HETEROGENEOUS CATALYTIC COPOLYMERIZATION REACTIONS OF CARBON DIOXIDE AND PROPYLENE OXIDE OVER POLYALCOHOLS UNDER SUBCRITICAL CONDITIONS

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Dirigida por:

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Que la Ingeniera Química **MARÍA PINILLA DE DIOS** ha realizado en el Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid, bajo nuestra dirección, el trabajo que, para optar al grado de Doctorado Internacional, presenta con el título *"Heterogeneous catalytic copolymerization reactions of carbon dioxide and propylene oxide over polyalcohols under subcritical conditions"*, cuyo título en castellano es *"Reacciones de copolimerización en catálisis heterogénea entre dióxido de carbono y óxido de propileno sobre polialcoholes en condiciones subcríticas"*

Valladolid, a _____ de _______ de 2016

Fdo. Juan García Serna Fdo. Tapio Salmi Fdo. José Román Galdámez Peña

Reunido el tribunal que ha de juzgar la tesis doctoral titulada “*Heterogeneous catalytic copolymerization reactions of carbon dioxide and propylene oxide over polyalcohols under subcritical conditions”* presentada por la Ingeniera MARÍA PINILLA DE DIOS y en cumplimiento con lo establecido en el Real Decreto 1393/2007 de 29 Octubre ha acordado conceder por ____________ la calificación de ________________.

Valladolid, a _____ de _______ de 2016

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1er VOCAL 2º VOCAL 3er VOCAL

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ABSTRACT

Carbon dioxide (CO_2) is one of the main gases that cause the Greenhouse Effect. As a way to attenuate this damage, CO_2 could be used as a building block for copolymerization reactions; precisely as C1 feedstock (monomer of the reaction) and as the pressurizing gas in these copolymerization reactions. The required monomer that was involved in the reactions was propylene oxide (PO) that possesses great reactivity, enabling the CO_2 bonding.

Through the mechanism of Ring Opening Polymerization (ROP), the incorporation of CO_2 in the polymer chain can be possible.

During this research, two different types of heterogeneous catalysts were used for the copolymerization reactions. Zinc glutarate (ZnGA) and Double Metal Cyanide (DMC) were selected as possible suitable catalysts to perform the reactions.

The goal of this PhD thesis was to study these heterogeneous catalysts in copolymerization reactions between PO and CO_2 in order to understand how the catalyst and the process can be improved for a possible future industrial application.

To characterize the catalysts, several techniques were used such as Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).

The goal of these copolymerization reactions was to get a liquid CO_2/propylene oxide copolymer, looking for the creation of carbonate bonds (polypropylene carbonate, PPC) and trying to minimize the cyclic carbonate production (byproduct, PC).

Fourier transform infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR) and Size Exclusion Chromatography (SEC) techniques were used to analyse the copolymers obtained from these reactions.

The first catalyst used for the study was Zinc glutarate (ZnGA), as it is shown in **Chapter 1**. An exhaustive characterization of this heterogeneous catalyst was done with a complete study of its behaviour in copolymerization reactions.

This catalyst was synthesized by mixing properly zinc oxide, glutaric acid and toluene. ZnGA proved to be a catalyst without porosity and without Brøwnsted and/or Lewis acid sites. The active area is the outer surface area of the catalyst, where the Zn^{2+} active sites were. In this catalyst the average amount of Zn^{2+} amount was around 353 mg Zn / g catalyst, being the sample very disperse on particle sizes showing, also, a rectangular plate shape morphology with an average size of 321.6 nm was found.

Several different reaction conditions were studied for the formation of the copolymers from propylene oxide, carbon dioxide and propylene glycol (as initiator, PPG of 425 g/mol). The study included changes on the amount of ZnGA (0.3, 0.6, 1.0, 1.5 g), reaction temperature (60, 80 ºC), reaction pressure (6, 25 barg), final expected molecular weight of the copolymer (725, 3000 g/mol) and in the reaction time (20, 40 h).

