Polymer 51 (2010) 5674–5679

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymerization of ethylene oxide initiated by lithium derivatives via the monomer-activated approach: Application to the direct synthesis of PS-*b*-PEO and PI-*b*-PEO diblock copolymers

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ARTICLE INFO

Article history:
Received 11 May 2010
Received in revised form
21 September 2010
Accepted 21 September 2010
Available online 8 October 2010

Keywords:
Anionic polymerization
Monomer activation
Poly(styrene-*b*-ethylene oxide)

ABSTRACT

The anionic polymerization of ethylene oxide (EO) initiated by lithium derivatives is extremely sluggish and only yields very low molar mass EO oligomers because of the low reactivity of lithium alkoxide species. We show here that using the monomer-activated anionic polymerization approach, one can activate the C–O–Li bonds towards EO polymerization at low temperature and in non polar media. Starting from living polystyryllithium and polyisoprenyllithium, addition of triisobutylaluminum (i-Bu_3Al) in excess to lithium species triggers the propagation reaction of EO, allowing the direct synthesis, in a few hours, of poly(styrene-*b*-ethylene oxide) and poly(isoprene-*b*-ethylene oxide) diblock copolymers, with a molar mass of the PEO block up to 10 000 g/mol.

1. Introduction

One of the most important applications of living anionic polymerization is the synthesis of well-defined block copolymers by sequential monomer addition [1]. Here we describe a new approach for the direct synthesis of poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) and poly(isoprene-*b*-ethylene oxide) (PI-*b*-PEO) diblock copolymers using polystyryllithium (PSLi) or polyisoprenyllithium (PILi) as macroinitiators for ethylene oxide (EO) polymerization. These diblock copolymers with a hydrophobic and a hydrophilic block have been largely studied and are of broad interest for their micellization and polymer emulgating properties [2].

The preferred route for the preparation of living and monodisperse polystyrene (PS) and polyisoprene (PI) blocks is the anionic polymerization initiated by alkyllithium. However when using this approach for the synthesis of PS-*b*-PEO and PI-*b*-PEO the strong lithium-oxygen bond formed after addition of one EO unit possesses a very low reactivity which makes it practically unable to add further EO units [3]. Different strategies have been developed to overcome this situation. The most general approach [4] consists in the preparation of PS–CH_2–CH_2OLi or PI–CH_2–CH_2OLi according to the following steps, i) addition of one EO molecule onto PSLi or PILi chain, ii) hydrolysis of the lithium alkoxide ends, iii) polymer drying, iv) transformation of the hydroxyl end into the corresponding sodium or potassium alkoxide in the presence of alkali metal salts, v) EO polymerization by the new alkali metal alkoxide [4–6]. Even in these conditions the anionic polymerization of EO requires long reaction times and is generally stopped before total monomer conversion. Despite its complexity, this process remains the main way for the preparation of PS-*b*-PEO and PI-*b*-PEO block copolymers.

An alternative approach recently developed consists in the addition of a phosphazene base t-BuP_4 onto butyllithium and living polystyryllithium, polybutadienyllithium (PButLi) or polyisoprenyllithium chains. This yields the formation of a lithium/t-BuP_4 complex and to the suppression of the lithium alkoxide aggregates. The large complex counterion allows the living polymerization of EO in THF [7–9] with molar masses up to 40 000 g/mol. Using hydrocarbon solvents, block copolymers were also prepared [8,10]. Long polymerization times (2–3 days) necessary at room temperature as well as the cost of the phosphazene base could be a limiting aspect for industrial purpose but the efficiency of this route and a one-step procedure places it to a high level of interest.

The present work deals with a third approach based on the synthesis of PEO, PS-*b*-PEO and PI-*b*-PEO block copolymers. Lithium precursors were used as initiators for the growth of PEO in short times using the monomer-activated anionic polymerization approach with triisobutylaluminum as additive.

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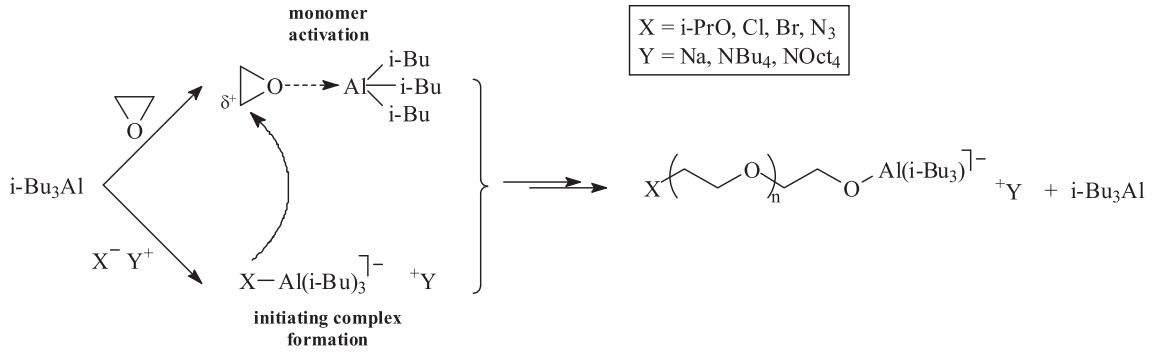
doi:10.1016/j.polymer.2010.09.061



Scheme 1. Polymerization mechanism via activation of ethylene oxide.

