

Towards a continuous process in heterogeneous coordinated anionic ring opening polymerization

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Summary. The current article deals with the initial developments of the use of a continuous plug flow reactor using an original heterogeneous catalyst system for the living coordinated anionic polymerization of certain oxygenated rings. This reactor is designed in order to maintain the essential characteristics of the original batch system. One of the pertinent parameters considered here is the residence time of the reactants inside the reactor. The column has been used to investigate ethylene oxide and ϵ -caprolactone oligomerization. Initial experiments have pointed out how the molecular weights can depend on the flow rate for a fixed bed length. Some theoretical problems relative to the reactive column are discussed in order to investigate more in depth the properties of this original continuous process and to model it to find the optimal working conditions.

Introduction

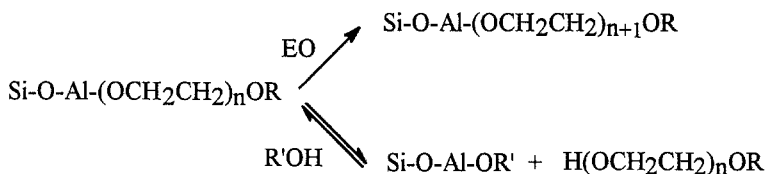
Some years ago, we developed a new heterogeneous catalytic system for the ring opening polymerization of oxygenated heterocycles such as oxiranes, lactones and lactides^{1,2}. The active centers are aluminium alcoholates, chemically grafted onto porous silica in order to prevent the aggregation which is often encountered in homogeneous systems^{3,4}. The active centers are then assumed to be in the same chemical environment, so that the same activity is expected for all of them. The separation of the active centers can also be achieved by making use of bulky substituents such as porphyrins⁵, and attempts to anchor these active centers have been made by grafting aluminium porphyrins on crosslinked polystyrenes⁶.

Adding protic molecules such as alcohols to the alcohols^{7,8}. This first exchange reaction yields a free alcohol functional group which can further be involved in another such reaction. Provided the rate of the exchange reaction is faster than the rate of the propagation reaction, all the growing chains spend the same fraction of time coordinated at the active centers and have the same probability of having a monomer inserting into the chain. As a consequence, the resulting polymer product will have a narrow molecular weight distribution with a living character. This transfer reaction brings a catalytic dimension to the system since there are more polymer chains produced than there are metal atoms. The polymerization maintains its living character in so far as the degree of polymerization increases with the conversion.

An important drawback is the possible decrease of the average molecular weight due to the transfer reactions. However, it must be pointed out that another quite interesting feature of this catalytic behaviour is that all the polymer chains are end-capped by a radical derived from the first free alcohol molecules. Furthermore, the chemically grafting of the active centers on a solid support allows us to remove them by simple

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filtration. This catalytic system thus offers an easy means of obtaining functionalized oligomers of both polyethers and polyesters in one reaction step, without the generation of any metallic residues, for example reactive surfactants, macromonomers⁹ as well as copolymers^{1,10}.



Until recently, the synthesis was carried out exclusively in a batch reactor. Another innovative aspect of this heterogeneous catalyst systems is to pass from a batch reaction to a continuous process by taking advantage of the exchange reaction which allows one to keep the same catalytic support over a long time in the reactor.

This innovative process displays some advantages. For instance, it allows one to use monomer solutions with relatively low concentration, which makes the process more sure when using gaseous and toxic products such as ethylene oxide. In order to obtain large quantities of products with a batch process, it would be necessary to add large quantities of monomer, which would increase the initial pressure and produce high viscosities as the conversion increases. A semi continuous process with continuous addition of a monomer solution will be a solution to this problem but requires relatively large reactors. Another inherent advantage in the continuous process is the self-acting separation of the products from the solid support after reaction. This step does not have to be neglected since it can take some time if the solid particles are stabilized by the polymer chains. For instance, this is observed with polyoxyethylene chains.

There are very few examples of the use of continuous reactors for anionic polymerization processes. Moreover, it must be stressed that the concept of continuous process as described in this paper is fundamentally different from those reported up to now, in which both initiator and monomers are added simultaneously and continuously in the reactor. The first examples are flow-tube reactors developed by Szwarc¹¹ and extensively used by Schulz¹² for following the kinetics of fast reactions. The same kind of reactors are employed for the polymerization of dienes with butyl lithium as initiator¹³, or for lactones and lactides with samarium triisopropoxyde¹⁴.