Finally, it was possible to conclude that the best conditions corresponded to 1.5 g of catalyst, 25 barg, 80 ºC, 40 h and 3000 Da of initial PO estimation. TON (Turnover Number) and TOF (Turnover frequency) values are really low which demonstrated the very slow behaviour of this catalyst.

A completely different behavior was observed when a Double Metal Cyanide catalyst (DMC) was used.

In Chapter 2 and Chapter 3 several DMC catalysts were synthesized and characterized in order to determine which one was the most catalytically active.

Chapter 2 showed the effect of varying the initial amounts of $ZnCl_2$ on the catalytic activity, in order to determine the influence of the catalyst preparation method.

Five DMC catalysts were synthesized from $ZnCl_2$, $K_3[Co(CN)_6]_2$, tert-butanol (tBuOH, as complexing agent (CA)) and PEG 1000 (as co-complexing agent (co-CA)).

Zn/Co ratio was changed during the synthesis, having one reagent always in excess in order to clear up its impact on the catalytic activity, crystallinity and other properties.

The presence of K^+ produced a dramatic decrease on the catalyst activity, while an increase on Zn^{2+} made the catalyst had more spherical agglomerations of particles (DMC E).

Only two of the catalysts prepared were successfully activated (D and E catalysts, according to our nomenclature). Their morphology was lamellar with spherical particle agglomerations.

After the copolymerization reactions, all the copolymers were analysed showing that the most active catalyst was DMC E. With DMC E it was possible to achieve a high catalytic activity (2.5 kg polymer / g catalyst) with more CO_2 incorporation (6.7 %) and a lower production of the cyclic carbonate, PC (0.3%).

The implementation of a mechanical stirring instead of the initial magnetic one caused the PDI values decrease from 5.97 and 13.09 to values around 1 to 1.1. This means obtain short dispersed copolymer chains in the bulk reaction medium instead of high polydispersity.

Chapter 3 was focus on the catalyst activation stage previous to the copolymerization reaction process.

This catalyst was named as DMC A and it was exactly the same as the DMC E discussed in Chapter 2. This catalyst had only 0.0002 mol/ g cat of K^+ while the amount of Zn was 0.0036 mol/ g cat.

The experiments that were carried out for these DMC catalyst activation study were 12, modifying the amount of catalyst using 10, 20, 40 and 80 mg of DMC and 4, 8 and 18 g of propylene oxide (PO) in total.

This type of catalysts were the least selective and higher concentrations of the by-product (PC) were obtained after the reaction. When DMC amount was increased, PC amount also increased at the same CO_2 incorporation in the final copolymer.

Using only 20 mg of catalyst per batch, the reaction produced more PPC and PC with the highest vales of TON and TOF and the lowest PDI value. These results were also confirmed by the FTIR spectrum for 20 mg of DMC A catalyst.

Apart from these chapters, the current PhD thesis has also one appendix. Appendix shows the solubility of CO_2 in different polycarbonates. Several experiments at different temperatures, trying to charge the same initial pressure, were done to show how the solubility is influenced by temperature and pressure.

REFERAT

Koldioxid (CO_2) är en av de viktigaste gaser som orsakar växthuseffekten. Som ett sätt att minska denna skada, kanCO_2 användas som en byggsten för sampolymerisationsreaktioner. Precis som C1 råmaterial (monomer) och som tryckgas i dessa reaktioner. Den erforderliga monomeren som är involverad i de reaktionerna är propylenoxid (PO) som har hög reaktivitet, vilket möjliggör att CO_2 kan bindas.

Genom mekanismen för ringöppningspolymerisationen (ROP), kan inkorporering av CO_2 i polymerkedjan bli möjlig.

I denna forskning användes två olika typer av heterogena katalysatorer för sampolymerisationsreaktioner. Zink glutarat (ZnGA) och dubbelmetallcyanid (DMC) valdes som potentiella lämpliga katalysatorer för att utföra reaktionerna.

