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Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum

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ABSTRACT: The conventional anionic polymerization of propylene oxide (POx) proceeds at a very slow rate in low polar media and is characterized by an important transfer reaction to monomer. This only allows the formation of poly(propylene oxide) oligomers. A new polymerization strategy allowing the fast and controlled anionic polymerization of POx has been developed. It is based on the formation of complexes with both the anionic initiator and the monomer. The influences of alkali metal alkoxides (*i*-PrONa), ammonium salts (NBu₄Cl and NOct₄Br), and phosphonium salts (PBu₄Cl) as initiators, in combination with triisobutylaluminum, have been investigated in terms of reactivity, molar mass control, livingness, and polymerization mechanism. PPOx with narrow polydispersities and controlled molar masses, up to 150 000 g/mol, have been obtained in hydrocarbon media, at low temperature, and in short reaction times.

Introduction

Poly(propylene oxide) (PPOx) finds important applications as functional oligomer, block co-oligomer, and high molar mass elastomer. However, its use remains limited due to the lack of control of its polymerization.

It is well-known that alkali metal derivatives are efficient initiators for the anionic polymerization of cyclic ethers. However, the high nucleophilicity of the corresponding propagating species may result in important transfer reactions.¹ In the case of propylene oxide (POx) only low molar mass polymers are obtained as a consequence of proton abstraction on the POx methyl group, which leads to the formation of hydroxy-ended chains and new allyl alkoxide initiators.² The addition of crown ethers to alkali metal cations reduces the transfer to monomer;³ however, PPOx molar masses are limited and remain below 10 000 g/mol. With the aim to check softer counterions less prone to hydrogen abstraction from the monomer, Mülhaupt and co-workers have recently investigated the use of bulky phosphonium salts.⁴ Polymerization proceeds rapidly with a relatively good polymer molar mass control, but only the preparation of PPOx oligomers has been described (5000 g/mol). Another approach consists in the use of aluminum porphyrins initiators in association with bulky aluminum derivatives as activator. These systems yield PPOx with controlled molar masses in the range of 10 000–15 000 g/mol in short polymerization time.⁵ More recently, Okuda et al. have reported the possibility to replace aluminum porphyrins by bulky aluminate complexes formed between sodium alkoxides or tetrabutylammonium salts on the one hand and bulky bis-(phenoxy)aluminum compounds on the other.⁶ Controlled synthesis of POx oligomers (<5 000 g/mol) was described.

In a recent work we have shown that very simple initiators based on the association of alkali metal derivatives, typically sodium isopropoxide (*i*PrONa) and triisobutylaluminum (*i*-Bu₃-

Al), yield rapid POx polymerization, whereas transfer to monomer was significantly reduced.⁷ These last systems allow the synthesis of PPOx with relatively high molar masses (up to 50 000 g/mol) but still suffer from side reactions. Some improvement was found in a preliminary study using tetrabutylammonium chloride instead of *i*-PrONa.⁸ We report here the use of onium salts (NBu₄Cl, NOct₄Br, and PBu₄Cl) as initiators in association with *i*-Bu₃Al for the anionic polymerization of POx.

Experimental Section

Materials. Triisobutylaluminum (*i*-Bu₃Al, 1 M in toluene), tetrabutylammonium bromide (NOct₄Br, 98%), and tetrabutylphosphonium chloride (PBu₄Cl, 96%) were purchased from Aldrich, and tetrabutylammonium chloride (NBu₄Cl, ≥97%) was purchased from Fluka. *i*-Bu₃Al was used without further purification; NOct₄Br and NBu₄Cl were dried under dynamic vacuum for 2 h. PBu₄Cl was first dried under vacuum and dissolved in dry methanol, to remove traces of water by distillation under vacuum, followed by another distillation with dry toluene. NOct₄Br and PBu₄Cl powders were then solubilized in toluene at the desired concentration. NBu₄Cl, insoluble in toluene, was solubilized in dry propylene oxide. Sodium isopropoxide (*i*-PrONa) was synthesized by reaction of *i*-PrOH (99.5% anhydrous, Aldrich), previously dried and distilled over CaH₂, with sodium metal (99.95%, cubes in mineral oil, Aldrich), and dispersed in the mixture toluene/THF (2:1). The reaction mixture was left at 50 °C for one night and stored over a small excess of sodium metal. Propylene oxide (POx, 99%, Fluka) was dried over CaH₂ and distilled under vacuum before use. Toluene (99%, J.T. Baker) and cyclohexane (99%, J.T. Baker) were purified over polystyryllithium seeds and distilled under vacuum before use.

