Macromolecules **2004,** *37,* 4038−4043

"Controlled" High-Speed Anionic Polymerization of Propylene Oxide Initiated by Alkali Metal Alkoxide/Trialkylaluminum Systems

Cyrille Billouard,[†] Stéphane Carlotti,[†] Philippe Desbois,[‡] and Alain Deffieux*[,†]

Laboratoire de Chimie des Polymères Organiques, UMR 5629 CNRS-ENSCPB-Université Bordeaux 1, 16 avenue Pey Berland, 33607 Pessac Cedex, France, and Polymer Laboratory, BASF AG, D-67056 Ludwigshafen, Germany

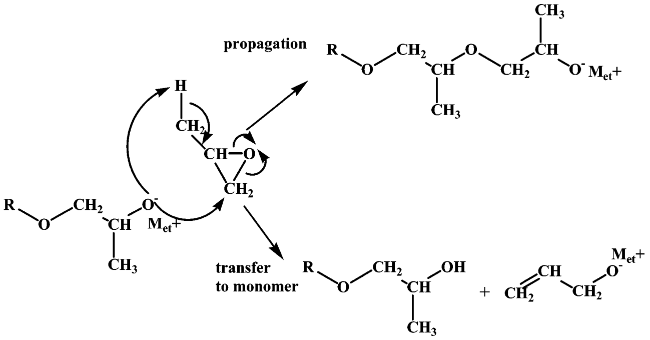
Received November 25, 2003; Revised Manuscript Received February 16, 2004

ABSTRACT: The anionic polymerization of propylene oxide initiated by alkali metal alkoxide suffers from several drawbacks such as a slow polymerization rate in nonpolar solvents and an important chain transfer reaction to monomer. We found that the addition of trialkylaluminum to the alkali metal alkoxide/propylene oxide system in hydrocarbon media strongly enhances the polymerization rate and strongly reduces the transfer reactions, thus allowing the controlled synthesis of poly(propylene oxide) with relatively high molar masses (up to 20 000 g/mol). At constant monomer and alkali metal alkoxide concentrations the polymerization rate increases with increasing trialkylaluminum concentration. Kinetic data and ^{1}H NMR studies indicate that the trialkylaluminum derivative is involved in the formation of two distinct complexes, one with the alkali metal alkoxide and another with the PO monomer. The strong electron-withdrawing on PO α-carbons associated with AlR_3 complexation makes the monomer much more susceptible to ring opening. Moreover, since the withdrawing effect is much less pronounced on the PO methyl group, the complexation also results in a higher selectivity of the nucleophilic species toward the ring-opening reaction to the detriment of the proton abstraction process yielding transfer to monomer.

Introduction

Since the first report of poly(propylene oxide) (PPO) synthesis by Levene in 1927,[1] many research efforts have focused on the polymerization of propylene oxide (PO) and on methods to control its living character. This may be explained by the great interest of PPO both as a functional oligomer and as a high molar mass elastomer. Despite significant progress, the anionic PO polymerization still suffers from several important drawbacks that must be overcome. The most widely used PO anionic polymerization initiators are alkali metal alkoxides and hydroxides.[2−4] Because of the high basicity of propagating species generated in these systems, proton abstraction from the PO methyl group can take place yielding a transfer reaction to monomer. This side process results in the exclusive formation of PO oligomers[3] with a large fraction that possesses a terminal allylic unsaturation (Scheme 1). The use of larger counterions (rubidium, cesium) or of crown ether additives slightly reduce the transfer process, but PO molar masses still remain low (<15 000 g/mol).[4] Very high molar mass PPO can be obtained, however, through coordinated anionic polymerization involving species of lower basicity.[5−11] In these systems, preliminary monomer coordination onto the electrophilic sites of the catalyst is assumed. The low solubility of these systems and the presence of various types of active species generally result in low initiation efficiency and yield PPO with multimodal or very broad molar mass distribution. PO polymerization can also be controlled by aluminum porphyrins.[12,13] The preparation of end-functional PPO with molar masses up to 10 000 g/mol with these initiators was reported. Addition of a bulky aluminum phenoxide drastically accelerates the polymerization; a complexation/activation of the oxygenated monomer by the electrophilic aluminum derivative was proposed.[14,15] Very recently, the highly colored porphyrin initiators, very difficult to remove from PPO, have been successfully substituted by simpler systems based on the association of ammonium salts, or alkali metal alkoxide/crown ethers, with a bulky bis(phenoxy)aluminum electrophile to synthesize PO oligomers with controlled molar masses ($\bar{M}_n < 5000$ g/mol).[16] Another interesting system is the so-called double cyanide catalytic system $Zn_3[Co(CN)_6]_2$ which recently found industrial applications for which the polymerization mechanism is not well established.[8]

Scheme 1. Propagation vs Transfer to Monomer in the Anionic Polymerization of PO Involving Alkali Metal Alkoxides as Active Species



We report here the use of new widespread initiating systems for the "controlled" high-speed anionic polymerization of propylene oxide, based on the combination of alkali metal alkoxides and trialkylaluminum.