The current article deals with the initial developments of the use of a continuous plug flow reactor using this new catalytic system for the polymerization of ethylene oxide (EO) and ϵ -caprolactone (CL).

Experimental part.

Reagents and catalytic system.

All the reactants were handled under argon. EO was distilled under vacuum and collected in a cooled trap. CL was mixed with sodium hydride, distilled under vacuum and stored under dry argon over molecular sieves (3 Å). Toluene and alcohols were dried over molecular sieves. Silica (Grace 432; pore volume : 1.2 ml/g; surface area : 320 m²/g; mean particle size around 1 mm) was dehydrated under vacuum at 450°C. The content of silanol groups was determined by titration with triethylaluminium (TEA) and found to be equal to 1.2 mmol/g. TEA was reacted at room temperature on a suspension of 5 g silica in toluene for 15 mn. The excess of TEA was then removed by washing three times with toluene. The initiating alcohol was added and allowed to react at 45°C for 2 hours.

Polymerization in continuous process.

The lab-scale column was designed from a Liebig condenser (100 mm length, 13 mm diameter) with a water jacket and modified with a sintered disk added at the bottom of the column in order to support the silica. Teflon stopcocks were adapted at both ends of the column in order to be able to purge it with argon.

The functionalized silica is transferred under argon in the column. The reactor is then continuously fed with a solution of monomer and alcohol in toluene with a [monomer]/[alcohol] ratio chosen according to the desired degree of polymerization.

When working with low vapor pressure monomers such as caprolactone, a simple peristaltic pump (Gilson pump) was used to feed the reactor. However, ethylene oxide solutions have high vapor pressures which make the use of such peristaltic pumps impossible. In this case, the reservoir of the monomer solution is kept under an argon pressure and the flow is regulated by a control valve at the top of the column. This technique allows one to keep the column under a slight pressure that prevents the evolution of gas bubbles that can disturb the catalytic bed.

Samples are collected at the column outlet and weighed. After elimination of the solvent, the polymer is analyzed by ^1H NMR (Bruker AC250 spectrometer; CDCl_3 as solvent) to determine its average number molecular weight, as well as the amount of unreacted starting alcohol (when the boiling point is high enough).

The residence time distributions were evaluated with a tracer injected through a « T » mixer connected to the bottom of the column. The measurements were performed by gas chromatography (Intersmat IGC 112F with a FID detector; column SE30 on Chromosorb W-HP at 120°C).

Results and discussion.

Designing the reactor : from a batch to a continuous process.

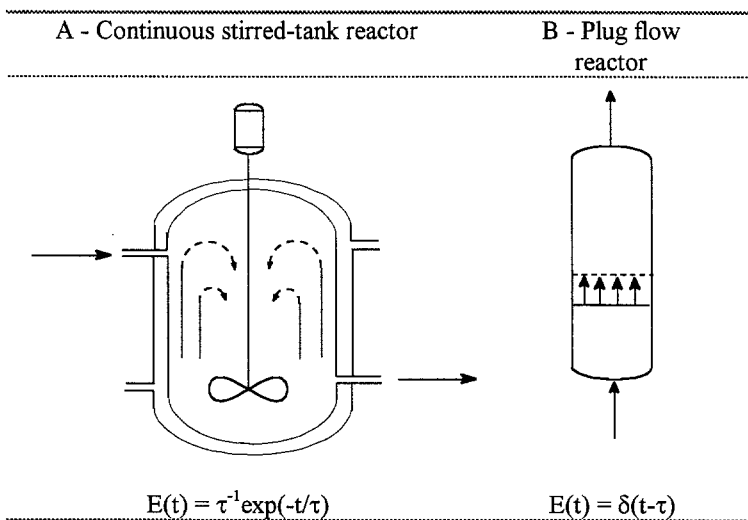
In order to successfully pass from a batch reaction to a continuous process, it is necessary to design a continuous system which will allow us to maintain the essential characteristics of the original batch system. One of the pertinent parameters to consider in any continuous process is the residence time of the reactants inside the reactor. As discussed in the introduction, our catalytic system has the characteristics of a living polymerization : the degree of polymerization increases with conversion, that is as long as the polymer chains are in the presence of the supported active centers (in the event there is still free monomer in the reactor). Therefore, the growth time of a given chain depends on the time this chain spends on the active centers.