Procedures. All polymerizations were performed between –30 and 50 °C under argon in a glass reactor equipped with a magnetic stirrer and fitted with PTFE stopcocks. The reactor was previously flamed under vacuum. Then, solvent and monomer were successively introduced under vacuum through connected glass tubes. After addition of the onium salt solution, the polymerization was triggered by addition of *i*-Bu₃Al via a syringe under argon. Polymerizations were stopped with EtOH or EtOH/HCl. Conversions were determined gravimetrically after a complete drying of the polymer under vacuum at room temperature.

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Table 1. Propylene Oxide Polymerization Initiated by Different Onium Salts (I) in the Presence of Triisobutylaluminum, in Toluene

onium salt (I)	[<i>i</i> -Bu ₃ Al]/[I]	[POx]/[I]	[POx] (mol/L)	<i>T</i> (°C)	time (h)	yield (%)	$\bar{M}_{n,th}$ (g/mol)	$\bar{M}_{n,exp}$ (g/mol)	\bar{M}_w/\bar{M}_n
NBu ₄ Cl	0	360	4	20	24	0			
NBu ₄ Cl	1	360	4	20	24	0			
NBu ₄ Cl	1.3	350	4	0	2	100	20 000	21 100	1.07
NBu ₄ Cl	1.8	360	4	0	1	100	20 700	19 800	1.34
NBu ₄ Cl	3	350	4	0	1 ^{1/2}	100	20 300	13 800	1.77
NOct ₄ Br	0.8	482	4	20	24	0			
NOct ₄ Br	1.3	300	4	0	2	100	20 000	17 500	1.12
NOct ₄ Br	1.4	345	2	20	2	100	20 600	20 500	1.11
PBu ₄ Cl	1.2	517	4	20	2	100	25 200	23 000	1.10
PBu ₄ Cl	1.2	345	4	50	2	100	20 100	12 000	1.32

Table 2. Propylene Oxide Polymerization Initiated by Different Onium Salts (I) and *i*-PrONa as Reference in the Presence of Various Amounts of Triisobutylaluminum, in Cyclohexane, at 0 °C ([POx] = 5 mol/L; $\bar{M}_{n,th}$ = 11 000 g/mol)

onium salt (I)	[<i>i</i> -Bu ₃ Al]/[I]	[POx]/[I]	<i>t</i> _{1/2} ^a (min)	<i>k</i> _p [M*] ^b (min ⁻¹)	<i>k</i> _p (L mol ⁻¹ min ⁻¹)	$\bar{M}_{n,exp}$ (g/mol)	\bar{M}_w/\bar{M}_n
<i>i</i> -PrONa	5.1	170	34.2	280	2 300	11 200	1.24
<i>i</i> -PrONa	3.4	170	67.7	120	1 700	10 500	1.21
NBu ₄ Cl	1.5	192	70.0	140	10 700	11 000	1.18
NOct ₄ Br	1.3	192	2.6	3850	493 300	12 800	1.15
NOct ₄ Br	1.2	193	16.0	1350	258 800	11 000	1.16
PBu ₄ Cl	1.3	161	3.5	3 050	327 400	13 200	1.12

^a Time for 50% monomer conversion. ^b [M*] = activated propylene oxide concentration.

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

Kinetic Measurements. Dilatometry measurements were performed using a similar synthesis procedure. The glass dilatometer was previously flamed under vacuum. After introduction of toluene under vacuum through connected glass tubes, NOct₄Br and *i*-Bu₃Al were added using a syringe. The system was thermostated at 0 °C, and POx was finally introduced via a syringe. Monitoring of the reaction was immediately followed by recording the volume level of the solution in the capillary tube attached to the reactor.

Analysis. PPOx 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 three TSK columns HXL (G2000, G3000, G4000) at an elution rate of 1 mL/min. Polystyrene was used as standards. Complementary PPOx measurements were performed by MALDI-TOF analysis for low molecular weight samples (≤10 000 g/mol) and osmometry for higher ones. According to these techniques, a 0.6 corrective factor was applied to molar masses obtained by SEC.

MALDI-TOF spectra were acquired using a Bruker REFLEX III mass spectrometer. The instrument is equipped with a pulsed N₂ laser (337 nm) and a time-delayed extracted ion source. A dithranol matrix and NaI as cationization agent were used.