Målet med denna doktorsavhandling var att studera dessa heterogena katalysatorer i sampolymerisationsreaktioner mellan PO och CO_2 med syfkt att förstå hur katalysatorn och processen kan förbättras med tanke på en möjlig framtida industriell tillämpning.

För att karakterisera katalysatorerna, användes flera metoder, såsom FTIR (FTIR och FTIR med pyridin), induktivt kopplad plasma optisk emissionsspektroskopi (ICP), ljusspridning (med luft och destillerat vatten), Fysisorption av kväve, svepelektronmikroskopi och energiröntgenspektroskopi (SEM-EDX), termogravimetrisk analys-masspektrometri (TGA-MS), röntgenfotoelektronspektroskopi (XPS) och röntgendiffraktion (XRPD).

Målet för dessa sampolymerisationsreaktioner var att erhålla en CO_2 / propylenoxid sampolymer genomatt skapa karbonatbindningar (polypropylenkarbonat, PPC) och genom att försöka minimera cyklisk karbonatproduktion (biprodukt, PC).

FTIR (FTIR), kärnmagnetisk resonans spektroskopi (NMR) och size exclusion kromatografi (SEC) användes för att analysera de sampolymerer som erhållits från dessa reaktioner.

Den första katalysatorn som användes för detta studium var zinkglutarat (ZnGA), vilket diskuter i kapitel 1. En uttömmande karakterisering av denna heterogena katalysator gjordes samt en fullständig undersökning av dess beteende i sampolymerisationsreaktioner.

Denna katalysator syntetiserades genom att blanda zinkoxid, glutarsyra och toluen. ZnGA visade sig vara en katalysator utan porositet och utan Brøwnsted och Lewis-syraställen. Det aktiva området är den yttre ytan av katalysatorn, där aktiva säten bestående av Zn^{2+} finns. I denna katalysator den genomsnittliga mängden $Zn^{2\,+}$ belopp var cirka 353 mg Zn/g katalysator. Provet hade en bred partikelstorleksfördelnin bestod morfologiskt av rektangulära plattor en medelstorlek på 321,6 nm.

Flera olika reaktionsbetingelser studerades för bildningen av sampolymererna från propylenoxid, koldioxid och propylenglykol (som initiator, PPG av 425 g / mol). I studiet ingick olika mängder ZnGA (0,3, 0,6, 1,0, 1,5 g), olika reaktionstemperatur (60, 80 ° C) och reaktionstryck (6, 25 barg), förväntade värden på molekylviken av sampolymeren (725, 3000 g / mol) och samt olika reaktionstider (20, 40 h).

Slutligen var det möjligt att dra slutsatser beträffande de bästa betingelserna som motsvarade 1,5 g katalysator, 25 barg, 80 ° C, 40 h och 3000 Da som PO peliminär uppskattning. Omsättningstalet (TON) och omsättnings rekvensen (TOF) värdena var verkligen som visade dent mycket långsamma beteendet av denna katalysator.

Ett helt annorlunda beteende observerades när dubbelmetallcyanidkatalysatorn (DMC) användes.

I kapitel 2 och 3 syntetiserades flera DMC-katalysatorerer som karakteriserades för att avgöra vilken ar dem var katalytiskt den mest aktiva.

I kapitel 2 visads effekten av att variera initiamängderna av $ZnCl_2$ på den katalytiska aktiviteten. Detta gjordes för att bestämma inverkan av katalysatorframställningsmetoden på aktiviteten.

Fem DMC-katalysatorer syntetiserades utgående från $ZnCl_2$, $K_3\,[Co(CN)_6]_2$, tert-butanol (tBuOH, som komplexbildningsmedel (CA)) och PEG 1000 (som co-komplexbildande medel (sam-CA)).

Zn / Co-förhållandet ändrades under syntesen, med en reagens alltid i överskott för att avslöja dess inverkan på katalytisk aktivitet, kristallinitet och övriga egenskaper.