In a batch process, the narrow molecular weight distribution is a consequence of an exchange reaction, which, compared to the propagation reaction, is relatively fast. This ensures that all the polymer chains spend the same fraction of time on the active centers and therefore have the same probability of inserting a new monomer molecule. Since the degree of polymerization depends on the residence time, the molecular weight distribution will be a direct function of the residence time distribution.

A continuous stirred-tank reactor (Scheme 1A) leads to a wide residence time distribution, going from zero to infinity. Thus, some of the initiating alcohol molecules will pass directly from the inlet to the output of the reactor without any reaction. The resulting molecular weight distribution would then be very broad. Therefore, this type of reactor cannot be used in our case.

On the other hand, a packed column having flow characteristics approaching those of a plug flow reactor (Schema 1B) has the same residence time as a batch reactor, i.e. a Dirac-delta function. If axial and radial dispersion can be minimized (length/diameter sufficiently high, with no by-passing) a narrow molecular weight distribution could be obtained with this type of reactor. It is for this reason that we decided to develop the continuous process in a packed column reactor.

Scheme 1. Two possible reactors for a continuous process with the residence time distribution provided the injection of the tracer is assumed to be a Dirac delta impulsion. τ is equal to V/Q where V is the reactional volume and Q the flow rate.



The problem of what tubing to use to feed the column is not easily resolved since it is necessary to maintain a constant flow of reactants in order to assure the desired residence time. Peristaltic pumps are well suited to controlling the low flow rates, but require elastomeric pipes which can swell when organic solvents such as toluene or dichloroethane are used. Such swelling means that the flow cannot be controlled over a long period of time. Also, ethylene oxide has a high vapor pressure which makes it difficult to handle with peristaltic pumps.

In order to prevent high-pressure drop over the catalytic bed, very small particle sizes must be avoided. Fortunately, silica is quite a versatile support and is commercially available in a wide range of particles sizes, specific surface areas and pore volumes. Because of this, it was possible to preselect a silica support that was well-adapted for use in the column reactor, use it in batch experiments, and to transpose the kinetic results to the continuous flow reactor. The support used in the current study was GRACE 432 silica with an average particle size of 1mm, a pore volume of 1.2 ml/g and a specific surface area of 320 m²/g.

Residence time distributions and exchange processes.

The average residence time can be regulated either by changing the length of the catalyst bed for a fixed reactor diameter or by altering the flow rate. It is clear that the

experiments with the same catalyst bed. The residence time distributions were determined using tracers injected into the solvent stream via a "T" mixer.

Samples are collected at various times at the outlet of the column and the amount of tracer is determined by UV or gas chromatography. Different tracers have been used, namely dodecane, toluene and some alcohols in order to investigate the interactions between the molecules and the silica. The mean residence time of an alcohol is more important than that of dodecane because of both polar interactions with the oxygen atoms of the silica and the exchange processes with aluminium alcoholates. Other experiments have been carried out in order to highlight the exchange process, such as the displacement of a grafted aluminium alcoholate by another free alcohol continuously injected at the bottom of the column. Such an experiment is shown in Fig. 1 where phenylethanol has been used to displace the grafted benzyl alcoholate which appears as benzyl alcohol at the column outlet.

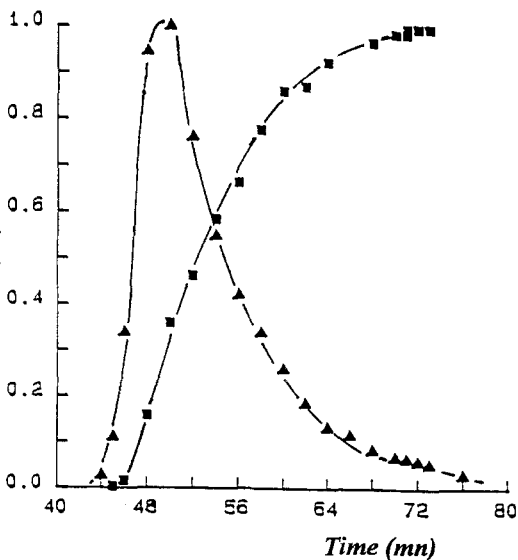


Fig. 1. Exchange of grafted benzyl alcoholate by phenylethanol (■). Benzyl alcohol (▲) appears at the column outlet and then disappears.

Syntheses of functionalized oligomers.