Results and Discussion

The replacement of RONa initiators by various onium salts (I) was investigated to determine the influence of the nature and size of the counterion on the control of both the initiation and propagation reactions as well as on the polymerization reactivity. A series of polymerization experiments were first performed in toluene with tetrabutylammonium chloride (NBu₄Cl), tetraoctylammonium bromide (NOct₄Br), and tetrabutylphosphonium chloride (PBu₄Cl) as initiators, associated with *i*-Bu₃Al as activator in different proportions. For triisobutylaluminum/sodium derivative systems in hydrocarbons the polymerization is only effective with an excess of *i*-Bu₃Al with respect to alkali metal derivatives.^{7,8} As it may be seen in Table 1, these new systems are also inactive at ratios [Al]/[onium salt] lower than or equal to one, even after a long polymerization time, typically 24 h. In contrast, in the presence of an excess of the aluminum compound, polymerization proceeds rapidly, up to complete monomer conversion. In the temperature ranging from 0 to 20 °C, experimental PPOx molar masses are close to the expected values, assuming the formation of one PPOx chain

per onium salt, while polydispersities of PPOx are narrow. Best results are observed at low [Al]/[I] ratios (1.2 or 1.3). Higher amounts of activator (1.8 or 3 equiv) or higher reaction temperatures (50 °C) yield broader molar mass distributions: some deviation from theoretical molar mass, indicating the occurrence of side reactions in these conditions, is also observed. Chain transfer processes will be discussed in the final part of the text named Analysis of Chain Ends.

1. Kinetic Study. Kinetic experiments were conducted to scale the reactivity of the different systems studied and to compare them with *i*-Bu₃Al/alkali metal alkoxides ones.^{7,8} As shown in Figure 1, the highest rates of polymerization (*R*_p) are obtained with the bulkiest ammonium NOct₄Br and the phosphonium PBu₄Cl salts. Even NBu₄Cl, which exhibits a lower reactivity, yields higher polymerization rate than the alkali metal alkoxides. Moreover, the required amount of *i*-Bu₃Al is lower in the case of onium salts. For example, a similar polymerization rate is obtained with 2.3 times less activator with NBu₄Cl than with *i*-PrONa. As a first approach to their relative reactivity, the half monomer conversion times have been determined for the different systems (see Table 2).

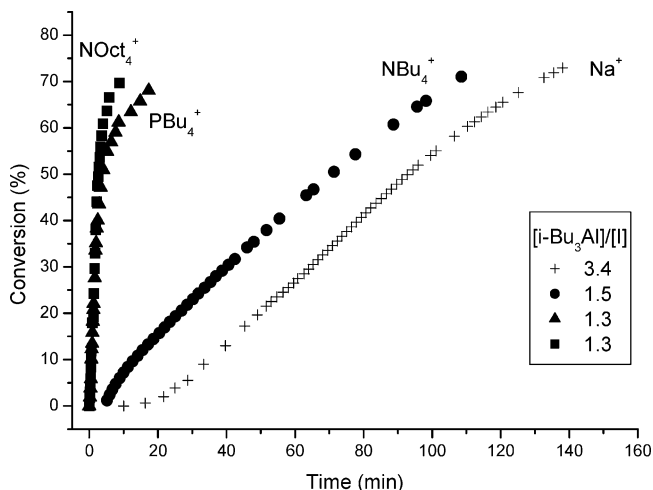


Figure 1. Conversion vs time curves of propylene oxide (POx) polymerization initiated by *i*-PrONa (+), NBu₄Cl (●), NOct₄Br (■), and PBu₄Cl (▲) in the presence of *i*-Bu₃Al; [POx]/[I] = 170–193, [POx] = 5 mol/L, at 0 °C in cyclohexane (I = initiator).

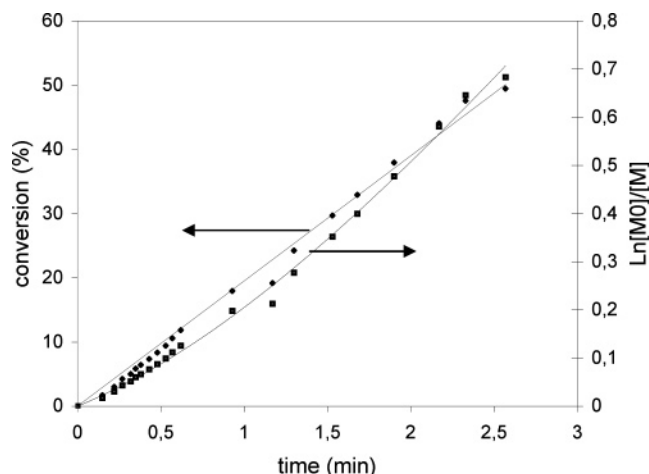
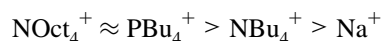


