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Heterogeneous cationic polymerization of 1,3-dioxolane and 1,3-dioxepane using grafted BF_3 on silica

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Summary

A BF_3 complex has been grafted onto silica and used as initiator to polymerize 1,3-dioxolane and 1,3-dioxepane. Grafting the active centers leads to a decrease of the reaction rate. The molecular weight increases steadily, parallel to the monomer conversion and the polydispersity is rapidly stabilized at a low value. MALDI-TOF mass spectrometry analysis shows that most of the polymer chains are initiated by a proton and lost a CH_2O unit. An exchange process between polymer chains bound to the silica and those remaining in the reactional medium was proposed. Finally, a semi-continuous process was investigated by adding continuously dioxolane during a 100 hours period.

Introduction

Lewis acids are widely used as initiators (with or without a coinitiator) for cationic polymerization of olefins and heterocycles. Some attempts have been made to immobilize such Lewis acids onto an inorganic substrate in order to reduce polymer contamination as well as the pollution by the production of waste. Another advantage is that the catalyst systems can be used for multiple cycles without regeneration.

The grafting of Lewis acids onto solid substrates to give supported superacids such as Al_2O_3-BF_3 or SiO_2-BF_3 has already been reported [1,2]. $AlCl_3$ has also been chemically grafted onto silica particles in order to polymerize isobutene [3]. In that case, higher molecular weights were obtained as well as an increase in the amount of terminal insaturations, probably due to the decrease of the transfer reactions.

On the other hand, carbocationic species have also been grafted onto solid supports for the polymerization of heterocycles. For example, the use of chloromethylated polystyrene as the initiator in the polymerization of 2-methyl-2-oxazoline has been described for a long time [4]. More recently, 1,3-divinylimidazolid-2-one and vinylfuran were recently polymerized using triphenylmethylium cation grafted on silica [5,6]. The modification of silica by cationic intermediates has recently been reviewed [7]. Nevertheless, it must be emphasized that the active center itself is grafted onto the surface of the silica particles. As a consequence, the polymer chain is immobilized on the solid particle. On the contrary, when using BF_3, the counter-ion is grafted onto the silica so that the polymer can easily be recovered after reaction.

This paper is dealing with the polymerization of 1,3-dioxolane and 1,3-dioxepane with BF_3 grafted onto silica as the initiator by using batch and semi-continuous processes. This latter experiment was carried out in order to investigate the possibility to perform continuous polymerization as previously demonstrated in the anionic polymerization field [8]. Kinetics was investigated by gas chromatography (GC) and SEC; the polymers were characterized by NMR, SEC and MALDI-TOF mass spectrometry.

Experimental Part

Materials

1,3-Dioxolane (DXL, 99,8% from Aldrich) was submitted to the standard purification for cationic polymerization. 1,3-dioxepane (DH) was synthesized from butylene glycol and formaldehyde [9]. Boron trifluoride di-n-butyl ether ($BF_3.BU_2O$) complex was synthesized by bubbling gaseous BF_3 (diluted 1:5 with dry argon) directly into purified di-n-butyl ether (with less than 10 ppm total impurities as detected by both GC and Karl-Fisher method water analysis). Cyclohexane and toluene (HPLC grade) were kept over molecular sieve under argon. Silica (type 432 from Grace GmbH) was heated at 200°C under vacuum for 2 hours and kept under argon.

Heterogeneous initiator

Grafted initiator was prepared in a three-necked flask and connected to an argon line. 0.5 g silica was suspended in 10 mL cyclohexane and contacted for 30 min at 30 °C with BF_3. Bu_2O (in an excess of 1.5 mole of complex to 1 mole of silanol groups). After the reaction time elapsed, the liquid phase was carefully withdrawn and a new quantity of cyclohexane was added for washing the silica, stirred for 10 min then withdrawn again. Washing operations were repeated three times.