Närvaron av K^+ producerade en dramatisk minskning på katalysatoraktiviteten, medan en ökning på Zn^{2+} ledde till att katalysatorn hade flera sfäriska agglomerat av partiklar (DMC E).

Endast två av de katalysatorer som framställdes kunde med framgång aktiveras (D och E-katalysatorer, enligt vår nomenklatur). Deras morfologi var lamellär med sfäriska partikelagglomerat.

Efter sampolymerisationsreaktionerna analyserades alla sampolymerer vilket visade att den mest aktiva katalysatorn var DMC E. Med DMC E var det möjligt att uppnå en hög katalytisk aktivitet (2,5 kg polymer / g katalysator) med en högre inkorporering av CO_2 (6,7%) och en lägre produktion av det cykliska karbonatet, PC (0,3%).

Implementering av en mekanisk omrörning i stället för den ursprungliga magnetiska omröringen ledde till at PDI värden minskade från 5,97 och 13,09 till runt 1 till 1,1. Detta innebär å korta sampolymerkedjor förekommer i bulkreaktionsmediet i stället för enhög polydispersitet.

Kapitel 3 var fokuserar på katalysatoraktiveringssteget före sampolymerisationsprocessen.

Denna katalysator kallades DMC A och den var exakt densamma som DMC E diskuteras i kapitel 2. Denna katalysator hade bara 0,0002 mol / g katalysator K^+ medan mängden Zn var 0,0036 mol / g katalysator.

Totalt 12 experiment genomfördes för dessa DMC-katalysatoraktiveringsstudier genom at, modifiera mängden katalysator och genom att användna av 10, 20, 40 och 80 mg av DMC och 4, 8 och 18 g propylenoxid (PO) totalt.

Denna typ av katalysatorern var de minst selektiva vaurd högre koncentrationer av biprodukter (PC) erhölls efter reaktionen. Då mängden av DMC ökades, öleade aver mänden av PC som skulle inkorporera CO_2 i den slutliga sampolymeren.

Genom att enbart använda 20 mg katalysator för ett fatsförföll, producerade reaktionen mer a PC och PC med de högsta vänden på TON och TOF och det lägsta PDI värdet. Dessa resultat bekräftades också av FTIR spektrum för 20 mg av DMC katalysatorn.

INTRODUCTION

This PhD thesis research started with the aim of producing polypropylene carbonates in copolymerization reactions using two different types of heterogeneous catalysts, Zinc glutarate (ZnGA) and Double Metal Cyanide (DMC) catalysts.

Zinc glutarate catalyst ($C_5H_6O_4Zn$) is an odourless white powder catalyst synthesized by the chemicals zinc oxide (s, ZnO), glutaric acid (s, GA) and toluene (l). Where s and l means, solid and liquid, respectively.

Double Metal Cyanide (DMC) is a heterogeneous catalyst synthesized, in this research, from zinc chloride ($ZnCl_2$), potassium hexacyanocobaltate (III) $K_3[Co(CN)_6]_2$, tert-BuOH (t-BuOH) and polyethylene glycol (PEG 1000, Mw=1000 g/mol).

A complete study of these two catalysts and the characterization of the polycarbonates obtained from the reactions is included in this thesis work

These reactions are copolymerization reactions, which means that two monomers are involved: one is propylene oxide and the other is carbon dioxide. The reactions are going to be carried out at subcritical conditions, in a batch mode.

One of the most interesting aspects in this field and particularly in this PhD research is the use of CO_2 not only as the pressurizing gas but also as a C1 feedstock [1-12].

To reduce or to eliminate the use of hazardous substances is the objective of Green Chemistry. Trying to have a sustainable society in the future is capital nowadays.