Experimental Section

Materials. *i*-Bu_3Al (1 mol/L in toluene) and Et_3Al (1.9 mol/L in toluene) were purchased from Aldrich and used without further purification. Propylene oxide (PO) (99%, Fluka) was purified over CaH_2, distilled under vacuum, and stored for 15 min in glass flask equipped with PTFE stopcocks in the

---

* Corresponding author: e-mail: deffieux@enscpb.fr.

[†] Université Bordeaux 1.

[‡] BASF AG.

10.1021/ma035768t CCC: $27.50

Table 1. Propylene Oxide (PO) Polymerization Initiated with Alkali Metal *tert*-Amyloxide ROM_{Et} (I) in the Presence of *i*-Bu_3Al in Cyclohexane

run	initiator ROM_{et} (I)	[PO] (mol/L)	[PO]/[I]	[$^iBu_3Al$]/[I]	time	T (°C)	conv (%)	$\bar{M}_{n,theo}$ (g/mol)	$\bar{M}_n{}^a$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	ROK	6.5	500	5	1 h	20	93	26 970	18 000	1.4
2	RONa	6.5	480	5	25 min	20	100	27 840	15 100	2
3	RONa	6.0	238	5	2 h	0	100	13 800	11 500	1.3
4	ROLi	6.5	510	10	22 h	20	57	16 860	1 600	1.6

[a] Number-average molar mass estimated by SEC on the basis of polystyrene standards.

Table 2. Propylene Oxide (PO) Polymerization Initiated by *i*-PrONa (I) in the Presence of Trialkylaluminum in Cyclohexane

run	R_3Al	[PO] (mol/L)	[PO]/[I]	[R_3Al]/[I]	T (°C)	polym time	conv (%)	$\bar{M}_{n,theor}$ (g/mol)	$\bar{M}_n{}^c$ (g/mol)	$\bar{M}_w/\bar{M}_n$
5[a]		6.2	360	0	25	7 days	0			
6[b]	*i*-Bu_3Al	5.5			25	10 days	0			
7	*i*-Bu_3Al	4.0	382	1	25	10 days	0			
8	*i*-Bu_3Al	4.0	87	3.5	0	2 h	100	5000	7100	1.1
9	*i*-Bu_3Al	4.0	173	3.5	0	2 h	70	7000	8800	1.1
10	*i*-Bu_3Al	4.0	258	5.2	0	3.5 h	100	15000	16800	1.3
11	*i*-Bu_3Al	4.0	382	7.6	0	3.5 h	100	22100	23600	1.3
12	Et_3Al	6.5	274	5.5	0	1 h	17	2700	2500	1.2
13	Et_3Al/TMEDA (1/1)	6.5	272	5.2	0	2 h	12	1800	1900	1.1

[a] Experiment performed in the absence of R_3Al. [b] Experiment performed in the presence of R_3Al alone. [c] Number-average molar mass estimated by SEC on the basis of polystyrene standards.

presence of *i*-Bu_3Al to remove traces of impurities. PO was finally distilled under vacuum and stored under vacuum at room temperature in graduated glass tubes until use. Cyclohexane (99%, J.T. Baker) was purified with polystyryllithium seeds, distilled under vacuum, and then stored in graduated glass tubes under vacuum.

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. Sodium, potassium, and lithium *tert*-amyloxide (2-methylbutan-2-oxide) were synthesized in a similar way from 2-methylbutan-2-ol.

Procedures. All polymerizations were performed at 0 or 20 °C under argon in a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks previously flamed under vacuum. Cyclohexane and PO were introduced under vacuum through connected glass tubes followed by the alkali metal alkoxide initiator in toluene solution and finally the trialkylaluminum catalyst 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 off the polymer under vacuum at 50 °C.

Typically, in a 50 mL glass reactor equipped with a magnetic stirring bar previously flamed under vacuum, 6.6 mL of cyclohexane and 3.0 mL of PO (42.9 mmol), both stored in graduated tubes, were introduced under vacuum through glass connectors to the reactor which was externally thermostated at 0 °C. Then, 0.25 mL of a solution of *i*-PrONa in cyclohexane (0.45 mol/L, 0.11 mmol) was added by a syringe, and the system was left for 10 min under stirring. Finally, triisobutylaluminum (1 mol/L in toluene) (0.86 mL, 0.86 mmol) was added to start the polymerization, and the system was maintained under stirring in the thermostated bath. The reaction was stopped after 3.5 h by adding 0.5 mL of a solution of HCl in ethanol (1:5 v/v). Residual PO and solvent were then evaporated under vacuum, and the polymer was dried until constant weight. Yield of recovered PPO = 2.5 g; conversion = 100%; experimental $\bar{M}_n$ = 23 600 g/mol, PDI = 1.3.

Poly(propylene oxide)s were obtained as a colorless, odorless, viscous liquid or as a gum for highest molar masses.