2. Experimental section

2.1. Materials

Toluene (98%, J.T. Baker) and dichloromethane (98%, J.T Baker) were purified respectively over polystyryllithium seeds and CaH_2, distilled and stored under vacuum in graduated glass tubes equipped with PTFE stopcocks. Ethylene oxide (99.8%, Fluka) was purified under vacuum over sec-Butyllithium (s-BuLi), distilled under vacuum and stored at room temperature in high pressure graduated glass tubes. Isoprene and styrene (99% Aldrich) were purified over n,s-dibutylmagnesium (1M in heptane, Aldrich) and distilled before use. s-BuLi (1.4M in cyclohexane, Aldrich) was filtered and used without further purification. 1,1-diphenyl-3-methylpentyllithium also called diphenylhexyllithium and abbreviated DPHLi was prepared by addition of a slight excess of diphenylethylene (95%, aldrich) onto the required amount of s-BuLi (1.1 eq) in THF at −40 °C and the solution was allowed to gradually attain room temperature. Triisobutylaluminum (1M in toluene, Aldrich) was used without further purification.

2.2. Procedures

All (co)polymerizations were performed at 25 °C under argon in a high pressure glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks, previously flamed under vacuum. Solvent and monomer(s) were introduced in the reactor under vacuum through connected glass tubes. Then the lithium derivative initiator and finally the aluminum derivative were added via a syringe under argon. HCl/EtOH was added to stop the reaction and the remaining monomer and solvent were stripped off under vacuum. Conversions were determined gravimetrically after complete drying off the polymer under vacuum.

Typically the synthesis of PS-*b*-PEO block copolymer was achieved as follows; in a 100 ml high pressure glass reactor equipped with a magnetic stirring bar, 10 ml of toluene and 0.5 ml of styrene (4.4 mmol), both stored in graduated tubes, were introduced into the reactor under vacuum through glass connectors. Then, 0.065 ml (0.091 mmol) of s-BuLi was added by a syringe under argon to start the polymerization of styrene at 25 °C. After 1 h, 1 ml of EO (19.5 mmol) was distilled directly into the reactor and 0.54 ml of i-Bu_3Al (0.54 mmol), corresponding to a ratio [Al]/[s-BuLi] = 6, was added via a syringe. After 3h reaction, HCl/EtOH was finally added to stop the reaction. The polymer was recovered by solvent evaporation under vacuum and characterized.

2.3. Kinetic measurements

Dilatometry measurements were performed using a similar synthesis procedure. Polystyryllithium was prepared directly into the glass dilatometer reactor then EO and i-Bu_3Al were added as indicated previously and the system was thermostated at 25 °C. The reaction was immediately monitored by recording the volume level of the solution in the capillary tube attached to the reactor.

2.4. Polymer characterization

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) at 20 °C in THF on a Jasco apparatus equipped with a Varian 2510 HPLC-pump, a refractive index Jasco detector, and three TSK gels HXL columns (2000, 3000, 4000), at an elution rate of 0.8 ml/min. Columns were calibrated with poly (ethylene oxide) and polystyrene standards.

MALDI-TOF spectra were acquired using a Bruker REFLEX III mass spectrometer (Bruker Daltonics, Bremen, Germany). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. The dithranol matrix solution was prepared by dissolving 10 mg in 1 ml of THF. A methanolic solution of cationisation agent (LiI + potassium salts, 10 mg/ml) was also used.

^{1}H NMR (400 MHz) measurements were performed on a Bruker Avance 400 spectrometer, in $CDCl_3$ at room temperature.

Table 1
EO polymerization initiated by lithium derivatives in the presence of i-Bu_3Al ([Al]/[Li] = 4, T = 25 °C).

Initiator (I)	Solvent	Time (h)	[EO] (mol/l)	Yield (%)	$\overline{M}_n$ (th.)[a] (g/mol)	$\overline{M}_n$ (exp.)[b] (g/mol)	$\frac{\overline{M}w}{\overline{M}n}$
s-BuLi	toluene	3	1.6	100	3000	2400	1.11
DPHLi	toluene	3	1.9	100	3000	2900	1.09
DPHLi	toluene	10	1.2	100	10 000	8900	1.14
s-BuLi	CH_2Cl_2/toluene[c]	24	1.7	80	16 000	8500	1.20
DPHLi	CH_2Cl_2/toluene[c]	24	2.8	70	14 000	7000	1.21

[a] Theoretical number average molar masses.
[b] Number average molar masses measured by SEC calibrated with PEO standards.
[c] Solvent mixture 50/50 vol.