Polymerization

Polymerizations were conducted in the same flask as for the preparation of the initiator. A reaction mixture of monomer and toluene (as the solvent of polymerization) was prepared in a separate vessel connected to an argon line. A sample withdrawn of this mixture was used as reference for the initial composition of the mixture. 10 mL of the reaction mixture was transferred into the reaction flask containing the functionalized silica and maintained at 30 °C under stirring. A second batch was eventually run by adding a new quantity of reaction mixture to the first one after the required reaction time. Homogeneous polymerizations were carried out according to the same procedures.

Semi-continuous process was conducted by adding a continuous flow (1 mL/h) of monomer solution after 1 hour reaction of a primary batch. This addition went on during 100 hours and the reaction was allowed to continue during another 100 hours.

Samples were withdrawn at different times and the polymerization was quenched with

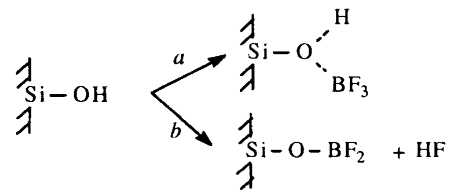
Ba(OH)$_2$ suspended in acetone for kinetic measurements or in THF for polymer characterization. The unreacted monomer was determined by GC (4 m length and 1/6 inch internal diameter column, filled with 10% Carbowax 20M on Chromosorb P 60/80 mesh, 72 °C, FID, toluene as internal standard).

Characterizations

Size exclusion chromatography (SEC) was performed in THF on a Waters chromatograph (PSS Gel mixed B 120 column and refractometer detector; polystyrene standards). Some samples have been analyzed by MALDI-TOF mass spectrometry (linear mode, calibration with polyethylene oxide; matrix : dithranol/NaI).

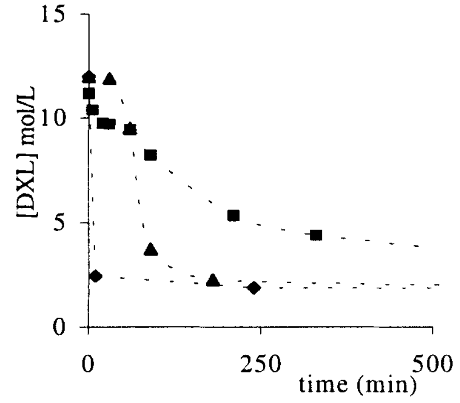
Results and discussion

The active centers have been grafted by adding the BF$_3$.Bu$_2$O complex in a silica suspension. Silica has been previously dehydrated at 200°C. In that case, the silanol content is 4 mmol/g, as checked by titration with AlEt$_3$. BF$_3$ can react [7] with the silica according to scheme 1.



Scheme 1. The possible reaction of BF$_3$ with the silanol groups.

According to our experimental procedure, the concentration of BF$_3$ can be estimated at 0.2 mol/L, assuming all the silanol groups react with BF$_3$. After adding the monomer, polymerization occurs gently and an equilibrium monomer concentration ([DXL]$_e$ = 1.8 mol/L) is reached (Figure 1). Kinetics data are satisfactorily plotted according to the usual modified first-order rate equation Ln([M]$_0$-[M]$_e$)/ ([M]-[M]$_e$) = f(time) (Figure 2). Assuming [BF$_3$] = 0.2 mol/L, the rate constant is estimated to around 3.4x10^{-4} L·s/mol. The polymerization starts again when adding a new amount of monomer.



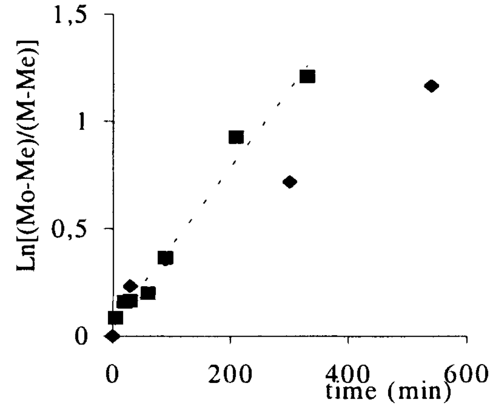


Figure 1. Kinetics of DXL polymerization in homogeneous (▲ [BF$_3$] = 0.03 M; ◆ : 0.2 M) and heterogeneous processes (■ : 0.2 M)

Figure 2. Modified first-order plot for the heterogeneous process (■ : 1st addition; ◆ : 2nd addition of DXL).

