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ANIONIC RING OPENING POLYMERIZATION OF OXYGENATED HETEROCYCLES WITH SUPPORTED ZIRCONIUM AND RARE EARTHS ALKOXIDES AS INITIATORS IN PROTIC CONDITIONS. TOWARDS A CATALYTIC HETEROGENEOUS PROCESS

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Summary.

The polymerization of ε-caprolactone and 2,2-dimethyltrimethylene carbonate (DTC) initiated by various Lewis acid metal alkoxides (Zr and rare earths) in the presence of alcohol molecules has been investigated. Adding alcohol induces a fast transfer reaction which allows to synthesise functionalized oligomers. The polymerization can be described according to a living process with fast transfer reaction, so that the molecular weight is easily controlled.

In the case of lactones, rare earths alkoxides allow to get higher activities so that functionalized oligomers can be obtained within less than 5 minutes. Some transesterification are noticed if the polymer chains are left in contact with the active centers after polymerization.

These active centers have been grafted onto porous supports. These solids act as actual chemical ligands able to modify drastically the kinetic behaviour, particularly with regard to the controlled polymerization of ethylene and propylene oxides. Supported Y and Nd alkoxides are the best active centers for the polymerization of DTC.

Finally, the heterogeneous character has been used to develop a new continuous polymerization process by using a plug flow reactor filled with grafted silica. The conversion as well as the degree of polymerization depend either on the height of the bed or on the flow rate.

Introduction

The ring-opening polymerization of some oxygenated heterocycles such as oxiranes, ε-caprolactone (CL) and 2,2-dimethyltrimethylene carbonate (DTC) has widely been investigated because of the large number of applications of their polymers.

Lewis acid metal alkoxides are versatile compounds to initiate living polymerizations of lactones and carbonates without transesterification reactions. Among them, aluminium or zinc

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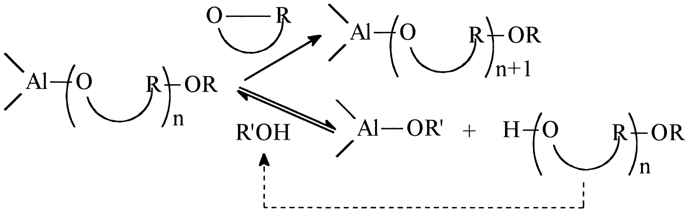
derivatives such as aluminium isopropoxide[1,2], μ-oxo-bimetallic alkoxides[3], porphyrins[4,5,6] and dialkylaluminium alkoxides[7,8] deserve to be mentioned. More recently, zirconium and rare earth alkoxides have been described as quite interesting initiators for the polymerization of ε-caprolactone[9,10,11] and lactides[12,13] and trimethylene carbonate[14]. As an example, polymerization carried out with yttrium isopropoxide at room temperature is very fast, and a living character has been observed with low polydispersities. The synthesis of poly(lactide-b-lactone) has also been reported[15], that highlights the living character of the polymerization.

In apolar or low polar solvents, these initiators are usually aggregated, that may lead to a decrease of the number of the active centers and a possible distribution of their activity. Bulky ligands have been proposed to avoid these aggregated structures. The aluminium porphyrins is a well-known illustration of this concept [4] and there is a clear relationship between the chemical structure of the porphyrin ligand and its activity [16]. The (2,6-di-tert-butyl phenoxy) ligand has been proposed to dispose of mononuclear yttrium alkoxide[17] for the polymerization of lactide, but this initiator seems unable to give well-controlled polymerization so that the addition of isopropanol is required to allow such polymerization, in order to exchange the alkoxides ligands.

The addition of protic compounds like alcohols or amines was already proposed many years ago by Teyssié [3] to dissociate the aggregates. The alcohol induces a transfer reaction place between the free alcohols and the aluminium alkoxides (Scheme 1) and consequently a decrease of molecular weights[18]. Nevertheless, thanks to this reaction, the polymer chains are end-capped by a functional group issued from the transfer agent.



Scheme 1. Propagation vs. transfer reactions in the polymerization of heterocycles. The arrow shows that the released ω-hydroxy-oligomer can act as a transfer agent in a subsequent reaction.

Another way to separate the active centers is to graft them on a solid support. The combination of a grafted alkoxide with a transfer reaction as described above leads to a quite versatile tool to synthesise functionalized oligomers. As a first example, we reported the great efficiency of aluminium alkoxides grafted on porous silica for the ring opening polymerization of oxiranes and lactones when working in the presence of alcohols or carboxylic acids[19,20)].