Dilatometry measurements were performed using a similar procedure. The dilatometer was previously flamed, and an *i*-Bu_3Al solution was first added using syringes. The system was thermostated at 0 °C, and a prepared solution of *i*-PrONa, cyclohexane, and PO prechilled at 0 °C was then added. Monitoring of the reaction was immediately followed by recording the volume level of the solution in the capillary tube attached to the reactor.

Analysis. PPO molar masses were determined by SEC at 20 °C using THF as eluant on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU and a dual refractive index/UV Varian detector and fitted with four TSK columns (250, 1500, 10^4, 10^5 Å), at an elution rate of 1.5 mL/min. Complementary PPO molar mass measurements were performed by tonometry on selected samples to check that PS calibration of SEC is appropriate for PPO in the examined molar mass range (<20 000 g/mol).

^1H measurements of PPO oligomers and [PO]/[*i*-Bu_3Al] mixtures were performed on a Bruker AC 200 spectrometer, in $CDCl_3$ at room temperature. ^{13}C NMR of PPO was performed on a Bruker Avance 400 spectrometer, in $CDCl_3$ at room temperature.

The MALDI−TOF mass spectrometry (matrix-assisted laser desorption/ionization time-of-flight) measurements were performed on a BIFLEX III instrument (Bruker Daltonik GmbH, Bremen). Polymers were dissolved at a concentration of 10 g/L in THF and the matrix dithranol (1,8,9-trihydroxyanthracene) at 20 g/L. Polymer and matrix solutions were then mixed in a 1:1 ratio (i.e., 20 μL each). 5 vol % (2 μL) of NaTFA (sodium trifluoroacetic acid 0.02 M in THF) was added as cationizing agent, and this mixture was then spotted on the sample holder.

Results and Discussion

PO polymerizations were performed under argon at 20 or 0 °C. Solvent, monomer, and alkali metal alkoxide (I) were successively introduced, and trialkylaluminum (AlR_3) was added to start the polymerization. Some care should be taken to avoid a possible runaway reaction at high reagent concentrations and at polymerization temperatures higher than 20 °C.

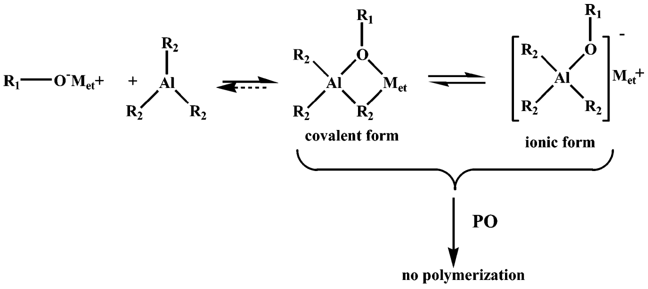
The results of a first set of PO polymerizations, performed at 20 °C, in the presence of various alkali metal *tert*-amyloxides (I) and triisobutylaluminum as initiating systems, [*i*-Bu_3Al]/[I] = 5−10, are collected in Table 1. In the presence of Na or K *tert*-amyloxide, a fast PO polymerization followed with a temperature increase is observed. Completion of the polymerization is reached in less than 25 min in the case of Na counterion at 20 °C (run 2). A better PO polymerization control is achieved at 0 °C as illustrated by run 3. With Na as counterion, although at 20 °C experimental molar masses $\bar{M}_n$ are not in close agreement with theoretical

Table 3. Kinetic Data of Propylene Oxide (PO) Polymerization Initiated by *i*-PrONa (I) in the Presence of Increasing Amounts of *i*-Bu$_3$Al in Cyclohexane ([*i*-PrONa] = 2.65 × 10^{-2} mol/L, [PO] = 5 mol/L, *T* = 0 °C; $\bar{M}_{n,theor}$ = 11 000 g/mol)

10^{-1}[*i*-Bu$_3$Al] (mol/L)	[*i*-Bu$_3$Al]/[I]	polym induction time^a (min)	Rp^b (min^{-1})	$^1/_2$ polym time^c (min)	$\bar{M}_{n,exp}$^{d} (g/mol)	$\bar{M}_w/\bar{M}_n$
0.090	3.4	25	0.7	67.7	10 500	1.2
0.135	5.1	20	1.6	34.2	11 200	1.2
0.180	6.8	12	2.9	18.2	10 500	1.3
0.225	8.5	8	4.6	11.7	11 200	1.2
0.307	11.6	5	50.1	2.0	6 800	1.5

[a] Estimated time of induction period corresponding to the intersection of the linear monomer conversion law at 0% conversion with the time axis. [b] Slope of conversion vs time curves calculated for the linear part. [c] Time for 50% conversion of monomer without taking account of the induction period. [d] Number-average molar mass estimated by SEC on the basis of polystyrene standards.

Scheme 2. Formation, Postulated Structures, and Reactivity (Cyclohexane, 0 or 20 °C) for *i*-PrONa:*i*-Bu$_3$Al [R$_1$OM$_{Et}$:Al(R$_2$)$_3$] Aluminate Complexes



ones (assuming the formation of one PPO chain per alkali metal alkoxide) and polydispersities are broad (1.4−2), relatively high molar mass PPO is obtained compared to reported values for the corresponding pure alkali metal alkoxide initiating systems ($\bar{M}_n$ < 6000 g/mol). Polymerization also proceeds in the presence of the lithium counterion, but kinetics are much slower and only oligomers are formed, suggesting the contribution of a transfer reaction.