Figure 2. Comparison of conversion = $f(t)$ and $\ln([M]_0/[M]) = f(t)$ curves for the polymerization of propylene oxide (POx) at 0 °C in toluene. $[i\text{-Bu}_3\text{Al}]/[\text{NOct}_4\text{Br}] = 1.3$; $[\text{POx}]/[\text{NOct}_4\text{Br}] = 158$; $[\text{POx}] = 3 \text{ mol/L}$.

Typical kinetic curves are presented in Figure 1. In contrast to RONA initiators for which an induction period attributed to aggregation of alkali metal alkoxides is observed, with onium counterions polymerization proceeds immediately. An almost linear conversion vs time plot is observed up to 60% with $\text{NOct}_4\text{-Br}$ and PBu_4Cl and 70% with NBu_4Cl . Besides the direct influence of the activator concentration, results reveal a strong influence of the nature of the counteranion and yield the following reactivity order:



Decreasing both the size of the counterion and the amount of R_3Al would allow to decrease the polymerization rate and maintain an advantageous k_p/k_{tr} at higher temperatures.

At high conversions a curvature of the kinetic plots indicating a decrease of the polymerization rate is observed. This was attributed to a decrease of the free $i\text{-Bu}_3\text{Al}$ concentration, part of it being trapped by the oxygens of the PPOx chains.

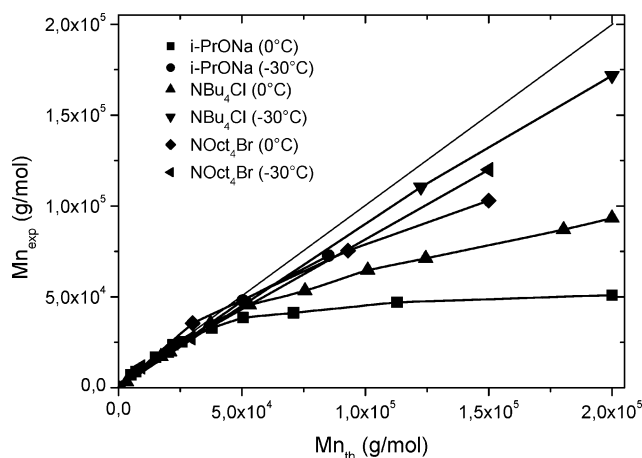


Figure 3. Comparison of experimental and theoretical molar masses in propylene oxide (POx) polymerizations initiated by $i\text{-PrONa}$ ($[i\text{-Bu}_3\text{Al}]/[\text{POx}] = 0.02$) and by NBu_4Cl ($[i\text{-Bu}_3\text{Al}]/[\text{POx}] = 0.005$) at 0 and -30 °C in toluene; $[\text{POx}] = 4 \text{ mol/L}$.

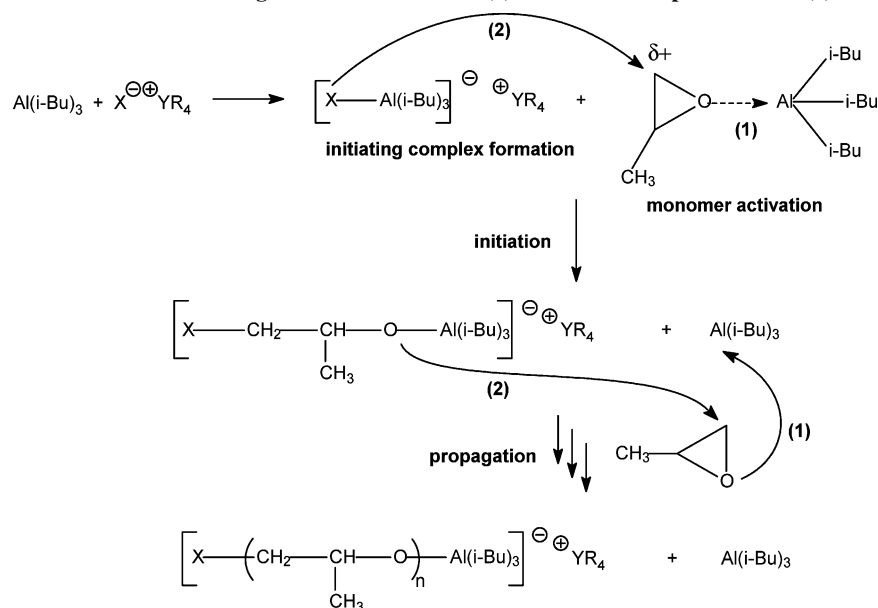
In order to determine the monomer order of the polymerization, at least in the first 50% monomer conversion, both the variation of POx consumption and of $\ln([M]_0/[M])$ were plotted as a function of reaction time. They can be compared in Figure 2: a much better linearity is observed for the conversion = $f(t)$ plot, suggesting a zero monomer order dependence of the polymerization. Since onium salts alone or onium salt/ $i\text{-Bu}_3\text{Al}$ (1:1) systems are inactive, these results sustain the selective insertion of a $i\text{-Bu}_3\text{Al}$ complexed monomer which is electrophilically activated.