In addition, a sample was withdrawn from the reaction mixture after one hour time and carefully separated from the heterogeneous initiator. This homogeneous mixture was kept under argon for several hours but no further polymerization was observed, indicating that all active sites are actually grafted onto silica. For sake of comparison, this initiator was also used in homogeneous batch process in the same concentration. It was observed that grafting the active centers leads to a decrease of the polymerization rate (Figure 1). The same equilibrium concentration was observed in both homogeneous and heterogeneous processes.

Figure3 displays some SEC chromatograms. The presence of oligomers is clearly detected at high elution volumes. The average molecular weights increase gently with the conversion and the oligomer/polymer ratio is decreasing. If taking into account the only polymer, Mn is around 4600 g/mol at 80% conversion (Polystyrene standards). According to a living process, the average molecular weight would be equal to $74\times[\mathrm{DXL}]_0\times\mathrm{yield}/[\mathrm{BF}_3] = 3550$ g/mol. This discrepancy could be explained by a lower amount of active centers, may be due to an incomplete grafting on the silanols groups or formation of HF unable to initiate the polymerization [10] (step *b* in scheme 1). After reaching the equilibrium, a slight decrease of these molecular weights is observed (Figure 4). Adding a new amount of monomer does not alter noticeably the molecular weights. For the same conversion, the molecular weight obtained with homogeneous initiator is slightly higher, around 5000 g/mol and the decrease of the molecular weights appears more pronounced than in the heterogeneous process.

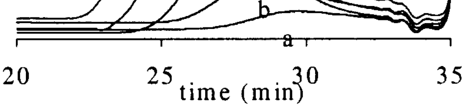


Figure 3. Evolution of the SEC curves with conversion (before the 2nd addition) from 1h (a) to 5 h (e).

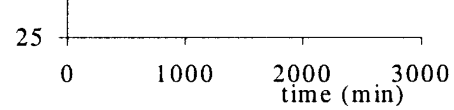
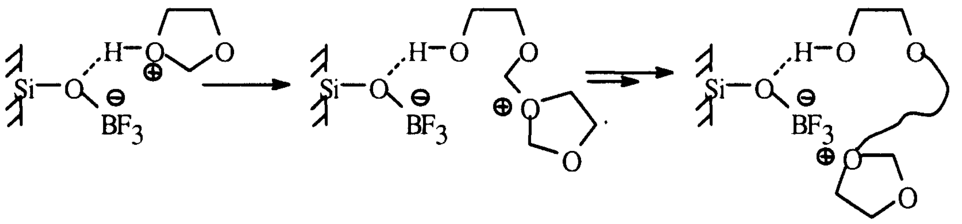


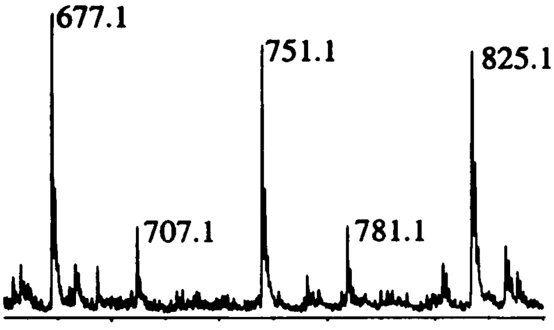
Figure 4. Evolution of the elution volume of the maximum (M_{peak}); the 2nd monomer addition occurs at t = 1140 min.

It was mentioned that no polymerization occurs when adding new monomer to a solution previously withdrawn from the reactional medium. That means the growing chains are not actually disconnected from the silica. They remain bound to the silica owing to both the hydrogen bonds and electrostatic interactions with the counterion. Scheme 2 displays such a mechanism, by analogy with that proposed for the isobutene polymerization initiated by $AlCl_3$ grafted onto silica [3].