To examine further PO polymerization initiated by these binary systems, a second series of experiments were performed at 0 °C using sodium isopropoxide (*i*-PrONa) in the presence of two distinct trialkylaluminums (*i*-Bu$_3$Al and Et$_3$Al) as the catalytic system. Results are collected in Table 2. When *i*-PrONa (run 5) and *i*-Bu$_3$Al (run 6) are used separately as initiator or catalyst, PO polymerization does not proceed even after several days at 25 °C. A similar situation also prevails when the molar ratio [*i*-Bu$_3$Al]/[*i*-PrONa] is less or equal to 1 (run 7). This suggests for [AlR$_3$]/[I] ≤ 1 that the trialkylaluminum is completely involved in the formation of an aluminate complex (Scheme 2), which is unable to initiate and/or propagate the PO polymerization. In contrast, in the presence of an excess of *i*-Bu$_3$Al with respect to *i*-PrONa, a fast polymerization of PO takes place and reaches completion in a few hours at 0 °C, suggesting an important activating effect of the “free” trialkylaluminum derivative. 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 (Table 2 and Figure 1). This suggests a PO living-like polymerization (runs 8−11) without any significant contribution of the monomer transfer process, observed with pure alkali metal alkoxide initiators. Although yielding active polymerization systems in similar conditions (run 12), Et$_3$Al proves to be much less efficient than *i*-Bu$_3$Al. The addition of a chelating agent does not improve the reactivity (run 13).

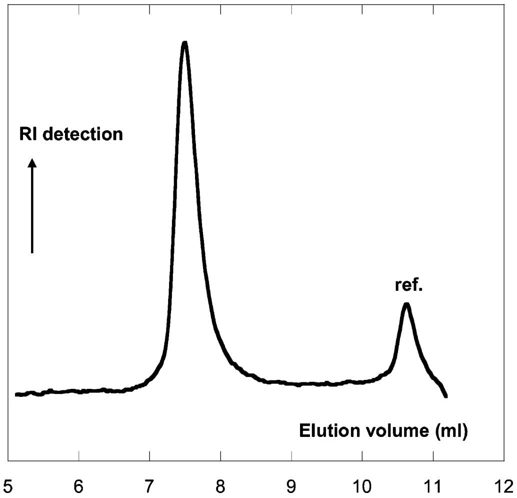


Figure 1. SEC curve of PPO obtained with *i*-PrONa/*i*-Bu$_3$Al at 0 °C, run 11, Table 2: $\bar{M}_n$ = 23 600 g/mol, $\bar{M}_w/\bar{M}_n$ = 1.3.

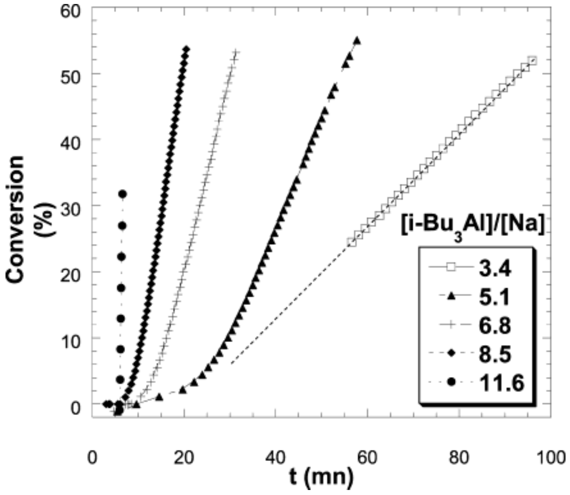


Figure 2. Conversion vs time curves of PO polymerizations initiated by *i*-PrONa (I) in the presence of increasing amounts of *i*-Bu$_3$Al in cyclohexane at 0 °C; [PO]/[I] = 189, [PO] = 5.0 mol/L. $\bar{M}_n$(theor) = 11 000 g/mol; $\bar{M}_n$(exp) are given in Table 3.

These results are consistent with a strong activation of the polymerization by R$_3$Al present in excess with respect to *i*-PrONa. As previously reported for PO polymerization performed in the presence of bulky aluminum phenoxide electrophiles,[14−16] we can also postulate monomer activation through complexation.