Accordingly, the polymerization rate R_p could be expressed by the equation

$$R_p = k_p[I]_0[M^*] \quad (1)$$

where k_p is the propagation rate constant and $[I]_0$ and $[M^*]$ are respectively the initiator and activated monomer concentrations. $[M^*]$ depends on the available $i\text{-Bu}_3\text{Al}$ concentration, $[Al]_a = [Al]_0 - [I]_0$, since 1 equiv of $i\text{-Bu}_3\text{Al}$ is trapped in the 1:1 "ate" complex formed with the initiator.

Scheme 1. Polymerization Mechanism Involving Monomer Activation (1) Prior to Nucleophilic Attack (2) of the Aluminate Complex



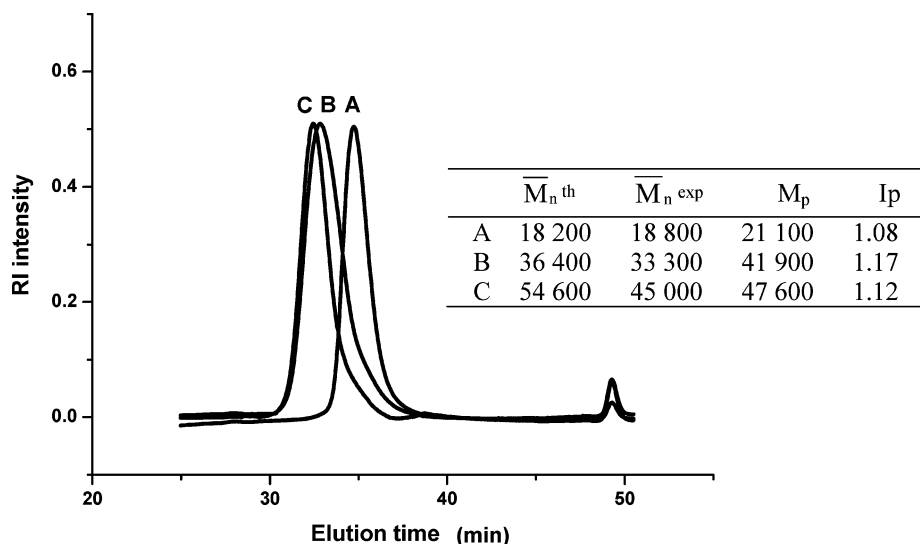


Figure 4. SEC curves of poly(propylene oxide) obtained after sequential propylene oxide (POx) additions (NBu₄Cl as initiator, [POx] = 4 mol/L, [*i*-Bu₃Al]/[POx] = 0.5 mol %, in toluene, at 0 °C, 100% conversion).