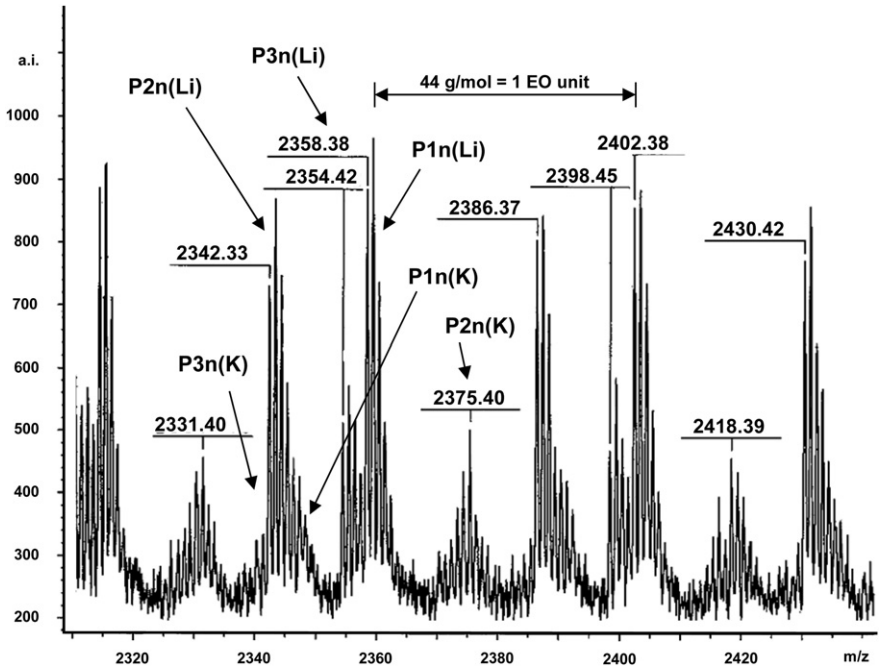
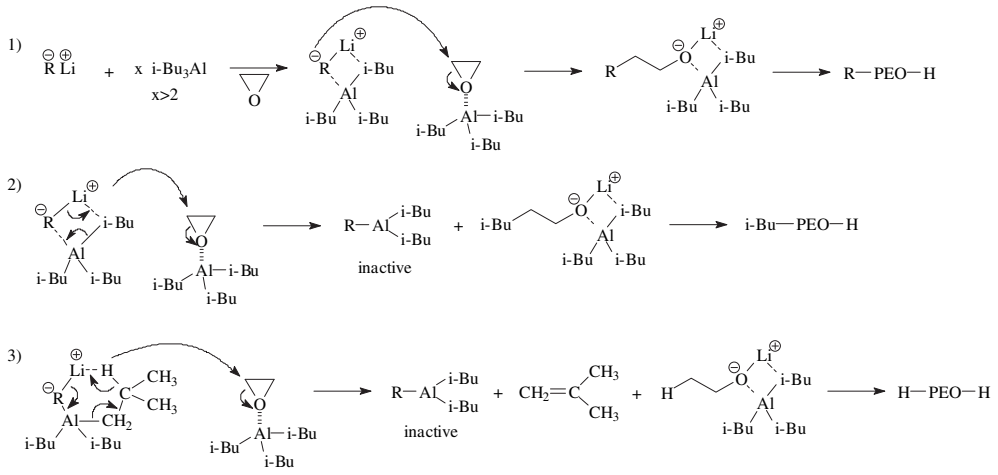


Fig. 1. Enlarged region of the MALDI-TOF mass spectrum of a PEO synthesized with DPHLi:i-Bu_3Al ([Al]/[I] = 4), [EO] = 0.8 mol/l at 25 °C (run 2, Table 1).