The activating role of R$_3$Al was further investigated by studying polymerization kinetics at various amounts of trialkyaluminum. It is worthy of note that the number of PPO chains is independent of the initial R$_3$Al con-

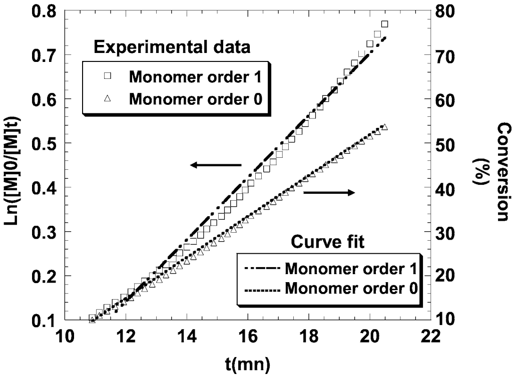
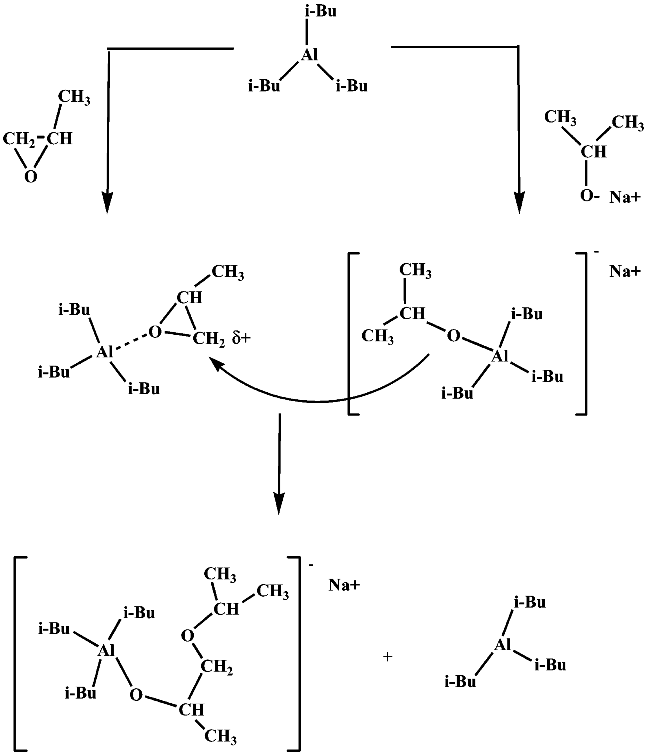


Figure 3. Monomer consumption with time according to first-order (logarithmic concentration dependence) and zero-order (concentration dependence) rate laws for the PO polymerization initiated by *i*-PrONa (I) in the presence of *i*-Bu_3Al ([Al]/[I] = 8.5) in cyclohexane at 0 °C.

Scheme 3. Reaction Mechanism Involving Monomer Activation Prior Insertion into the Growing "ate" Complex



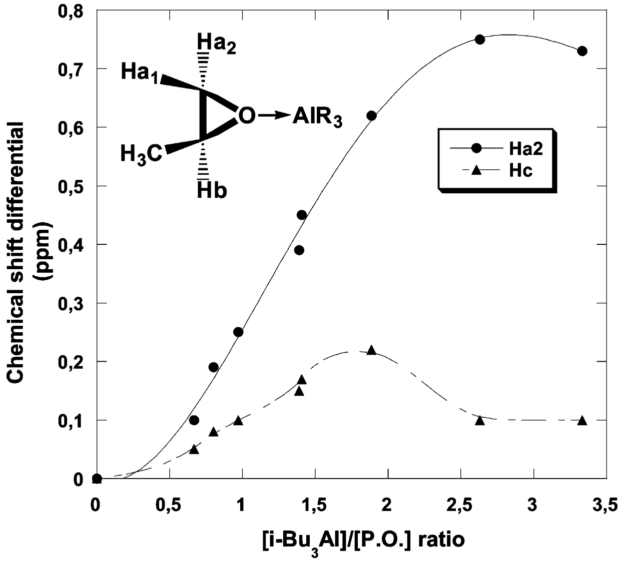


Figure 4. Chemical shift differential (Δ, ppm) of PO α-methylene Ha_2 and of β-methyl Hc protons prior to and after addition of increments of *i*-Bu_3Al; T = 20 °C; solvent $CDCl_3$. The same chemical shift differential is also observed for Ha_1 and Hb.

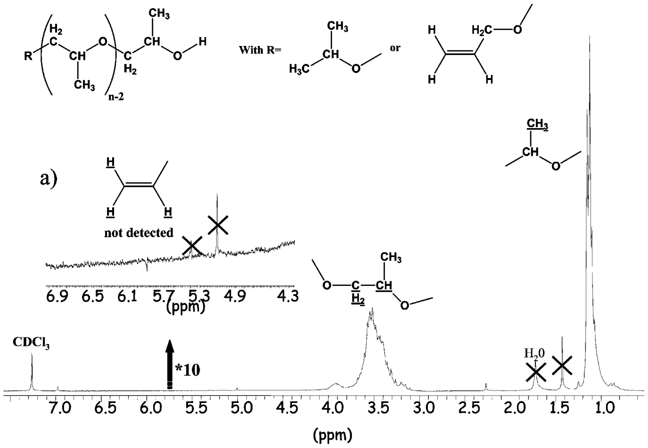


Figure 5. ^1H NMR spectrum of PPO oligomers ($\bar{M}_n$(exp) = $\bar{M}_n$(theor) = 500 g/mol) obtained in the presence of *i*-PrONa and *i*-Bu_3Al ([Al]/[I] = 5) as initiating system, in cyclohexane, at 0 °C; (a) expansion of the ethylenic region.