Carbon dioxide as a feedstock for polymerization

Carbon dioxide (CO_2) causes the Greenhouse Effect, among other gases like methane (CH_4) and nitrous oxide (N_2O). Anthropogenic actions as burning coal or other fuels are increasing the concentration of CO_2 in the atmosphere year after year.Several regulations are established to control the emissions, like Montreal Protocol or Kyoto Protocol. In fact, at the Paris climate conference (COP21) in December 2015, 195 countries adopted the first-ever universal, legally binding global climate deal. This agreement has been signed by 175 countries on the 22nd April 2016 [13].

The concentration in the atmosphere in 2015 raised up to 400 ppm of CO_2. This concentration was less than 320 ppm of CO_2 in 1962 (National Oceanic & Atmospheric Administration, 2015) [14, 15].

As a chemical or solvent CO_2 can be considered environmentally friendly with relatively low cost, high purity, nontoxic and non-flammable. It can be captured, storage and used in copolymerization reactions as a C1 feedstock [16, 17].

Using CO_2 as a feedstock is not only because of the green point of view of using a reaction by-product as a monomer but because of the economical aspect. Using CO_2 as a C1 feedstock assures lower OPEX in carbon sources from other chemicals, as epoxides in this case [18]. The point is to substitute the weight of other organic monomers by the incorporation of CO_2.

The “reactive” monomer that was involved in these researched copolymerization reactions was Propylene oxide (PO). Propylene oxide (C_3H_6O) is a colourless liquid with an ether-like odour.

Through the mechanism of Ring Opening Polymerization (ROP), the epoxide (PO) opens itself and the incorporation of CO_2 in the polymer chain can be possible [19-21]. This process is based on thermodynamic preferences.

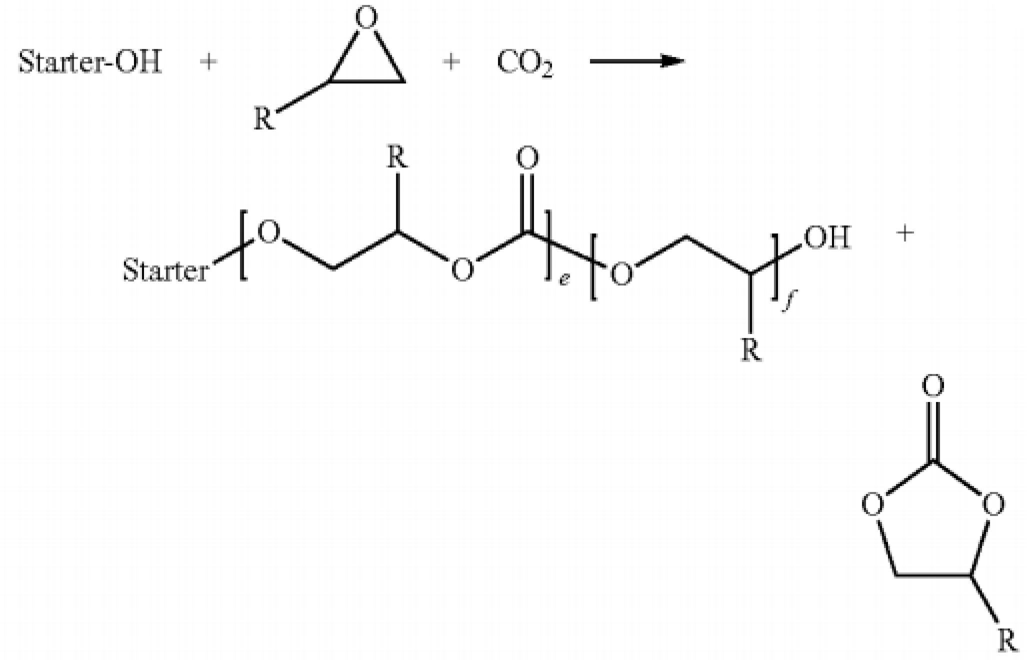

Figure 1. Copolymerization reaction among propylene oxide and carbon dioxide [22].

