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Activation Mechanisms of Trialkylaluminum in Alkali Metal Alkoxides or Tetraalkylammonium Salts / Propylene Oxide Controlled Anionic Polymerization

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Summary: The anionic polymerization of propylene oxide (PO) initiated by alkali metal alkoxides is in non polar solvents a very slow and non controlled reaction process. Transfer reaction to monomer is predominant, allowing only the preparation of low molar masses PPO. The influence of the addition of trialkylaluminium to either an alkali metal alkoxide or a tetraalkylammonium salt used as initiator for PO polymerization in hydrocarbon media was investigated. A strong enhancement of the polymerization rate accompanied by a drastic decrease of the transfer reactions is observed, allowing the synthesis of PPO with well controlled molar masses. At constant monomer and alkali metal alkoxide concentrations, the polymerization rate increases with increasing trialkylaluminium concentration. Results indicate that the trialkylaluminium derivative is involved in the formation of two distinct complexes, one with the alkali metal alkoxide or the tetraalkylammonium salt and another one with the PO monomer which is strongly activated towards nucleophilic active species. Significant differences between the alkali metal and tetraalkylammonium based initiators are observed. In particular much less trialkylaluminum activator is needed with the ammonium salt to get the same rate of propagation and controlled polymerization.

Keywords: anionic polymerization; monomer activation; polyethers; propylene oxide; trialkylaluminum

Introduction

Improvement of propylene oxide (PO) polymerization and the ways to control its living character are still the object of important research efforts since polypropylene oxide (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[1]. This side process results in the exclusive formation

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of PPO oligomers, a large fraction of which possesses a terminal allylic unsaturation. The use of larger counterions (rubidium, cesium) or of crown ether additives slightly reduces the transfer process but PPO molar masses still remains limited (<15 000 g/mol)[2]. Very high molar mass PPO can be obtained however through coordinated anionic polymerization involving species of lower basicity[3]. 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. Indeed controlled PO polymerization has been achieved with aluminum porphyrin initiators[4] allowing the preparation of end-functional PPO with molar masses up to 10 000 g/mol. Addition of a bulky aluminium phenoxide to the aluminum porphyrin initiator was shown to drastically accelerate the polymerization; a complexation/activation of the oxygenated monomer by the electrophilic aluminium derivative was proposed[5]. Very recently, the possibility to substitute porphyrin initiators, very difficult to remove from PPO, by simpler systems based on the association of ammonium salts, or of crown ether complexed alkali metal alkoxide, with a bulky bisphenoxy aluminum electrophile was described[6]. However, up to now, only the controlled synthesis of PPO oligomers with molar masses of less than 5 000 g/mol was described. Another interesting initiating system for which the polymerization mechanism is not well established is the so-called double cyanide catalytic system $Zn_3[Co(CN)_6]_2$ which recently found industrial applications[7].

The present study deals with the use of new initiating systems based on the combination of simple alkali metal derivatives or tetraalkylammonium salts and trialkylaluminum for the "controlled" high speed anionic polymerization of propylene oxide.

Experimental

Materials *i*-Bu_3Al (1 mol/l in toluene) was 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 presence of *i*-Bu_3Al to remove traces of impurities. PO was finally distilled under vacuum and stored under vacuum at R.T. 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 *t*-Amyloxide (2-methylbutan-2-oxide) were synthesized in a similar way from 2-methylbutan-2-ol. *i*-BuNa and *n*-BuNa were synthesized by reaction of *i*-BuCl (98%, Aldrich) and *n*-BuCl (99.5% anhydrous, Aldrich), respectively dried and distilled over CaH_2, with sodium dispersion in cyclohexane. The mixture was reacted at 25°C for one hour and the supernatant liquid recovered by filtration. NBu_4Cl hydrate was dried under vacuum, dissolved in dry methanol and remaining traces of water were removed by co-distillation with methanol. NBu_4Cl was then recristallized in a solution of dried PO/toluene (4/1) and finally solubilized in PO at the desired concentration.

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. Cyclohexane and PO were introduced under vacuum through connected glass tubes followed by the 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 of the polymer under vacuum at 50°C. Dilatometry measurements were performed using a similar procedure.

Analytical techniques PPO molar masses were determined by SEC at 20°C using THF as eluant and polystyrene as standards. The nature of PPO chain ends was determined by MALDI-TOF mass spectrometry measurements on a BIFLEX III instrument.