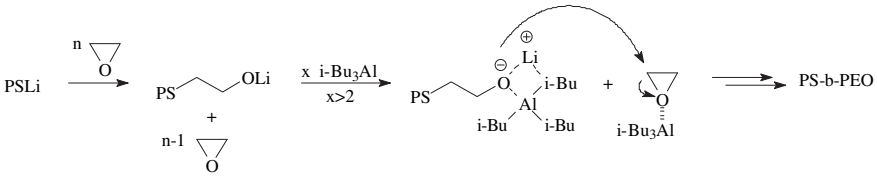
3. Results and discussion

3.1. Homopolymerization of EO with alkyllithium/triisobutylaluminum systems

As previously reported for sodium alkoxides [11,12] or ammonium salts based initiating systems [13–15], ethylene oxide and propylene oxide polymerization takes place in a few minutes to a few hours when a slight molar excess of triisobutylaluminum (i-Bu_3Al) with respect to the initiator is added to the polymerization medium. It was proposed that i-Bu_3Al first form an aluminate 1:1 complex with alkali metal derivatives or ammonium salts, whereas the excess of i-Bu_3Al yields a second complex with the epoxide monomer, increasing its reactivity towards nucleophilic species (Scheme 1). It was of large interest to verify if EO polymerization could also takes place using lithium alkoxides as initiator in presence of i-Bu_3Al. Series of experiments in which sec-butyllithium (s-BuLi) or diphenylhexyllithium (DPHLi) were used as initiators in association with triisobutylaluminum were thus implemented. Results collected in Table 1 show that EO is polymerized in relatively short time at 25 °C in toluene, indicating that it is possible to activate $-CH_2-CH_2-O-Li$ species towards EO ring opening polymerization using the monomer-activated anionic polymerization approach. Both s-BuLi and DPHLi associated to i-Bu_3Al in 4 M excess behave as efficient polymerization initiators. PEO with molar masses up to about 10 000 g/mol and a low dispersity were obtained quantitatively in a few hours in toluene. Experimental molar masses, given by Size Exclusion Chromatography (SEC) with PEO standards, are in good agreement with theoretical values assuming the formation of one PEO chain per lithium derivative. However, when molar masses higher than 10 000 g/mol were targeted, EO conversion was not quantitative



Scheme 2. Synthesis of PEO initiated by alkyllithium/triisobutylaluminum systems: 1) expected initiation by an alkyl group (R = s-Bu, DPH), 2) initiation by a butyl group coming from i-Bu_3Al, 3) initiation by a hydride coming from i-Bu_3Al.



Scheme 3. Synthesis of PS-b-PEO: formation of the "ate" complex between PSOLi and i-Bu_3Al.

after 24 h and a deviation was observed from expected molar masses. The use of a mixture of dichloromethane and toluene (50/50%vol.) (runs 4 and 5 Table 1) was explored to improve the PEO solubility despite a possible side reaction between alkyllithium and dichloromethane [16] during the initiation of the polymerization. This would decrease the initiator concentration. However it did not permit the preparation of PEO with higher molar masses suggesting the contribution of secondary reaction processes with the method used.

Investigation of these side reactions was conducted using MALDI-TOF analyses of PEO. Polymers initiated with DPHLi were selected in order to characterize the presence of the initiator fragment i.e. the diphenylhexyl group and distinguish it clearly from head groups representative of other initiation mechanisms mainly resulting from transfer processes to i-Bu_3Al [13]. Indeed both PEO chains resulting from termination upon addition of MeOH/HCl or from a transfer to i-Bu_3Al should have an hydroxyl terminus.

These considerations yield for PEO chains peak molar masses expressed by the general formula: $P(PEO_n) = M_{Met+} + M_{initiator\ fragment} + n \times M_{EO} + M_H$, where Met+ is the cationizing metal, i.e, Li^+ containing a small fraction of K^+ in the present case. As suspected the observed PEO peak mass series reveal the presence of PEO chains with different head groups: DPH-PEO-H, H-PEO-H and Bu-PEO-H, that confirm several modes of initiation (Fig. 1). The main PEO polymer fraction (cationized either by Li^+ or K^+) with formula $P1n = M_{Met+} + M_{DPH} + n \times M_{EO} + M_H$, corresponds to initiation by diphenylhexyllithium as expected ($P1(n = 48)(Li)exp = 2358.38 \approx P1(n = 48)(Li)th = 2358.85$). The second polymer fraction P2n exhibiting a H-head as initiator fragment, $P2n = M^+_{Met} + n \times M_{EO} + 2 \times M_H$, corresponds to PEO chains initiated by an hydride coming from an isobutyl group of i-Bu_3Al with formation of isobutene [13] ($P2(n = 53)(Li)exp = 2342.33 \approx P2(n = 53)(Li)th = 2343.76$). A third population, in a much lower proportion, bears a butyl head group ($P3n = M_{Met+} + M_{Bu} + n \times M_{EO} + M_H$) and is consistent with transfer/initiation by an isobutyl group of i-Bu_3Al ($P3(n = 52)(Li)exp = 2354.42 \approx P3(n = 52)(Li)th = 2355.81$).

The reaction yielding the different PEO head groups are illustrated in Scheme 2. In the proposed mechanisms, reactions #1 and #2, one i-Bu_3Al molecule is involved in the formation of a four-center 1:1 aluminate-type complex with diphenylhexyllithium. Reaction #1 highlights the nucleophilic attack of the diphenylhexyl group to activated EO, yielding the expected initiation step. Reaction #2 illustrates ligand exchange inside the complex with formation of complexed i-Bu_2AlDPH and isobutyl-lithium moities, followed by ring opening of activated EO by the more nucleophilic iBu group. Finally release of a hydride of an isobutyl group of i-Bu_3Al, reaction #3, suggests DPH/H ligand exchange between the two metals [17,18] with departure of isobutene, in a six–center complex. The complexed Li–H species then attacks activated EO yielding PEO chains with an H-head group. These last two side initiation processes would explain the formation of a PEO homopolymer fraction during the diblock copolymer synthesis described in the next section.