centration but is only determined by the sodium isopropoxide concentration (see Table 3). The lower molar mass obtained at the highest AlR_3 concentration ([*i*-Bu_3Al]/[I] = 11.6) can be attributed to side-reaction transfer associated with the important temperature increase due to very fast polymerization (see below). Conversion vs time curves for a series of experiments performed at increasing *i*-Bu_3Al concentration and constant monomer and initiator concentrations are shown in Figure 2. One may notice first the presence of an important induction period which becomes shorter while increasing the R_3-Al concentration. This can be tentatively assigned to the tendency of sodium isopropoxide and alkoxide termini of short PPO oligomers to strongly aggregate. After insertion of several monomer units, a solvation of propagating ends with oxygens of the growing polyether chains allows deaggregation. Enhancement of the overall reactivity at this stage then yields fast PO polymerization. As may be noticed in Figure 3, in this second stage the monomer consumption vs time ($[M]_0 - [M]_t/[M]_0$) follows a linear rate law up to high PO conversion, whereas the ln($[M]_0/[M]_t$) vs time plot is not linear. This suggests an apparent zero monomer order for the propagation reaction. Slopes of conversion vs time curves (Rp), keeping constant initial concentration of PO and alkoxide initiator, clearly show that the aluminum derivative strongly activates the propagation reaction (see Table 3). Once the induction period is over, 50% PO conversion requires about 70 min at a ratio [*i*-Bu_3Al]/[I] of 3.4, almost 10 min at ratio 8.5, and about 2 min for a ratio of 11.6. Indeed, the polymerization rate increase is so important that a temperature raise in the reactor likely takes place and contributes also to the observed reactivity enhancement, yielding an apparent reaction order of the polymerization of about 2 with respect to *i*-Bu_3Al concentration. In this calculation, the fraction of the electrophilic trialkylaluminum involved in the alkoxytriisobutyl aluminate sodium complex of presumed 1:1 stoichiometry (Scheme 2) was subtracted.

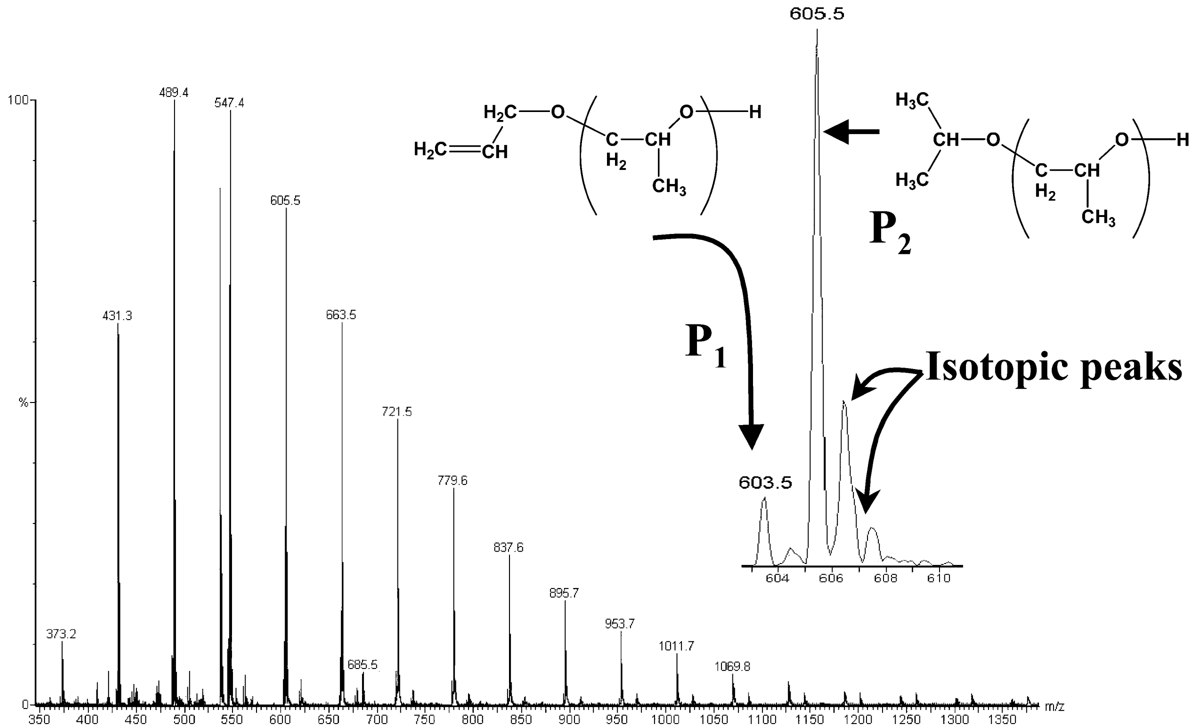


Figure 6. MALDI−TOF spectrum of PPO oligomers ($\bar{M}_{\rm n}$(exp) = 500 g/mol) obtained in the presence of *i*-PrONa and *i*-Bu_3Al ([Al]/[I] = 5) as initiating system in cyclohexane at 0 °C. P_1 and P_2 peak series correspond respectively to PPO with isopropoxy and allyloxy headgroups and H terminus.