This paper is dealing with the polymerization of ethylene and propylene oxides, CL and DTC by using some metal alkoxides as initiators, such as Zr and rare earths (Y, Sm, Nd) in the presence of benzyl alcohol in excess. Some of these metal alkoxides have been grafted onto porous solids such as silica, alumina and zinc oxide to give heterogeneous initiators. Finally, an example of continuous polymerization of DTC by using a plug flow reactor will be shown.

Results and discussion

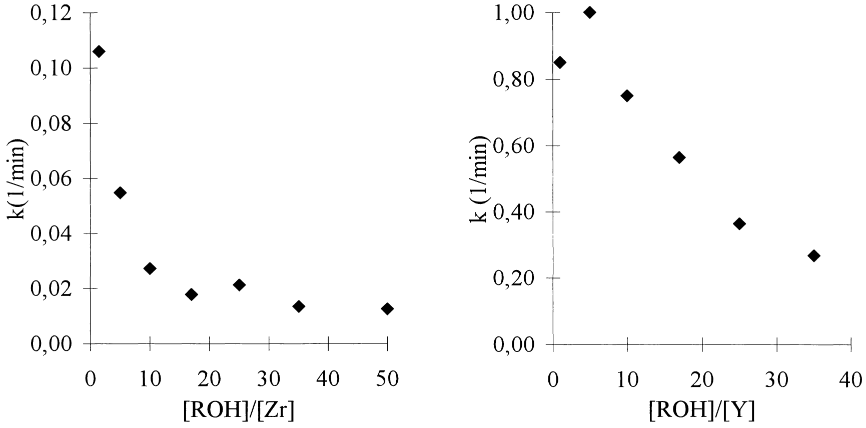
The benzyl alcohol has been used as transfer agent because of its great versatility as end-group tracer. Kinetics have been monitored by gas chromatography (GC), ^1H NMR and SEC analysis of samples taken from the reaction mixture, according to procedures previously described[20,21,22)]. GC analysis as well as ^1H NMR showed the fast and complete consumption of the benzyl alcohol molecules during the polymerization, that demonstrates the existence of a fast exchange reaction between free alcohols and metal alkoxides.

^1H NMR allowed us to estimate the average molecular weight as well as the conversion. In addition, the analysis of the end-group showed that the polymerization proceeds through acyl-oxygen bond cleavage (benzyl group singlet at 5.16 ppm).

1 - Homogeneous processes

The polymerization of ε-caprolactone polymerization with $Zr(OnBu)_4$ as initiator was first investigated. After a short induction period, a first-order kinetic is observed. There is a good agreement between the values of the degree of polymerization obtained from SEC, NMR and those deduced from GC, if assuming a living character (i.e. $\overline{DP_n} \propto \text{Conversion}$). The polydispersity index is low, around 1.1, indicating the absence of transesterification reactions. The effect of the [alcohol]/[Zr] ratio on the rate constant is depicted in Fig. 1a: increasing the alcohol content leads to a continuous decrease of the catalytic activity.

Sm, Nd and Y alkoxides have also been used as initiators. The catalytic activities are generally better than those observed with the aluminium or zirconium-based initiators and depend also on the [ROH]/[Y] ratio, but displaying an optimum, as for the aluminium-based systems (Fig. 1b). In addition, the activity depends on the metal (Tab. 1). Kinetics are very fast, but a broadening of the molecular weight is noticed if the polymer chains are left in the reactional medium after the complete consumption of the monomer. This observation suggests that some transesterification reactions probably occur. The rate constant of this side reaction is low enough and does not influence the molecular weight distribution during the monomer consumption, so that the consequences appear only at the end of the polymerization. This fact was already reported by McLain and Drysdale [12]. More recently, Baran *et al.* reported propagation and transfer rate constants related to a Sm and some Al derivatives as initiators [23]: the higher reactivity of the Sm derivative with respect to the Al compound ($k_p = 2.0$ L.mol^{-1}.s^{-1} instead of 0.5) is balanced by a transfer rate constant which is 1000 times higher.



(a) *(b)*

Figure 1. Experimental rate constants for ε-CL polymerization in toluene at 50°C using Zr *(a)* or Y *(b)* alkoxides as initiator and benzyl alcohol as transfer agent. Notice the difference in activities between Zr and Y. $[\varepsilon\text{-CL}]_0$ = 2mole/L. $[\varepsilon\text{-CL}]_0/[ROH]_0 = 10$.