Results and discussion

As shown in Table 1, polymerization of propylene oxide in cyclohexane initiated by soluble Na or K *tert*-amyloxide occurs readily in the presence of triisobutylaluminum at 20°C.

Table 1. Propylene oxide (PO) polymerization initiated with alkali metal *tert*-amyloxide ROM_{ct} (I) in the presence of *i*-Bu_3Al ($[iBu_3Al]/[I] = 5$) in cyclohexane.

Initiator (I)	[PO] (mol/l)	[PO]/[I]	Time	T (°C)	Yield (%)	$\overline{M}_n$ th (g/mol)	$\overline{M}_n$ (g/mol)	$\overline{M}_w/\overline{M}_n$
ROK	6.5	500	1h	20	93	26 970	18 000	1.4
RONa	6.5	480	25min	20	100	27 840	15 100	2
RONa	6.0	238	2h	0	100	13 800	11 500	1.3
ROLi[a)]	6.5	510	22h	20	57	16 860	1 600	1.6

a) $[iBu_3Al]/[I] = 10$

Completion of the reaction can be reached in less than 25 min in the case of Na counterion, however the control of the polymerization is not achieved and temperature has to be decreased to 0°C to improve the reaction livingness. With lithium counterion kinetics are much slower and only oligomers are formed suggesting a transfer reaction.

According to these preliminary data, a more detailed study of PO polymerization by bimetallic systems was performed at 0°C using sodium isopropoxide (*i*-PrONa) in the presence of triisobutylaluminum (Table 2) as well as other aluminum derivatives (Et_3Al and Me_3Al - results not shown) as initiating systems.

Table 2. Propylene oxide (PO) polymerization initiated by *i*-PrONa (I) in the presence of triisobutylaluminum in cyclohexane.

[PO] (mol/l)	[PO]/[I]	$[R_3Al]/[I]$	Time	T (°C)	Yield (%)	$\overline{M}_n$ th (g/mol)	$\overline{M}_n$ (g/mol)	$\overline{M}_w/\overline{M}_n$
6.2[a)]	360	0	7 days	25	0	-	-	-
5.5[b)]	-	-	10 days	25	0	-	-	-
4.0	382	1	10 days	25	0	-	-	-
4.0	87	3.5	2h	0	100	5 000	7 100	1.1
4.0	173	3.5	2h	0	70	7 000	8 800	1.1
4.0	258	5.2	3h30	0	100	15 800	16 800	1.3
4.0	382	7.6	3h30	0	100	22 100	23 600	1.3

a) experiment performed in the absence of R_3Al

b) experiment performed in the presence of R_3Al alone

When *i*-PrONa and *i*-Bu_3Al are used separately PO polymerization does not proceed even after several days at 25°C. A similar situation also prevails when the molar ratio [*i*-Bu_3Al]/[*i*-PrONa] is less or equal to 1. This suggests for $[AlR_3]/[I] \leq 1$ that the trialkylaluminum is completely involved in the formation of an aluminate complex, which is unable to initiate and/or propagate the PO polymerization. In contrast, in the presence of an excess of i-Bu_3Al in respect to *i*-PrONa, a fast polymerization of PO takes place and reaches completion in a few hours at 0°C, indicating 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. This suggests a PO living-like polymerization without any significant contribution of the monomer transfer process, which is typically observed with pure alkali metal alkoxide initiators.

These results are also consistent with a strong activation of the polymerization by R_3Al present in excess in respect to *i*-PrONa. As previously reported for PO polymerization performed in the presence of bulky aluminium phenoxide electrophiles [5-6], we can also postulate monomer activation through AlR_3 complexation. The activating role of R_3Al was further investigated by studying polymerization kinetics at various amounts of trialkylaluminum. Conversion versus time curves for a series of experiments performed at increasing *i*-Bu_3Al concentration and constant monomer and initiator concentrations are shown in Figure 1. The induction period which appears at the beginning of the polymerization can be tentatively assigned to the tendency of sodium isopropoxide and alkoxide termini of short PPO oligomers to strongly aggregate. Then reactivity rapidly increases yielding fast PO polymerization. As it may be seen increase in the concentration of the aluminium derivative strongly enhances the propagation reaction rate. These results are in agreement with a reaction mechanism in which the monomer is activated by the electrophilic aluminium compound, prior its insertion into the poly(propylenoxy) triisobutylaluminate sodium growing chain end (Scheme 1). Dissociation of $ROAlR_3^-$ into RO^- and AlR_3 is not favorable due to non polar solvent and no reaction at ratio $[Al]/[I] \leq 1$.