These results are in agreement with a reaction mechanism in which the monomer is activated by the electrophilic aluminum compound, prior its insertion into the poly(propylenoxy)triisobutyl aluminate sodium growing chain end (Scheme 3).

The complexation of PO with triisobutylaluminum was investigated by ^{1}H NMR at various [PO]/[*i*-Bu_3Al] ratios, ranging approximately from 0.5 to 3. Coordination of PO onto *i*-Bu_3Al induces a strong downfield chemical shift ($\delta > +0.7$ ppm) of the Ha_1 and Ha_2 protons of the α-methylene PO carbon atom (see Figure 4). Although not shown in the figure, an identical strong downfield chemical shift ($\delta > +0.7$ ppm) is also observed for the proton of the α-methine carbon. This indicates a strong electron withdrawing on the α-carbons as a result of electron transfer from the PO oxygen atom to the aluminum. Assuming the formation of a 1:1 complex, the complexation constant has been estimated from the chemical shifts: in $CDCl_3$ at 20 °C, $K_c = 1$ mol L^{-1}.

Protons of the PO methyl carbon in the β-position (Hc) also exhibit a downfield shift. However, Hc protons are much less shifted ($\delta \sim +0.2$ ppm), indicating a smaller influence of the complexation effect at longer distance. As a main consequence of the electronic density decrease, the PO α-carbons should exhibit an enhanced reactivity toward nucleophiles and in particular toward PPO propagating species. Since neither the alkali metal alkoxide alone nor the 1/1 alkali metal alkoxide/aluminate complex is able to polymerize PO in the present conditions (see Table 2, runs 5 and 6), it can be concluded that only R_3Al complexed PO molecules react with growing polymer ends.

The presence of trialkylaluminum induces strong monomer activation toward nucleophiles, which results in the observed drastic increase of the polymerization rate. Besides, as indicated by the “living-like” behavior of the PO polymerization observed (PPO with controlled $\bar{M}_{\rm n}$ up to 20 000 g/mol), the important transfer reaction to PO, which characterizes alkali metal alkoxide initiators, is also strongly reduced. In other words, in the presence of R_3Al the $k_{\rm p}/k_{\rm tr_m}$ ratio, with $k_{\rm p}$ and $k_{\rm tr_m}$ respectively the rate constants of propagation and transfer to monomer, is strongly enhanced. This 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 process to monomer (Figure 4). Reduction of the basicity of alkali metal alkoxide species in alkoxy aluminate complexes may also contribute to the reduction of the proton abstraction reaction yielding transfer to monomer.

The ^{1}H NMR spectrum of a low molar mass PPO ($\bar{M}_{\rm n}$ = 500 g/mol) prepared with the system Na isopropoxide/*i*-Bu_3Al (1/5) at 0 °C is shown Figure 5. No trace of ethylenic protons from a possible allyloxy terminal group as a consequence of transfer to monomer is detected.

Because of higher sensitivity of MALDI−TOF mass spectroscopy to detect polymer end groups, the same PPO sample was analyzed. The corresponding spectrum is shown in Figure 6. A major peak series (P_1) of molar mass $P_1 = M_{\rm Na} + n(M_{\rm PPO}) + 2$ g/mol or $P_1 = M_{\rm Na} + (n - 1)(M_{\rm PPO}) + (M_{\rm isopropoxy}) + 1$, corresponding to PPO chains with isopropoxide and hydroxide end groups, is observed in agreement with isopropoxide initiation and proton termination. A second peak series P_2 in apparent very low proportion (≤10%) matches allyloxy-terminated and/or isobutyl-terminated oligomers $P_2 = M_{\rm Na} + n(M_{\rm PPO}) + (M_{\rm allyloxy}) + 1 = M_{\rm Na} + (n - 1)(M_{\rm PPO}) + (M_{\rm isobutyl}) + 1$). Although we cannot definitely conclude at this time on the origin of this second mode of initiation, involving an isobutyl group coming from trisobutylaluminum or an allyloxy group resulting from transfer to monomer, these results support the strong reduction, but may be

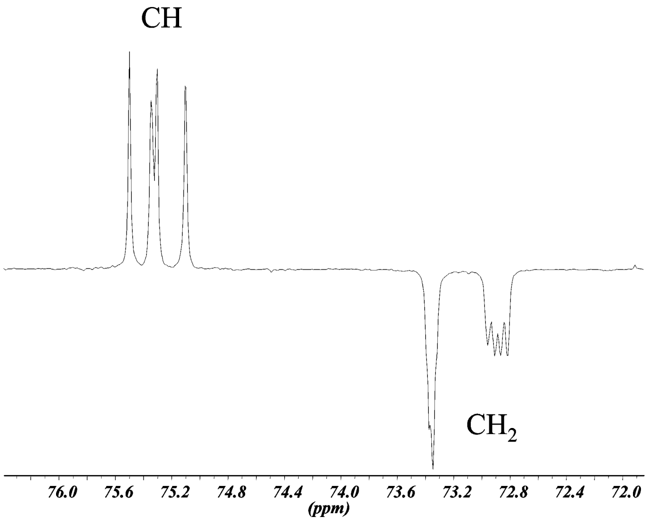


Figure 7. ^{13}C NMR DEPT spectrum of PPO ($\bar{M}_n$(exp) = 16 800 g/mol) obtained in the presence of *i*-PrONa and *i*-Bu$_3$Al ([Al]/[I] = 5) as initiating system, in cyclohexane, at 0 °C; expansion of methylene and methine region