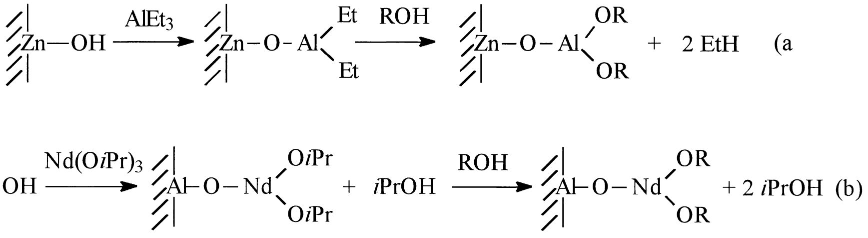
Initiator	reaction time for 100% conversion	$\overline{M_n}$ (g/mol)	$\overline{M_w}/\overline{M_n}$
$Y(OiPr)_3$	5 min	1950	1,55
$Nd(OiPr)_3$	10 min	1550	1,1
$Sm(OiPr)_3$	5 min	1100	1,9

Table 1 : Polymerization of ε-CL by some rare earth alkoxides and benzyl alcohol in toluene at 50°C. [metal] = 9.10^{-3} mol/L; $[ROH]_0$ = 0,09 mol/L; $[\varepsilon\text{-CL}]_0$ = 1,15 mol/L.

2 - Heterogeneous process

A - ε-caprolactone.

The alkoxides have been supported on porous supports according two different procedures. In the first case, the metal was grafted by reaction of triethylaluminium or diethylzinc on the hydroxyl groups located onto the surface of the support, followed by alcoholysis of the remaining alkyl groups (Scheme 2a). When the alkyl precursors were not commercially available, we took advantage of the exchange reaction between these OH groups and alkoxides functions (Scheme 2b). The same exchange reaction has been used to change the nature of the alkoxide groups on the metal. In all the cases, the amount of hydroxyl groups is previously determined by a thermic treatment.



Scheme 2. Grafting the active centers on a porous support.

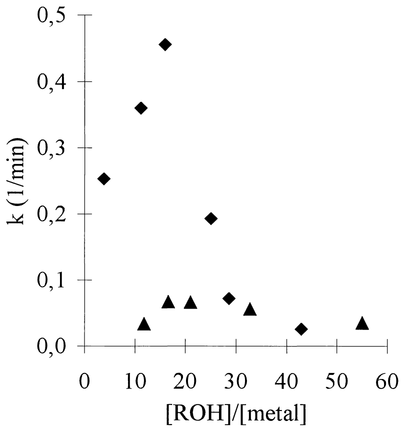


Figure 2. Heterogeneous polymerisation of ε-CL (T = 50°C).

(▲) Al; (◆) Sm grafted on silica (450°C).

As shown in Figure 2 and Table 2, the activity depends not only on the [alcohol]/[metal] ratio, but also on the support. Consequently, silica and alumina can no longer be seen as simple supports, but as actual chemical ligands, able to modify the acidity of the grafted metal through the oxygen atom. This feature had already been illustrated by the polymerization of ethylene oxide with the SiO_2/Al system whilst "homogeneous" aluminium isopropoxide is quite inefficient

Table 2. Heterogeneous polymerization of ε-caprolactone in toluene by using various metal alkoxides grafted on silica or alumina. T = 50°C.

Metal :	Al	Zr	Y	Sm	Nd
Silica 450°C	100% - 30 min	100% - 3h30	100% - 5 min	100% - 20min	100% - 30 min
Alumina 200°C	50% - 6h30	30% - 6h	50% - 20 min	80% - 20min	100% - 5 h

The activation energies were determined by investigating the effect of temperature on the rate constants. Fig. 3 displays the Arrhenius plot of the rate constants for the experiments carried out with the same [monomer]/[alcohol] ratio. For comparison are reported the rate constants related to the aluminium-based system grafted onto silica. Both systems exhibit roughly the same activation energy, between 30 and 33 kJ/mol, but grafting the active centers decreases the reaction rate. Using zirconium instead of aluminium increases the activation energy up to 51 kJ/mol. The activity is lower at room temperature but reaches the values displayed by aluminium systems at 85°C.