Scheme 2. Cationic polymerization of DXL initiated by BF_3 grafted onto silica

Some samples have also been analyzed by MALDI-TOF mass spectrometry (Figure 5). In the low molecular weight range, the analysis of the polymers shows two main macromolecular $(M\text{-}Na)^+$ species. The most important series is detected at $m/z = 74\times n + 62 + 23 = 74\times n + (44+18) + 23$ which can be assigned to polymer chains initiated by H^+, after elimination of CH_2O (nucleophilic attack of the monomer on the linear oxocarbenium active center) and deactivation by water (probably coming from adventitious water in the reaction mixture and from the quenching agent). The second series detected at $m/z = 74\times n + 18 + 23$ is assigned to the polydioxolane chains without CH_2O elimination. It was observed that the relative amount of this latter type is slightly more important in the heterogeneous process.

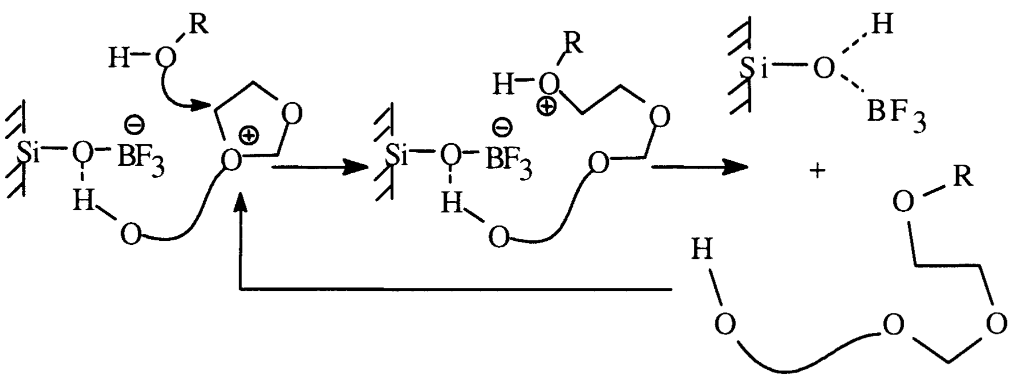


heterogeneous process

Figure 5. Maldi-Tof mass spectrometry of PDXL (low molecular weight domain) obtained from both processes. The main peaks are assigned to the $(M\text{-}Na)^+$ species. The $(M\text{-}K)^+$ are also present in the mass spectra.

This point confirms an initiation process by proton coming from the silanol groups. Polymer chains with formiate and methoxy end-groups (characteristic for the hydride abstraction occurring either in the initiation step or from the transfer to the polymer) has not been detected by MALDI-TOF spectrometry. The NMR spectra display a formiate end groups signal at 8,1 ppm representing less than 1% of total chain ends in the beginning of the process and slightly diminishing until the equilibrium concentration is reached. The formiate (and methoxy end-groups) regain importance if the polymer is kept in contact with the initiator after the equilibrium is reached.

Finally, as displayed in Scheme 3, taking into account the presence of both silanol groups and chains carrying hydroxyl end-groups, an exchange process can be proposed by analogy with that encountered in coordinated anionic ring opening [11]. But, in this case, the exchange frequency would be lower than in the anionic case.



Scheme 3. The exchange process between a grafted chain and a free one carrying an hydroxyl end-group.

Similar attempts have been performed with 1,3-dioxepane (DH). As in the homogeneous processes, it was observed that the rate of DH polymerization is higher than that of DXL. It was also interesting to proceed to sequential addition of DH and DXL. Figures 6 and 7 display the corresponding kinetic curves. A small decrease of [DH] is observed after the addition of DXL, indicating an equilibrium between the corresponding polymers (Equation 1) :

$$\text{polyDH} + \text{DXL} \rightleftharpoons \text{polyDXL} + \text{DH} \qquad (1)$$