Besides, as it can be noticed by the discrepancy observed between theoretical and experimental PEO molar masses, when relatively high molar masses are targeted, Table 1, the contribution of termination and/or transfer reactions during the propagation step appears to be more significant in lithium containing systems than when other alkali metals or ammonium salts are used. It is believed that the main side reaction that takes place involves again ligand exchanges within the aluminate complex or with the excess of i-Bu_3Al present. Transfer of the growing PEO chain end to the aluminum will results in the formation of new initiating species, likely LiH and/or Li-butyl, as well as diisobutylaluminum alkoxide a much weaker monomer activator than i-Bu_3Al [19] whereas the concentration of available i-Bu_3Al is decreased. This tends to decrease the rate of the polymerization and could even stop the reaction.

3.2. Alkyllithium-initiated sequential copolymerization of styrene (or isoprene) and ethylene oxide

As shown above complexation of EO by i-Bu_3Al allows its easy ring opening reaction by weak nucleophiles, such as complexed lithium alkoxides. This result was applied to the direct synthesis of PS-*b*-PEO (Scheme 3) and PI-*b*-PEO block copolymers.

A series of block copolymerizations was carried out by sequential monomer addition of styrene (or isoprene) and ethylene oxide using sec-butyllithium as initiator in toluene at 25 °C. After the synthesis of the first PSLi or PILi block, EO was introduced, followed by the addition of i-Bu_3Al. Results are collected in Table 2. As it may be seen when PEO blocks of 10 000 g/mol or less are targeted EO polymerization proceeds quantitatively in a few hours

Table 2
Synthesis of PS-b-PEO and PI-b-PEO initiated by alkyllithium species in the presence of i-Bu_3Al (reaction in toluene at 25 °C).

Run	[i-Bu_3Al]/[RLi]	Time (h)	Conv (%)	$\overline{M}_n$(SEC) 1st block (g/mol)	$\overline{M}_n$(th.) PEO (g/mol)	$\overline{M}_n$ (SEC[a]) Diblock (g/mol)	$\frac{\overline{Mw}}{\overline{Mn}}$ diblock	Diblock Efficiency[b] (%)
PS-b-PEO	2	10	80	2000	6000	7000	1.10	85
PS-b-PEO	4	8	100	5000	10 000	15 000	1.12	80
PI-b-PEO[c]	4	8	100	2500	6000	10 000	1.12	80
PS-b-PEO	6	3	100	5000	10 000	14 000	1.11	80
PS-b-PEO	10	1	100	5000	10 000	14 000	1.12	80
PS-b-PEO	5	48	50	3000	50 000	20 000	1.21	20

[a] apparent molar masses obtained by SEC with polystyrene as standards.
[b] reinitiation efficiency calculated from the ratio of the copolymer area over the homoPS area in UV SEC.
[c] PSLi seeds were used as a macroinitiator of isoprene ($\overline{M}_n$PSLi (exp) = 500 g/mol, $\overline{M}_n$PILi (exp) = 2000 g/mol).

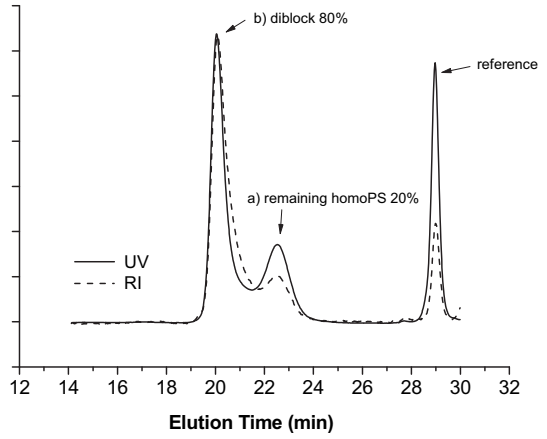


Fig. 2. UV and RI SEC traces corresponding to the synthesis of a PS-*b*-PEO diblock copolymer ([Al]/[Li] = 6, run 4, Table 2), a) residual PS ($\overline{M}_n$(exp) = 5000 g/mol), b) diblock PS-b-PEO ($\overline{M}_n$ (SEC) = 14 000 g/mol).