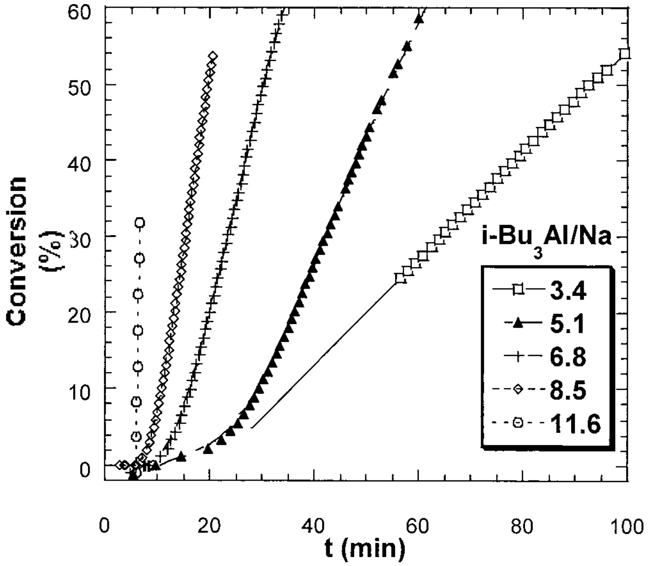
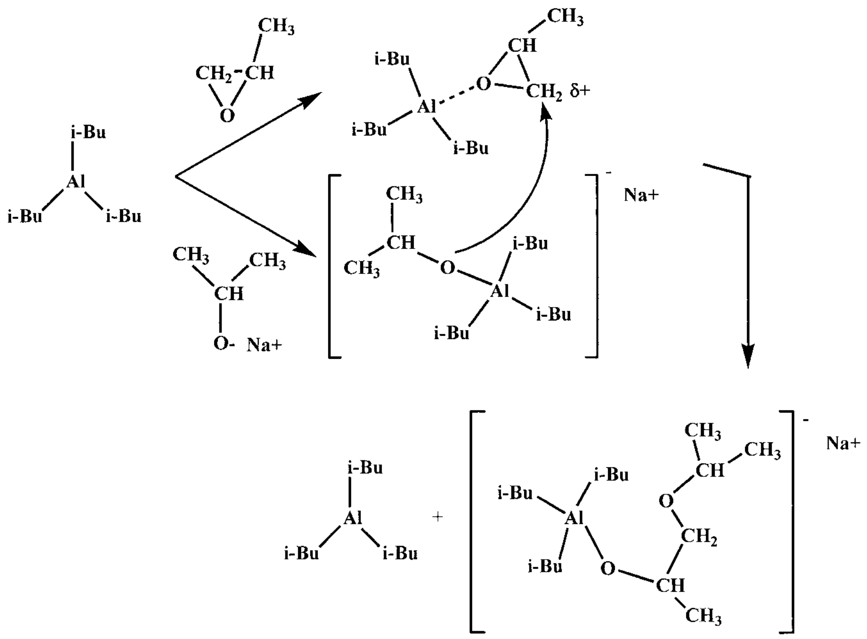


Figure 1. Conversion *vs* time curves of PO polymerizations initiated by *i*-PrONa with increasing amounts of *i*-Bu_3Al (cyclohexane, 0°C, $[PO]/[I]=189$, $[PO]=5$ mol/l, $\overline{M}_n$th = 11 000 g/mol).



Scheme 1. Reaction mechanism involving monomer activation prior insertion into the growing "ate" complex.

Besides, as indicated by the "living-like" behavior of the PO polymerization observed (PPO with controlled molar masses up to 20- 30 000 g/mol), the important transfer to monomer, that characterizes alkali metal alkoxide initiators, is also strongly reduced. 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 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.

Indeed when PPO of molar masses higher than 30 000 g/mol are targeted, the occurrence of transfer reactions at 0°C is clearly observed (Figure 2). Performing polymerizations at lower temperature (-30°C) allows to reduce significantly transfer but still some deviation from linearity is noticed for targeted PPO of molar masses higher than 100 000 g/mol. Attempts to initiate PO polymerization from alkyl derivatives of sodium confirm this tendency.