not complete, of the transfer process to monomer. Indeed, MALDI−TOF analysis of PPO initiated with the Na *tert*-amyloxide/*i*-Bu$_3$Al system at 20 °C shows that the situation is more complicated. In addition to the reported PPO molar mass series (P_1 and P_2), the presence of other PPO peak series suggests that different initiation mechanisms can also take place. Further studies are in progress concerning this point.

The regioregularity and stereospecificity of monomer insertion were further investigated by ^{13}C NMR. The DEPT spectrum of PPO ($\bar{M}_n$(exp) = 16 800 g/mol) obtained in the presence of *i*-PrONa and *i*-Bu$_3$Al ([Al]/[I] = 5) as initiating system, in cyclohexane at 0 °C, is shown in Figure 7. According to literature data,[17] the observed methine and methylene carbon signals can be unambiguously attributed to exclusive head-to-tail (H−T) enchainments. The absence of side peaks indicative of H−H or T−T junctions is indicative of an anionic coordinated type mechanism involving attack of a nucleophilic active species onto the PO methylene carbon. Besides, the relative peak intensities of the methine and methylene carbons respectively resolved into triads and diads (splitted into higher stereosequences) show that the PPO obtained is fully atactic.[18]

Conclusion

In conclusion, we have shown that catalytic systems obtained from the simple combination of alkali metal alkoxides (I) and trialkylaluminum at ratio [Al]/[I] > 1 are efficient initiators for the "controlled" high speed anionic polymerization of PO. Depending on the initial ratio [PO]/[alkali metal alkoxide], PPO with controlled masses (up to 20 000 g/mol) have been prepared in very short reaction times compared to other initiating systems described in the literature. The rate of polymerization is strongly dependent on the nature and proportion of the trialkylaluminum. This derivative acts as an activator of PO through oxygen coordination onto the electrophilic aluminum center, as already reported by Inoue et al.[14,15] and Braune[16] in the case of bulky phenoxyaluminum electrophiles. The second impact of the monomer activation process deals with the selectivity increase of active species toward the ring-opening polymerization to the detriment of the monomer transfer reaction. Further works are in progress to study the influence of initiator and aluminum catalyst nature and determine the parameters that govern this anionic polymerization involving an activation of the monomer (APAM).

References and Notes

(1) Levene, P. A.; Walti, A. *J. Biol. Chem.* **1927**, *75*, 325.
(2) Boileau, S. In *Comprehensive Polymer Science, Chain Polymerization*; 1989; Vol. 3, Part 1, pp 467−487.
(3) Gagnon, S. D. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kruschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Vol. 6, pp 273−307.
(4) Quirk, R. P.; Lizarraga, G. M. *Macromol. Chem. Phys.* **2000**, *201*, 1395−1404.
(5) Pruitt, M. E.; Baggett, M. M. U.S. Patent 2,706,181, 1955.
(6) Vandenberg, E. J. *J. Am. Chem. Soc.* **1961**, *83*, 3538−3539.
(7) Colclough, R. O.; Wilkinson., K. *J. Polym. Sci., Part C* **1964**, *4*, 311−322.
(8) Huang, Y. J.; Zi, G. R.; Wang, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1142−1150.
(9) Tsurata, T.; Hagiwara, T.; Ishimori, M. *Makromol. Chem.* **1981**, *182*, 501−511.
(10) Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 401−411.
(11) Jérôme, R.; Teyssié, P.; Taquet, A.; Masy, J. P.; Goethals, E. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1169−1176.
(12) Inoue, S.; Aida, T. *Macromolecules* **1981**, *14*, 1166−1169.
(13) Inoue, S.; Aida, T.; Sanuki, K. *Macromolecules* **1985**, *18*, 1049−1054.
(14) Sugimoto, H.; Aida, T.; Inoue, S.; Kuroki, M.; Sugimoto, H. *Macromolecules* **1994**, *27*, 2013−2018.
(15) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2820−2825.
(16) Braune, W.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 64−68.
(17) Antelmann, B.; Chislom, H. C.; Iyer, S. S.; Huffman, J. C.; Navarro-Llobet, D.; Pagel, M.; Simonsick, W. J.; Zhong, W. *Macromolecules* **2001**, *34*, 3159−3175.
(18) Chisholm, M. H.; Navarro-Llobet, D. *Macromolecules* **2002**, *35*, 2389−2392.

MA035768T