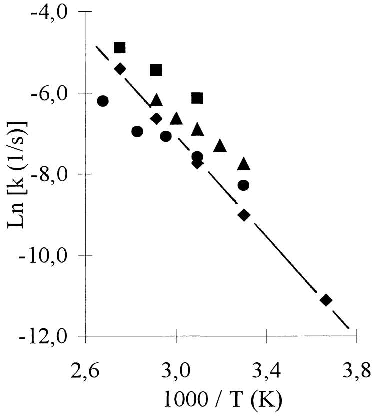


Figure 3. Arrhenius plots and activation energy for various systems :

(■) homogeneous aluminum : 30,2 kJ/mol.

(▲) heterogeneous aluminum : 32,9 kJ/mol.

(◆) homogeneous zirconium : 51,6 kJ/mol.

(●) heterogeneous samarium : 25,8 kJ/mol.

B - 2,2-dimethyltrimethylene carbonate (DTC)

The kinetics of the DTC polymerization depends both on the support and the alkoxide. The activity can be very high but a first-order law is rarely observed. In a lot of cases, more than more than 20% conversion can be reached during the first minute. After that, the kinetics slows down. The more striking result is that observed with the SiO_2/Y system, where a conversion around 95% is obtained in less than one minute, but levels off immediately after[24)].

SEC chromatograms display neither traces of lower molecular species nor broadening of the MWD, which could be related to cyclic molecules. Figure 4 shows that $\overline{M_n}$ increases roughly linearly with the conversion. If assuming a living character, this slope should be directly related to the number of polymer chains, that is the number of alcohol molecules :

$$\overline{M_n}(t) = 130 \times \overline{DP_n}(t) = 130 \times \frac{[\text{Monomer}]_0}{[\text{polymer chains}]}.Q(t) \rightarrow 130 \times \frac{[\text{Monomer}]_0}{[\text{alcohol}]}.Q(t)$$

where 130 is the molecular weight of DTC and Q(t) the conversion. The number of polymer chains is around that of starting alcohol molecules (provided [ROH]>[active centers]). In our conditions, [monomer]/[alcohol] = 10 and the expected "theoretical" value is 1300. This "ideal" behaviour has only been noticed with the ZnO/Zn system. With Al_2O_3(450°)/Y and ZnO/Y systems, the slope is around in the good range up 80% conversion and then increases. In some other cases, the slope is higher, that means the number of polymer chains involved in the transfer process is smaller than expected. This fact could be due to remaining aggregates.

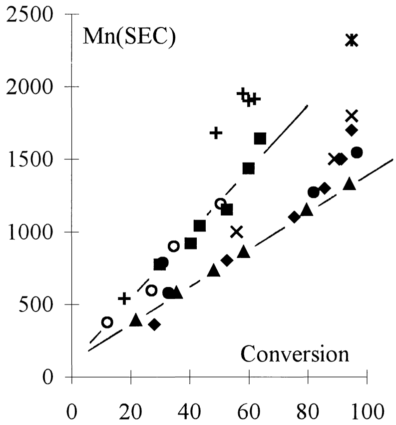


Figure 4. Polymerization of DTC by using different initiators grafted on various supports.

× SiO_2 800° - Al + SiO_2 800° - Zn

* SiO_2 800° - Y

▲ ZnO 130° - Zn ◆ ZnO 130° - Y

■ Al_2O_3 200° - Y ● Al_2O_3 450° - Y

o Al_2O_3 450° - Zn

C - Ethylene and propylene oxide

The Vandenberg's catalysts based on alkylaluminium - water systems are well-known for the polymerization of these oxiranes, but the polymers display generally large MWD [25], contrarily to ionic initiators. Our first attempts have shown that grafting aluminium alkoxides on silica could lead to very interesting initiators[19,20]. Nevertheless, the same alkoxides were quite inactive in the same experimental conditions if not grafted.

On the same way, we have grafted zirconium and rare earths alkoxides on various supports. It is generally impossible to deduce a rate constant from the EO polymerization kinetics, because of the heat released during the reaction. For PO polymerization, we found an activation energy around 65 kJ/mol, slightly lower than that reported in the literature for homogeneous polymerization (78 kJ/ml). Tables 3 and 4 report the main results. They show that the activity depends also both on the solid support and the grafted metal. Using Zr or rare earths alkoxides instead of Al alkoxides give better results. In the same way, the content of allylic double bonds in POP decreases when using these metals.

Table 3. Conversion of the ethylene oxide polymerization in toluene with benzyl alcohol as transfer agent. $[EO]_0 = 1.2$ mole/L. $[EO]_0/[ROH]_0 = 10$. $[Metal] = 0.006$ mole/l. T = 55°C.