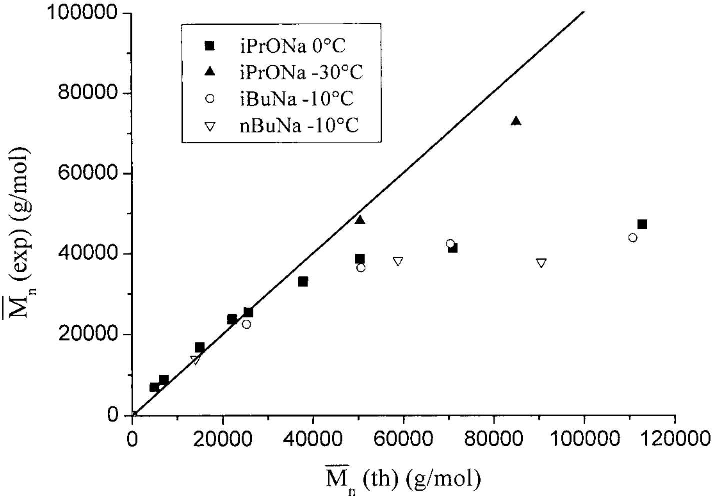


Figure 2. Experimental PPO molar masses from initiation by RONa or RNa and i-Bu_3Al at 0 and -30°C ([Al]/[Na] > 1, cyclohexane, [PO]=4 mol/l).

A similar study was performed using NBu_4Cl as initiator instead of *i*-PrONa. As previously observed with alkali metal derivatives, PO polymerization in the presence of NBu_4Cl and *i*-Bu_3Al takes place at a faster rate. This rate increases in direct relation with the concentration of *i*-Bu_3Al whereas the PPO molar masses remain constant and close to those expected for the formation of one chain per NBu_4Cl molecule, in agreement with an initiation involving the chloride anion and *i*-Bu_3Al catalysis. The conversion versus time curves for two typical polymerization experiments with iPrONa/*i*-Bu_3Al and NBu_4Cl/ *i*-Bu_3Al are shown in Figure 3. As it may be seen for almost similar rate the required amount of activator is much less with the ammonium salt. Moreover, the induction period observed with iPrONa initiator is suppressed with NBu_4Cl.

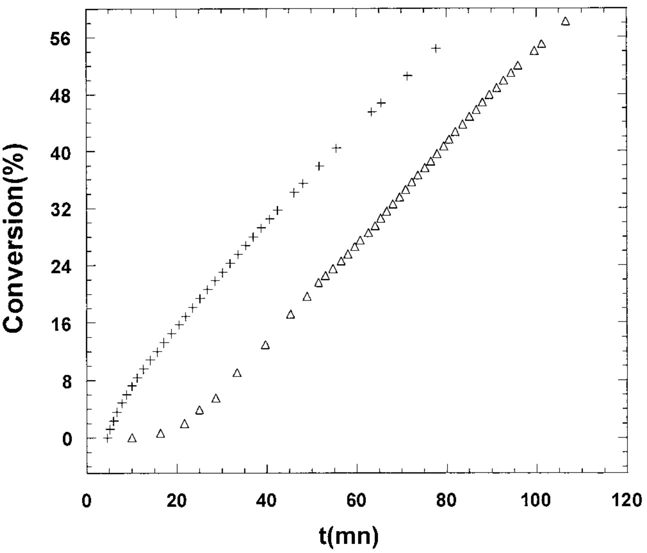


Figure 3. Conversion versus time curves of PO polymerization initiated by iPrONa ([Al]/[Na]=3.9) (Δ) and NBu_4Cl ([Al]/[NBu_4]=1.5) (+); [PO]/[Initiator]=189, [PO]=4 mol/l, 0°C in toluene, in the presence of different amounts of i-Bu_3Al.

Conclusions

The combination of simple alkali metal derivatives or tetraalkylammonium salts and trialkylaluminum yields binary complexes which are efficient initiators for the anionic polymerization of propylene oxide. The trialkylaluminum must be added in slight excess with respect to the initiator in order to activate the monomer and to allow a good control of PPO molar masses. The influence of reaction parameters such as the nature of the initiator and the activator are under investigation.

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