The column has been used to investigate ethylene oxide and ϵ -caprolactone oligomerization. These initial experiments were carried out with benzylic alcohol as transfer agent because its versatility as tracer for further ^1H NMR analysis. The benzylic hydrogen resonances are shifted when belonging to an ether or ester function, and can be used to check the total consumption of the alcohol molecules (δ $\text{C}_6\text{H}_5\text{-CH}_2\text{-OH}$ = 4.70 ppm; δ $\text{C}_6\text{H}_5\text{-CH}_2\text{-OCH}_2\text{-}$ = 4.55 ppm; δ $\text{C}_6\text{H}_5\text{-CH}_2\text{-OCO-}$ = 5.10 ppm) as well as the number average molecular weight (deduced from the $(\text{C}_6\text{H}_5\text{-CH}_2\text{-})/(\text{CH}_2\text{ of the polymer chain})$ ratio). The purity of the products can also be verified by NMR.

The silica is first functionalized under argon with aluminium benzylate in a Schlenk-type glass tube, and then transferred to the column. A mixture of monomer and benzylic alcohol in toluene is passed through the column. Samples are collected at the top of the column, weighed and analyzed by ^1H NMR to determine the molecular weight of the oligomers, as well as the amount of unreacted benzylic alcohol. A diol has also been used in order to obtain α - ω -hydroxytelechelic polymer chains. The monomer, alcohol, and solvent (toluene or dichloroethane) were mixed in a tank which can be heated to the reaction temperature.

The results of the experiments demonstrated how the molecular weight depends on the flow rate for a fixed bed length (Table 1), which is an other indication of the living character of the polymerization. Also, it is rare that a chemical reaction proceeds to

completion in a continuous reactor. This point, which may be seen as a simple question of yield in the case of organic reaction as $A \rightarrow B$, becomes crucial in our case since the average molecular weight is controlled by this yield. Nevertheless, this problem can be overcome by choosing an appropriately long column or decreasing the flow rate.

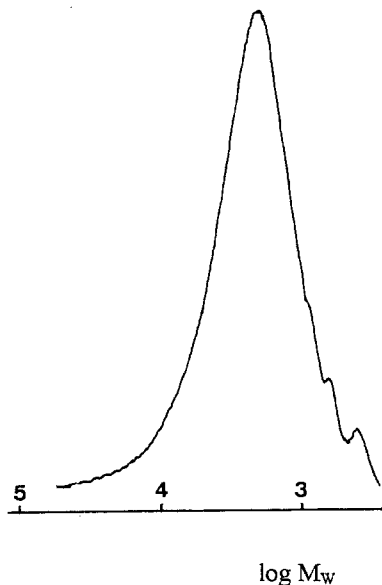


Table 1. Dependence of the degree of polymerization of EO on the flow rate.

Starting alcohol : benzyl alcohol.

Height of the silica bed : 5 cm.

Flow rate Q mL/mn	<DP>	Q* <DP>
4	8.8	35.2
5.3	6.9	36.6

Fig. 2. SEC of polycaprolactone oligomers with benzyl alcohol as starting alcohol. $M_n = 1100$, in agreement with the NMR determination¹⁵. Some residual tiny silica particles (a few nm in diameter) cause the broadening of the MWD¹⁶ ($I = 1.9$).

Computer Model

It is necessary to model this process in order to identify the optimal reactor dimensions and the working conditions. The model must take account of the problems related to the heterogeneous aspect of the catalysis, but also to the interactions of the macromolecules with the surface of the catalyst and to the diffusion of the reactants, i.e. the polymer chains inside a porous medium. In addition, it must be kept in mind that the viscosity of the polymer solution increases with conversion, in other words, with the length of the column.

Some theoretical problems relative to the reactive column must be addressed, some of which come from the polymerization process itself which proceeds in a heterogeneous porous medium (adsorption, viscosity, size exclusion), others are related to the chemistry (living character and transfer reaction), and finally others are related to the column itself (reactants, products and heat transfer). Provided there is no strong temperature gradient, a model for size exclusion chromatography could be a method of describing a suitable non-reactive system¹⁷, keeping in mind that the average molecular weight is increasing with the conversion so that the accessible pore volume fraction will decrease as the conversion increases.