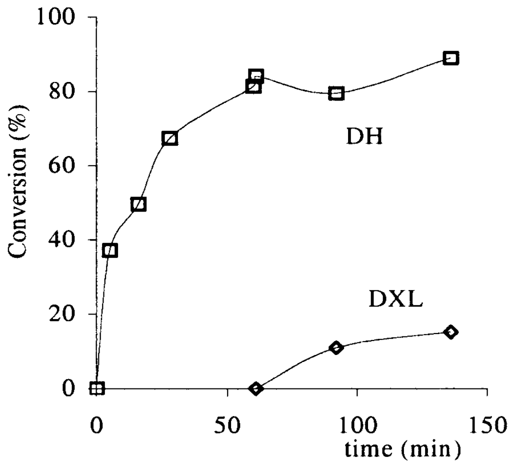


Figure 6. sequential additions of DH (5 mL) and DXL (5 mL). 1.43 g silica.

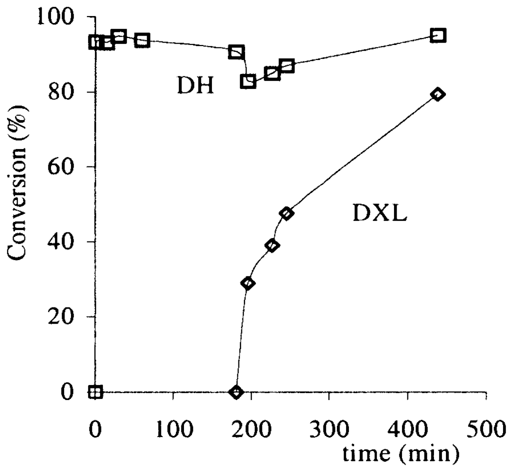


Figure 7. sequential additions of DH (10 mL) and DXL (10 mL). 4.3 g silica.

Finally, a semi-continuous polymerization was investigated by adding continuously dioxolane on the heterogeneous system. The molecular weight increases steadily in the first 100 hours, as long as the monomer is fed and its concentration is far from the equilibrium, then remains constant (Figures 8, 9). At the same time, the polydispersity slowly increases in the beginning and then is stabilized at a lower value than in the batch process (I = 1.8 after 8 hrs reaction).

It deserves to note that no significant deactivation of the polymerization occurred during the continuous addition of the monomer. The molecular weight increased continuously since there was no withdrawal from the reactional medium. Experiments by using a column filled with the functionalized silica, as it was previously done for continuous anionic coordinated polymerization [8], are now under investigation.

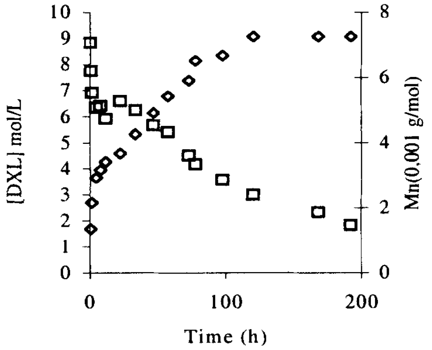


Figure 8. Semi-continuous process. ($[BF_3]_0$ = 0.2 mol/L); (continuous addition of monomer stopped after 100 hours).
□ : [DXL]; ◊ : Mn.

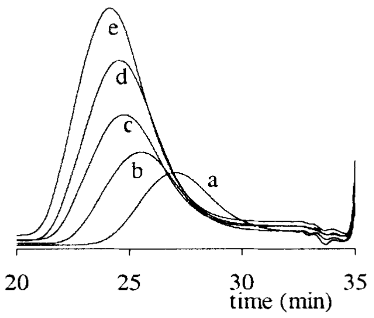


Figure 9. Evolution of the SEC curves with conversion from 1h 30 reaction (a) to 120 h (e).

As a conclusion, grafting a Lewis acid (a BF_3 complex) onto silica allowed to polymerize easily 1,3-dioxolane and 1,3-dioxepane. The average molecular weight increases steadily, parallel to the monomer conversion and the polydispersity is rapidly stabilized at low value, as a strong indication of a decrease or absent transfer to the polymer. The molecular weight seems to be controlled by a transfer agent. Therefore, we assume that the transfer to the polymer is sterically hindered. An exchange process between the polymer chains bound to the silica and those remaining in the reactional medium.

Acknowledgements.

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