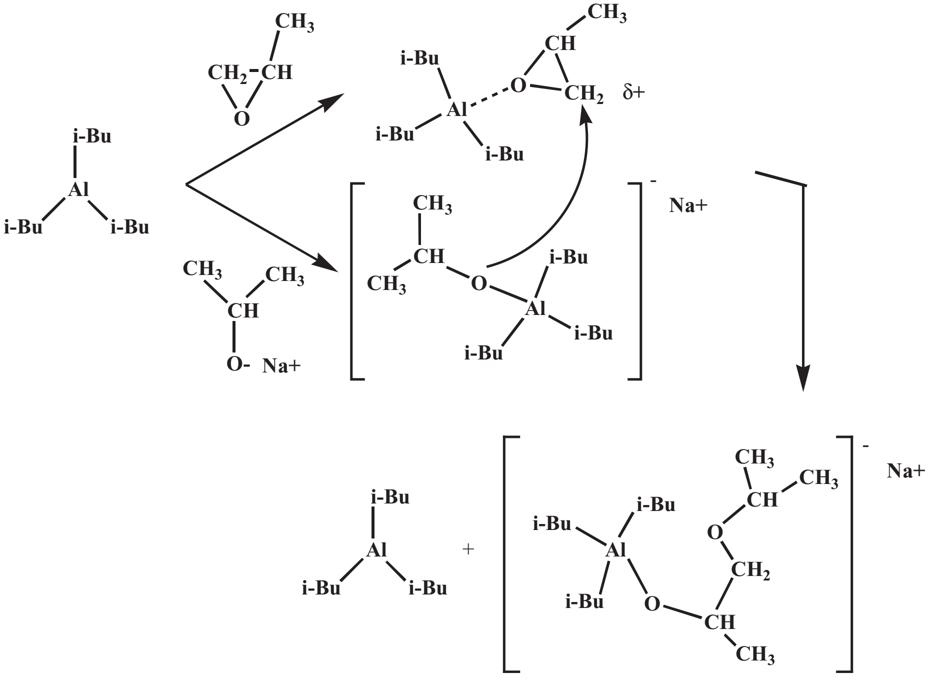
[PO] mol · l^{-1}	[PO]/[I]	[*i*-Bu$_3$Al]/[I]	Time	T °C	Yield %	$\overline{M}_n$th g · mol^{-1}	$\overline{M}_n$ g · mol^{-1}	$\overline{M}_w/\overline{M}_n$
6.2$^{a)}$	360	0	7 d	25	0	-	-	-
5.5$^{b)}$	-	-	10 d	25	0	-	-	-
4.0	382	1	10 d	25	0	-	-	-
4.0	87	3.5	2 h	0	100	5 000	7 100	1.1
4.0	173	3.5	2 h	0	70	7 000	8 800	1.1
4.0	258	5.2	3 h 30	0	100	15 800	16 800	1.3
4.0	382	7.6	3 h 30	0	100	22 100	23 600	1.3

a) Experiment performed in the absence of *i*-Bu$_3$Al.
b) Experiments performed in the presence of *i*-Bu$_3$Al alone.

present in excess with respect to *i*-PrONa and a reaction mechanism in which the monomer is activated by the electrophilic aluminum compound prior to its insertion into the poly(propylenoxy) triisobutylaluminate sodium growing chain end (Scheme 2). The strong reduction of the transfer to monomer can be assigned to the much larger electron withdrawing effect of R_3Al complexation onto the methylene and methine PO α-carbons, the two potential active sites in the ring opening process, than on the β-methyl hydrogens involved in the transfer reaction to monomer. Reduction of the basicity of alkali metal alkoxide species in aluminate complexes may also contribute to the reduction of the proton abstraction reaction yielding transfer to monomer.

Conclusion

Dialkylmagnesium and trialkylaluminum derivatives used as additives to PSLi are good retarding agents for high temperature styrene polymerization and allow kinetically controlled styrene polymerization up to 120 and 150 °C, respectively. Depending on the metal but also on the nature and structure of the alkyl ligands the retardation effect is more or less pronounced. This can be related to the ease of formation and strength of ate complexes, the quantitative complexation of PSLi species, and the structure and stoichiometry of the formed complexes. Whereas the strong retardation effect is generally observed in the presence of large excess of dialkylmagnesium with respect to PSLi ($r > 4$) corresponding to complexes constituted of one PSLi chain for one or several dialkylmagnesium, the retardation takes place at r lower than one ($0.8 < r < 1$) in the case of trialkylaluminum systems. It likely involves the formation of a complex of low activity constituted by one trialkylaluminum with 2PSLi, whereas the stronger 1:1 complex is inactive. The relatively narrow domain of existence of the 1:2 complex determines the



Scheme 2.
Polymerization mechanism involving monomer activation prior insertion into the growing "ate" complex.

reduced reactivity window where retardation is operational. It is however possible to overcome this problem by using dialkylaluminum alkoxides which yield the formation of a 1:1 Al:Li complex that remains active at high temperature for styrene polymerization. This results in a quite different and much broader reactivity profile.

Another important difference between magnesium and aluminum-based retarded systems concerns the number of PS chains formed per associated metal derivative. In dialkylmagnesium systems, the number of PS chains is governed by the amount of dialkylmagnesium present and the nature of their alkyl groups. In the case of aluminum systems, with some exception for aluminum hydride, for example,[6] no insertion takes place in the aluminum-alkyl bond and the number of PS chains is determined by the initial amount of lithium species.

The strong retardation effect observed for styrene polymerization, in relation with the formation of propagating species in the form of ate complexes, can be completely overturned by a second mechanism involving the Lewis acid additives. This is typically the case in oxirane polymerization in the presence of trialkylaluminum additives. The formation of a second type of complex between the aluminum derivatives and the monomer results in a strong enhancement of its reactivity, which predominates over the possible lower reactivity of the ate propagating species. The increase of both the reactivity and selectivity in the monomer insertion step allows a living-like polymerization to proceed even at low temperature in hydrocarbon media.

These results illustrate the versatility of Lewis acids additives in anionic polymerization and their very beneficial contribution to the control of polymerization for a broad range of monomers.

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