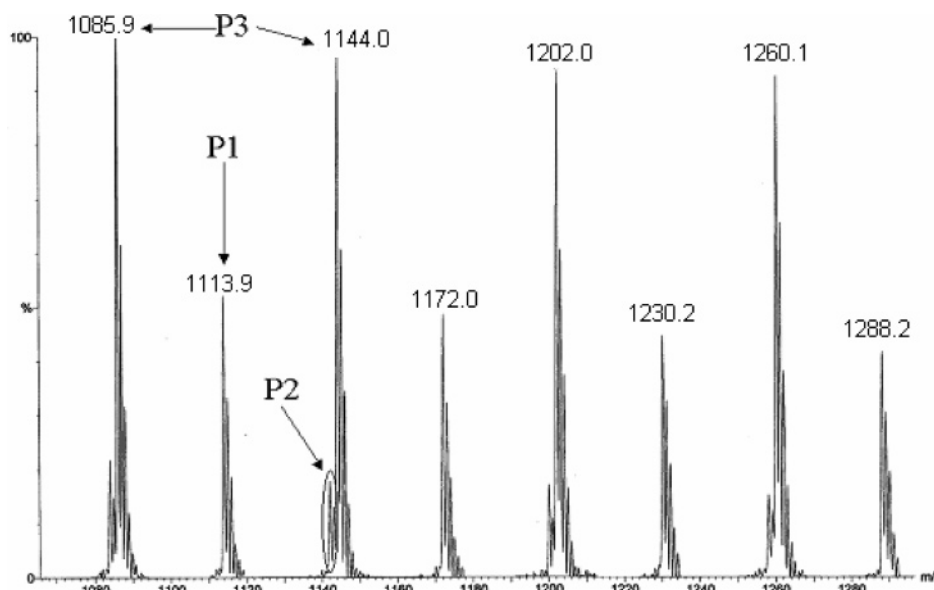


Figure 5. Enlarged region of the MALDI-TOF mass spectrum of poly(propylene oxide) (PPOx) synthesized with *i*-Bu₃Al:t-AmOK ([*i*-Bu₃Al]/[t-AmOK] = 5), [POx] = 4 mol/L at 20 °C in cyclohexane.

In polymerization conditions $[M]_0 \gg [Al]_a$; thus, we may assume that $[M^*] \approx [Al]_a$. This yields for the polymerization reaction

$$R_p = k_p[I]_0[Al]_a \quad (2)$$

The corresponding $k_p[M^*]$ and k_p values are collected in Table 2. The polymerization rate constant increases by a factor 5 going from Na to NBu₄ and by 30–50 times when PBu₄ or NOct₄ is used as counterion. The noticeable difference observed between the k_p values calculated with NOct₄Br can be related to the uncertainty in the available *i*-Bu₃Al concentration, in particular for experiments performed at [*i*-Bu₃Al]/[I] ratio close to one. Results confirm the reported reactivity order.

At high conversions (>50–60%), competitive *i*-Bu₃Al complexation by the polyether chains cannot be neglected anymore: $[M^*] = [Al]_a = [Al]_0 - [I]_0 - [Al]_{PPOx}$, with $[Al]_{PPOx}$ corresponding to *i*-Bu₃Al complexed by the PPOx chains.

As already proposed for R₃Al/ROMt, these results can be interpreted by a polymerization mechanism involving an activation of POx by *i*-Bu₃Al, through complexation, making the

activated monomer more prone to nucleophilic attack by the 1:1 [*i*-Bu₃Al]/[X[−]Y⁺] “ate” complex (X = Br, Cl and Y = NR₄ or PR₄) (see Scheme 1). After one monomer insertion, a new “ate” complex is formed between a *i*-Bu₃Al molecule and the growing chain end, whereas the second *i*-Bu₃Al molecule is released and can coordinate and activate a new POx molecule. At elevated monomer conversion (>60–70%) competitive complexation of *i*-Bu₃Al with the polyether chains reduces the activated monomer concentration and the polymerization rate.

The microstructure of PPOx obtained with the system NOct₄-Br/*i*-Bu₃Al provides some further information about the polymerization mechanism. The presence in the NMR spectra of regioregular head-to-tail enchainments and the absence of characteristic peaks of head-to-head and tail-to-tail linkages allow to conclude to a controlled and fully regiospecific monomer insertion process.^{7,9,10} Deconvolution of the methylene signal, which is resolved in three distinct peaks, yields the following triad sequences: isotactic (25%), atactic (50%), and syndiotactic (25%), in agreement with a nonstereoregulating polymerization process.