(1–10 h) at [Al]/[Li] ratios ranging from 4 to 10. A mass increase of the majority of the PS population and narrow molar mass distributions of the copolymers were observed. At a lower ratio ([Al]/[Li] = 2), a maximum of 80% conversion is observed after 10 h, meaning that monomer activation is not optimized. Increasing the amount of triisobutylaluminum allows to drastically decrease the EO polymerization time down to 1 h, without affecting the efficiency in the diblock formation. Fig. 2 shows at first the UV SEC chromatogram of a crude PS-*b*-PEO copolymer (run 4 Table 2) and of residual polystyrene. The block copolymerization efficiency, determined from the areas of the copolymer and homopolystyrene SEC UV absorbance peaks, corresponds to the growth of PEO blocks onto 80% of the initial PSLi or PILi chains. The introduction of a first short PS block (500 g/mol) prior to the PILi block synthesis was used as a tag to determine the block efficiency in the case of PI-*b*-PEO copolymer. The homopolystyrene fraction that could come in part from impurities introduced during EO addition results more likely from side initiation and transfer reactions reported for EO polymerization initiated by lithium derivatives (see Scheme 2). In addition to homoPS, both hydride and isobutyl initiations results in the formation of homoPEO, H-PEO-H and Bu-PEO-H respectively, in about the same proportion (20%) of the total PEO formed. A small

Table 3
Influence of [Al]/[Li] ratio on the EO polymerization rate constant initiated by PSLi chains ($\overline{M}_n$PS = 5000 g/mol) (toluene, 25 °C).

[i-Bu_3Al]/[PSLi]	[EO] (mol/l)	[EO]/[PSLi]	$t_{1/2}$ (min)	$k_p[M^*]$[a] (min^{-1})	k_p[b] ($l\ mol^{-1}\ min^{-1}$)
2	2.1	150	500	6	430
4	1.1	220	410	42	2800
6	1.1	220	120	137	5480
10	1.1	220	47	282	6270

[a] Determined from the slope of the conversion versus time plot (linear part): $k_p[M^*]$ = slope.$[M]_0/[I]_0$.
[b] $k_p = k_p[M^*]/[Al]_a$.

tailing of the block copolymer peak towards lower $\overline{M}_n$ observed with the RI signal (Fig. 2) can indicate the presence of homoPEO since its theoretical $\overline{M}_n$ is 10 000 g/mol, a value in between the PS and the block copolymer.

Trying to prepare PEO block of high molar mass was not successful (run 6 in Table 2). At low [Al]/[Li] ratio the reaction stops at low conversion. Even at a ratio of 10, used to tentatively maintain significant activity, the polymerization is not completed after 2 days. Limitation of the PEO number average molar mass to less than about 20 000 g/mol, broader chains distribution and low block efficiency are consistent with significant transfer reactions along the propagation step, likely via ligands exchange between the two metals as suggested in Scheme 2. This can be related to the higher amount of i-Bu_3Al necessary to activate the EO polymerization.

3.3. Kinetic study

Polymerization kinetics were implemented to scale the reactivity of RLi/i-Bu_3Al sytems toward EO polymerization. As shown in Fig. 3, EO polymerization rate strongly increases with the amount of i-Bu_3Al added and the [Al]/[Li] ratio. A curvature of the conversion vs time plots, corresponding to an induction period, was observed in particular at lower amounts of organoaluminum added ([Al]/[Li] = 2 and 4). This kinetic behavior has been also highlighted by Müller et al. [20] for the polymerization of EO in the presence of s-BuLi/t-BuP_4 as initiating systems and by us for propylene oxide polymerization initiated by sodium alkoxides and i-Bu_3Al [11]. This was explained by the presence of strong alkali metal alkoxide aggregates at the first stages of the propagation reactions. These aggregates should be broken by complexation of the Li^+ or Na^+

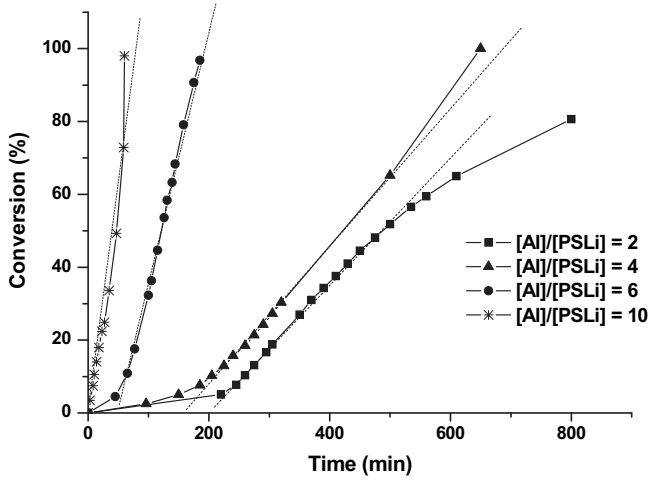


Fig. 3. Conversion vs time plots for the polymerization of EO initiated by PSLi:i-Bu_3Al systems at 25 °C in toluene: influence of the [Al]/[Li] ratio on the kinetics and rate of polymerization (see Table 3 for experimental conditions).