In a preliminary model, the column has been modelled as a succession of staged reactors which consist of a mixture of porous particles with various sizes. The polymer chain must enter, then reacts or not with the active centers bound onto the surface of the pore and finally diffuses out. All species of reactants as well as products are assumed to be

in equilibrium, the steady state being obtained by a material balance for each stage. The flow of materials into and out of any pore can be simply written as :

$$dn/dt = (dn/dt)_{out} - (dn/dt)_{in} + (dn/dt)_{reaction}$$

Monomer and solvent are assumed to go without any diffusion limitation. The diffusion coefficient of the polymer chain is estimated from Stokes' law. In the case of low polymer concentrations ($C < C^*$), the single coil approximation can be used and the diffusion coefficient of polymer chains in the porous structure is estimated from the Stokes-Einstein equation. Using the hydrodynamic radius $R_H = \left(\frac{3}{10\pi N}\right)^{1/3} ([\eta]M_v)^{1/3}$ where M_v is the viscosimetric molecular weight, the diffusivity of the polymer solute may be estimated from the following equation :

$$D = \frac{kT}{6\pi\eta R} = \frac{RT}{6\pi\eta N} \left(\frac{10\pi N}{3K}\right)^{1/3} (M)^{\frac{1+a}{3}}$$

In a porous medium, the molecular diffusion coefficient would be replaced by an effective diffusion coefficient D_e which accounts for the porosity ϵ ($\cong 0.74$ for silica), the tortuosity τ and steric exclusion¹⁸: $D_e = \frac{D_T \cdot \epsilon}{\tau}$. The value of the tortuosity factor cannot be obtained directly and is often employed as an adjustable parameter to fit the experimental chromatograms¹⁹. In a first approximation, the model assumes a straight passage without any tortuosity : adding this factor would only change the numerical values without altering the general features since τ values are generally in the 1 - 10 range¹⁸. D_T represents the pore structure dependence of the molecular diffusion.

In this model, we consider the only circulation of polymer chains in the pores which are characterized by an effective cross-section $S = \pi(R_i - 2\alpha R_v)^2$ where R_i is the pore radius. α is used to describe the non-rigidity of the polymer particle.

The "reaction" term means a growing step, that is the production of a chain, the degree of polymerization of which becomes $(n+1)$ while another chain of degree of polymerization n disappears. The model works with several loops in order to calculate the flow of material for every pore family and every polymer chain. The concentrations are then calculated. In Fig.3 is shown a characteristic result obtained from this computer model. As a comparison are also displayed the molecular weight distributions related to Poisson distribution. The simulated distribution appears narrower than a Poisson distribution, as expected from the size exclusion induced by the porous volume : the accessible pore fraction, and therefore the propagation probability, decreases as the chain length increases.

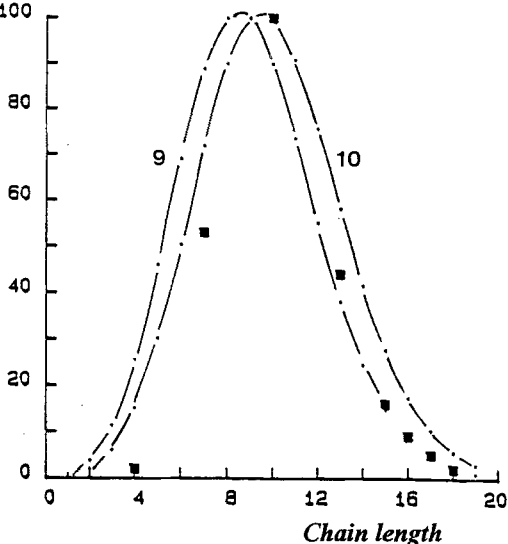


Fig.3. Simulation of the MWD of oligomers obtained by the continuous process (\square). The Poisson distributions centered on 9 and 10 are also displayed in order to underline how narrow is the simulated distribution.

Conclusion.

The heterogeneous character of the catalytic system allows one to easily pass from a batch to a continuous process while maintaining the characteristics of a living polymerization. As highlighted in the text, 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. Care must be taken in order to keep a narrow residence time distribution so that the MWD is not altered.

Some other problems are still to be solved, particularly the pressure drops and the heat exchange. As underlined above, adjusting the size of the solid support used can help to reduce the pressure drop. While in a batch reactor, the heat of reaction can easily be removed by stirring the mixture, care must be taken that single silica particles do not overheat in the column during the reaction ($\Delta H = 114$ kJ/mole) so that the heat exchange has to be controlled. This can be done by optimizing the surface to volume ratio of the column : the heat removal capacity increases as column diameter decreases. These last points demonstrate some differences which occur between a batch reactor and a reactive column in order to synthesize functionalized oligomers displaying the same characteristics.

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