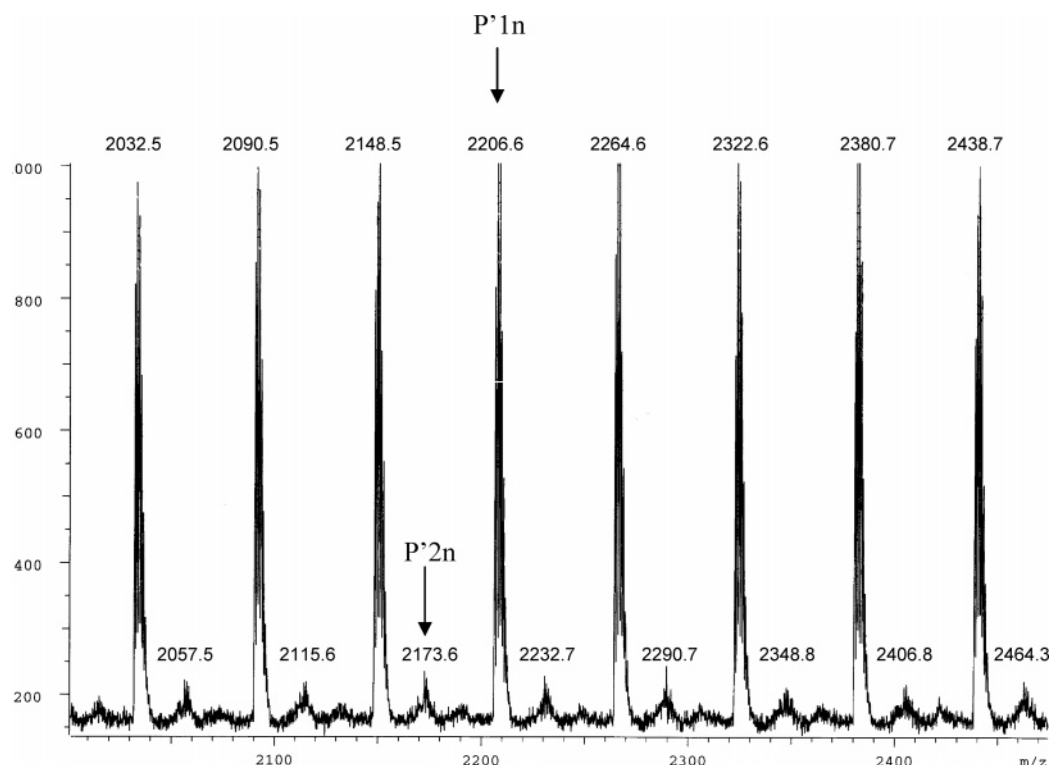
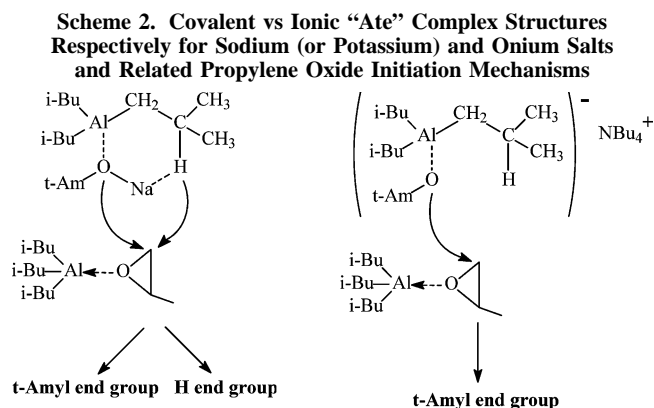


Figure 6. Enlarged region of the MALDI-TOF mass spectrum of a poly(propylene oxide) (PPOx) synthesized with $i\text{-Bu}_3\text{Al}:\text{NOct}_4\text{Cl}$ ($[i\text{-Bu}_3\text{Al}]/[\text{NOct}_4\text{Cl}] = 1.3$), $[\text{POx}] = 1 \text{ mol/L}$ at 0°C in toluene.

2. Polymerization Livingness. A series of polymerization experiments were carried out at 0 and -30°C targeting PPOx of increasing molar masses to check the living character of $i\text{-Bu}_3\text{Al}/\text{NR}_4\text{X}$ systems ($\text{R} = \text{Bu}$, Oct and $\text{X} = \text{Cl}$ or Br) and compare it with $i\text{-Bu}_3\text{Al}/i\text{-PrONa}$. Fits between experimental and theoretical molar masses are presented in Figure 3. With the onium salt, at low temperature (-30°C) and low $[\text{Al}]/[\text{I}]$ ratio, PPOx of very high molar mass, up to $170\,000 \text{ g/mol}$, was prepared. Indeed, a good agreement between theoretical and experimental molar masses is observed up to $100\,000 \text{ g/mol}$ at -30°C and $50\,000 \text{ g/mol}$ at 0°C . For comparison with $i\text{-Bu}_3\text{Al}/\text{RONa}$ molar masses are satisfactorily controlled only up to $50\,000$ and $20\,000 \text{ g/mol}$ at -30 and 0°C , respectively. This shows that transfer reactions are significantly reduced when replacing Na^+ by NR_4^+ counterions. This could be explained by the higher softness and the bulkiness of onium counterions as compared to alkali metal ones that are directly involved in the transfer-to-monomer process. In addition, formation of an “ate” complex decreases the nucleophilicity of the propagating chain ends, which likely contributes to limit proton abstraction on the POx methyl group.