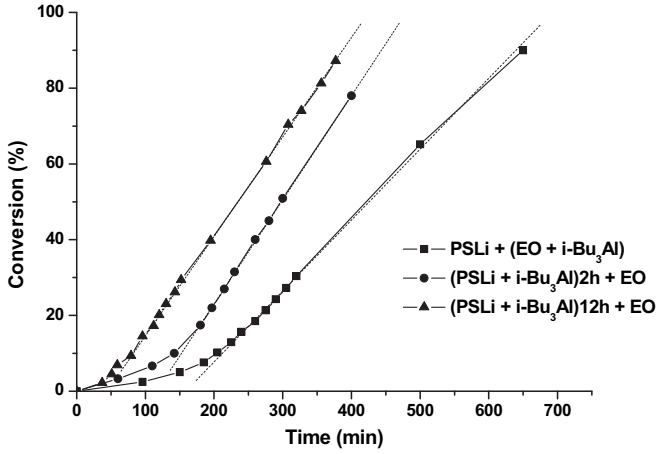


Fig. 4. Conversion vs time plots for the polymerization of EO initiated with PSLi:i-Bu_3Al systems ([Al]/[Li] = 4, 25 °C, toluene): influence of the aluminate complex preparation on EO kinetic.

Table 4
Effect of addition order of reactants and of deaggregation time on the polymerization rate on the of EO polymerization kinetic ($\overline{M}_n$PEO = 10 000 g/mol) initiated by PSLi chains ($\overline{M}_n$PS = 5000 g/mol) (toluene, 25 °C).

Reactants addition order	[EO] (mol/l)	[i-Bu_3Al]/[PSLi]	[EO]/[PSLi]	$t_{1/2}$ (min)	kp[M*][a] (min^{-1})	kp[a] ($l.mol^{-1}.min^{-1}$)
PSLi + (i-Bu_3Al + EO)	1.10	4	220	410	42	2800
(PSLi + i-Bu_3Al) 2h + EO	0.70	4	140	300	39	2600
(PSLi + i-Bu_3Al)12h + EO	0.75	4	150	220	39	2600

[a] Determined from the slope conversion versus time, after the end of induction period.

counterion with t-BuP_4 or i-Bu_3Al to enable the polymerization. A similar explanation can be proposed here. Breaking of PS–CH_2–CH_2–OLi aggregates to yield more reactive "ate" complexes PS–CH_2–CH_2–OLi:i-Bu_3Al is a kinetically limiting step. At higher amounts of activator ([Al]/[Li] = 6–10) the rate of deaggregation is increased and the induction period is limited or even suppressed.

If we exclude the induction period, kinetics are consistent with our previous data [13,14] or with those published by Müller and coworkers [21] on the polymerization of N,N-diethylacrylamide in the presence of triethylaluminum, which showed a zero monomer order dependence of the polymerization. Indeed, the typical variation of EO conversion ($[EO]_0$-$[EO]_t/[EO]_0$) vs time shows a linear dependence of the monomer consumption with time, up to high conversion. Since alkyllithium alone or alkyllithium/*i*-Bu_3Al (1:1) systems are inactive, these results sustain the selective insertion of a *i*-Bu_3Al complexed monomer which is electrophilically activated.

The half monomer conversion times ($t_{1/2}$) and polymerization rate constants (k_p) in toluene at 25 °C were determined for the different initiating systems compositions varying by the amount of i-Bu_3Al added to PSLi used as initiator (Table 3). The polymerization rate R_p can be expressed by the equation $R_p = k_p[Li]_0[M^*]$ where k_p is the propagation rate constant, $[Li]_0$ and $[M^*]$ respectively the initiator and activated monomer concentrations. $[M^*]$ depends on the *i*-Bu_3Al concentration available, $[M^*] = [Al]_a = [Al]_0$-$[I]_0$, since one equivalent of *i*-Bu_3Al is trapped in the 1:1 "ate" complex formed with the initiator. As indicated in Table 3, half reaction times decreases with increasing [Al]/[Li] ratios while $k_p[M^*]$ or calculated k_p increases. These observations suggest, as also shown in Fig. 3, that deaggregation of PS–CH_2–CH_2-O-Li is quite limited at low [i-Bu_3Al]/[Li] ratio and requires higher amounts of i-Bu_3Al to get rid of the induction period. In addition the propagation rate constant is directly related to the amount of Lewis acid added and therefore to the amount of activated monomer. This kinetic calculation does not completely fits with what it is observed and calculated k_p values will suffer from the simplification we have used for the quantification of [M*]. Indeed we can imagine that more than one molecule of aluminum derivative is needed to break the aggregates, as high [Al]/[Li] are needed to get polymerization, decreasing the activated monomer concentration.