Metal :	Al	Zr	Y	Sm	Nd
Silica 450°C	100% - 16h	60% - 44h	--	80% - 22h	--
Silica 800°C	100% - 10h	66% - 43h	40% - 45h	45% - 16h	
Alumina 200°C	75% - 22h	100% - 9h	100% - 12h	100% - 22h	100% - 5 h
Alumina 600°C	100% - 11 h	100% - 4h	100% - 5h	100% - 6h	

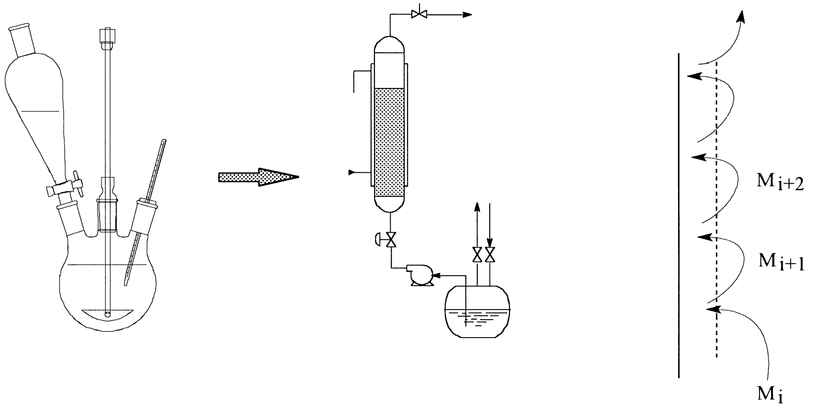
Table 4. Conversion of the propylene oxide polymerization. Same conditions as in Table 3.

Metal :	Al	Zr	Y	Sm	Nd
Silica 450°C	70% - 20h	--	--	--	--
Silica 800°C	70% - 16h	40% - 21h	--	--	--
Alumina 200°C	43% - 14h	55% - 18h	65% - 23h	63% - 25h	100% - 35 h
Alumina 600°C	66% - 10h	100% - 17h	100% - 20h	100% - 25h	80% - 63 h

3 - Towards a continuous process

Another innovative aspect of these heterogeneous systems is to pass from a batch reaction to a continuous process by taking advantage of the exchange reaction. In order to successfully pass from a batch reaction to a continuous process, it was necessary to design a system which allowed us to maintain the essential characteristics of the original batch system. One of the pertinent parameters to consider in any continuous process is the residence time of the reactants inside the reactor. As discussed previously, the degree of polymerization increases with conversion, that is as long as the polymer chains are in the contact of the supported active centers. We made use of a packed column having flow characteristics approaching those of a plug flow reactor. If axial and radial dispersion can be minimised (length/diameter sufficiently high, with no by-passing), a narrow molecular weight distribution could be expected with this type of reactor.

There are very few examples of the use of continuous reactors for anionic polymerization processes. This concept described here is fundamentally different from those reported up to now, in which both initiator and monomers are added continuously in the reactor. Besides its innovative aspect, this process displays some advantages. For example, the transition between two different functionalized oligomers is easier since washing the column with another alcohol can re-establish proper working conditions.



Scheme 3. The transfer reaction is the key to pass from a batch reaction to a continuous process.

The column has been used to investigate ethylene oxide[26)], ε-caprolactone and DTC oligomerization. Initial experiments have pointed out how the molecular weights can depend on the flow rate for a fixed bed length. Work is now in progress to model this process in order to design optimal reactor dimensions. The flow and mass transfer parameters have been estimated from residence time distributions (RTD) of a tracer [27)]. In a second stage, a contact time distribution was deduced from the RTD in order to know the actual time spent by the monomer in the contact of the active centers. Finally, a Monte Carlo simulation was used to model the polymerization process. Coupling both approaches allowed us to simulate the MWD of the polymer chains at the column output.

Conclusion

These results clearly show that zirconium and rare earths alkoxides are versatile initiators for the ring opening polymerization of oxygenated heterocycles when using in the presence of alcohol molecules. Functionalized well-defined oligomers can easily be obtained by this process.

Grafting these alkoxides on porous supports allows to polymerise ethylene and propylene oxides. The activity depends both on the solid support and the grafted metal. This feature is a general trend for all the supported systems and it becomes possible to design a system support/metal which would be specific for each monomer.

Finally, it is possible to propose a continuous polymerization process by making use of a plug flow reactor filled with grafted alkoxides. The MWD of the polymer chains can be simulated from a model which has been developed by combining a Monte Carlo approach and a contact time distribution of the monomer on the active centers.

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