To further confirm the “living” character of the POx polymerization initiated by onium salt/ $i\text{-Bu}_3\text{Al}$, sequential addition of POx was performed during one polymerization. Evolution of PPOx molar mass after polymerization of the successive monomer feeds indicates that almost all the chains formed in the first stage restart a second polymerization, as indicated by the shift of the polymer peak to higher molar masses (run B) on the SEC chromatogram (Figure 4). A third POx addition yields a new shift of the SEC peak (run C) although some deviation from theoretical \bar{M}_n is observed, indicating some deactivation due to the repeated reactor opening for sampling and/or to some residual transfer.

3. Analysis of Chain Ends. MALDI-TOF analysis of PPOx yields informations on chain ends from which initiation, transfer, and termination reactions can be well documented. In addition to hydroxyl terminus resulting from methanol deactivation, three



distinct PPOx populations with different head groups are formed with $t\text{-AmOK}/i\text{-Bu}_3\text{Al}$ (Figure 5). Formation of the main polymer fraction ($\text{P}2n = \text{M}_{\text{K}^+} + n\text{M}_{\text{POx}} + 2\text{M}_{\text{H}}$), with an H headgroup, can be attributed to hydride initiation involving $i\text{-Bu}_3\text{Al}$.^{7,11,12} The second polymer fraction with a $t\text{-AmO}$ head corresponds to expected initiation by $t\text{-AmOK}$ ($\text{P}1n = \text{M}_{\text{K}^+} + \text{M}_{t\text{-AmO}} + n\text{M}_{\text{POx}} + \text{M}_{\text{H}}$). Finally, in a much lower proportion, the third population characterized by an allyloxy headgroup ($\text{P}3n = \text{M}_{\text{K}^+} + n\text{M}_{\text{POx}} + \text{M}_{\text{H}} + \text{M}_{\text{allyloxy}}$) illustrates the residual contribution of the transfer to monomer process.

As shown in Figure 6, polymers obtained in similar conditions with $\text{NOct}_4\text{Cl}/i\text{-Bu}_3\text{Al}$ possess almost quantitatively a chloride head ($\text{P}'1n = \text{M}_{\text{K}^+} + \text{M}_{\text{Cl}} + n\text{M}_{\text{POx}} + \text{M}_{\text{H}}$) while only traces of the population resulting from hydride initiation ($\text{P}'2n = \text{M}_{\text{K}^+} + n\text{M}_{\text{POx}} + 2\text{M}_{\text{H}}$) can be detected. This supports a direct and selective initiation in the “ate” complex by the halide anions, in agreement with an anionic-type mechanism. Moreover, the population of PPOx resulting from transfer to monomer is not observed, which agrees with the possibility to prepare high molar mass PPOx. These results confirm the better control of the POx initiation and propagation reactions with onium salts compared

to alkali metal alkoxides. This can be related to the nature of the counteranion which likely affects the structure of the aluminate complex. Onium salt/trialkylaluminum “ate” complexes are known to preserve an ionic structure in the solid form¹³ which largely favors the expected halide initiation, as illustrated in Scheme 2 and in agreement with their large radius size calculated by molecular modeling (NOct_4^+ , $r = 11.2 \text{ \AA} > \text{PBu}_4^+$, $r = 6.3 \text{ \AA} > \text{NBu}_4^+$, $r = 6.1 \text{ \AA} \gg \text{Na}^+$, $r = 1.9 \text{ \AA}$). In contrast, because of its small size and its higher electrophilic character, the sodium counterion yields a more covalent “ate” complex in which the alkali metal cation directly interacts with the alkyl groups of trialkylaluminum, thus allowing hydride abstraction accompanied by side initiation.

Conclusion

Very efficient and well-controlled propylene oxide polymerization has been achieved using the simple combination of onium salts and triisobutylaluminum at low to room temperature. “High-speed” controlled anionic polymerization of POx takes place in the presence of a slight excess of $i\text{-Bu}_3\text{Al}$ Lewis acid with respect to the initiator. In comparison with alkali metal alkoxides/ $i\text{-Bu}_3\text{Al}$ systems, the use of tetraalkylammonium or tetraalkylphosphonium salts as initiators increases significantly the polymerization rate and the k_p/k_{tr} ratio, allowing the controlled synthesis of high molar mass poly(propylene oxide)s.

Application of these systems to the design of telechelics and PPOx-based copolymers will be reported in forthcoming papers.

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