Deaggregation of PS–CH_2–CH_2-O-Li by i-Bu_3Al was examined further by varying the addition order EO and i-Bu_3Al onto PSLi and studying its influence on the induction period, keeping as example the [Al]/[Li] ratio equal to 4. As shown in Fig. 4 simultaneous addition of EO monomer and i-Bu_3Al onto PSLi species results in a long induction period. This suggests a predominant or competitive reaction of PSLi with EO to yield lithium alkoxide species before formation of the PS–CH_2–CH_2-O-Li/i-Bu_3Al aluminate complex. In contrast, when i-Bu_3Al is introduced directly onto PSLi the PSLi:i-Bu_3Al aluminate complex first forms, limiting, but not suppressing, the formation of lithium alkoxide aggregates. Long complexation time (12h) between lithium and i-Bu_3Al before addition of EO reduces the induction period which is still present at such a [Al]/[Li] ratio. The average stoichiometry of the initiating complexes formed (Al:Li, 4:1) appears as not sufficient to prevent lithium alkoxides aggregation. A higher average Al:Li stoichiometry (6:1 or even better 10:1, Fig. 3) seems to be the key parameter to avoid it and therefore the induction period. Some free, or available, triisobutylaluminum are still necessary for the monomer activation. Propagation rate constants, determined after the end of the induction period with the simplification in the calculation of the activated monomer concentration, remain in the same range ($k_p \approx 2600$–$2800\ l\ mol^{-1}\ min^{-1}$) whatever the addition order of the reactants (Table 4), suggesting that all the systems have reached the same final equilibrium and a similar activation process due to an identical [Al]/[Li] ratio equal to 4. The decrease of the half reaction is indeed related to the decrease of the induction period.

4. Conclusion

The anionic polymerization of EO initiated by a lithium derivative proceeds in hydrocarbons at room temperature in a few hours in the presence of triisobutylaluminum as additive. i-Bu_3Al used in excess with respect to the lithium initiator, permits i) the deaggregation of lithium alkoxides chain ends to form lithium/aluminate complexes, ii) a strong activation of EO ring opening towards weak nucleophiles. PEO and PS-*b*-PEO or PI-*b*-PEO were prepared with relatively well controlled PEO molar masses up to 10 000 g/mol. Transfer reactions to a hydride or an isobutyl group coming from i-Bu_3Al still limit the diblock formation efficiency and the access of PEO of higher molar mass.

References

[1] Hsieh HL, Quirk RP. Anionic polymerization. Principles and practical applications. New York: Dekker; 1997.
[2] Yu K, Eisenberg A. Macromolecules 1996;29:6359–61.
[3] (a) Quirk RP, Ma JJ. J Polym Sci Part A Polym Chem 1988;26:2031–7;
(b) Quirk RP, Guo Y, Wesdemiotis C, Arnould MA. Polymer 2004;45:3423–8.
[4] Hillmyer MA, Bates FS. Macromolecules 1996;29:6994–7002.
[5] Candau F, Afchar-Taromi F, Rempp P. Polymer 1977;18:1253–7.
[6] Hruska Z, Hurtez G, Walter GS, Riess G. Polymer 1992;33:2447–9.
[7] Esswein B, Steidl NM, Möller M. Macromol Rapid Commum 1996;17:143–8.
[8] Esswein B, Möller M. Angew Chem Int Ed Engl 1996;35:623–5.
[9] Förster S, Krämer E. Macromolecules 1999;32:2783–5.
[10] Schmalz H, Knoll A, Müller AJ, Abetz V. Macromolecules 2002;35:10004–13.
[11] Billouard C, Carlotti S, Desbois P, Deffieux A. Macromolecules 2004;37:4038–43.
[12] Carlotti S, Billouard C, Gautriaud E, Desbois P, Deffieux A. Macromol Symp 2005;226:61–8.
[13] Labbé A, Billouard C, Desbois P, Carlotti S, Deffieux A. Macromolecules 2007;40:7842–7.
[14] Rejsek V, Sauvanier D, Billouard C, Desbois P, Deffieux A, Carlotti S. Macromolecules 2007;40:6510–4.
[15] Gervais M, Labbe A, Carlotti S, Deffieux A. Macromolecules 2009;42:2395–400.
[16] Closs G. J Am Chem Soc 1962;84:809–13.
[17] Schmitt B, Stauf W, Müller AHE. Macromolecules 2001;34:1551–7.
[18] Ihara E, Ikeda J-I, Inoue K. Macromolecules 2002;35:4223–5.
[19] Labbe A. Thesis: Université Bordeaux-1; 2007.
[20] Schmalz H, Lanzendörfer MG, Abetz V, Müller AHE. Macromol Chem Phys 2003;204:1056–71.
[21] André X, Benmohamed K, Yakimansky V, Litvinenko G, Müller AHE. Macromolecules 2006;39:2773–87.