Zinc glutarate the first active catalyst

One of the pioneers of this type of copolymerization reactions was Inoue back in the 60's [23]. Epoxides had not been used before as a monomer in alternating copolymerization until they used them with carbon dioxide to get polycarbonates using an organometallic compound.

First, the metal alkoxide reacts with the carbon dioxide and then, the epoxide with the metal carbonate bond. Propylene oxide was studied with acid anhydride or with α-amino acid N-carboxy anhydride, such as diethylzinc and ethanol.

Other epoxides were also copolymerized and characterized such as epiclorohydrin, and styrene oxide with carbon dioxide [12, 24, 25].

Ree and Kim et al, made several copolymerizations between propylene oxide and carbon dioxide studying the influence of several heterogeneous catalysts [26, 27]. They proposed a procedure for the synthesis of zinc glutarate catalyst (experimental procedure followed in Chapter 1 with some negligible differences).

Numerous catalysts were synthesized and tested in copolymerization reactions (using eleven different glutaric acid derivatives, they obtained different zinc dicarboxylate catalysts giving the highest yield of the poly (propylene carbonate) gotten (PPC) using zinc glutarate (ZnO/GA) as the catalyst. Also, the highest molecular weight was achieved by this heterogeneous catalyst.

Chisholm et al. , explained in detail the structure and conformation of the poly (propylene carbonate) from the reaction among carbon dioxide (CO_2) and propylene oxide (PO) [28]. The catalyst employed was zinc glutarate which has active Zn-OH groups that they synthesized from Ree et al. [29]. They chose zinc oxide and glutaric acid to synthesize it.

Morphological parameters are used for catalyst characterization. They found that the catalyst with the highest crystallinity and crystal quality but with the lowest surface area had the highest catalytic activity in copolymerization reactions. It was also concluded that the one obtained by using zinc oxide (ZnO) and glutaric acid (GA) was the most active for this type of copolymerization between CO_2 and PO (with a low surface area) [26, 30-35].

The research showed in **Chapter 1** using ZnGA as catalyst in copolymerization reactions was carried out at Åbo Akademi University (Åbo/Turku, Finland).

Double metal cyanide a novel highly active catalyst

Chapter 2 is focus on the use of DMC catalysts instead of Zinc glutarate for these type of copolymerization reactions.

Several catalyst systems have been developed for the synthesis of polycarbonates [36] and many studies have focused on finding new catalysts with improved activity and selectivity [37].

The main goal is to synthesize a catalyst fast enough to reduce the reaction time to make the process technically feasible, but at the same slow enough in PO incorporation to give CO_2 the opportunity to react and incorporate into the polymer chain [3, 38].

Several research groups have pursued this path on developing both homogeneous and heterogeneous catalysts for CO_2 fixation [39, 40] and one of the successful examples is double metal cyanide (DMC) catalyst [41, 42].

DMC catalyst generally referred to zinc hexacyanometalate prepared by reaction of zinc halide and hexacyanometalate salt [43] and a complexing agent in some cases [44].

DMC catalysts not only are effective for propylene oxide ring-opening (ROP) but also for CO_2-epoxides copolymerization [37, 42, 45-47].

These catalysts are highly active and give polyether polyols that have low unsaturation and narrow molecular weight distribution [45], yielding biodegradable polycarbonates with a wide potential for polyurethane applications [48].

Improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [45]. Copolymerization of propylene oxide (PO) and CO_2 using DMC complex based on $Zn_3[Co(CN)_6]_2$ has been successfully carried out by different researchers. Chen et al., 2004 demonstrated that $Zn_3[Co(CN)_6]_2$ enhances the catalytic activity higher than $Zn_3[Fe(CN)_6]_2$ [49].

Gao et al. (2012) [46] studied the effect of molecular weights of the initial polypropylene glycols (PPG) on polymerization and the reaction conditions.

Li et al. (2011) [47] studied the copolymerization process of CO_2 and PO without initiators.

Zhou et al. (2011) [50] showed high crystallinity catalysts and they studied the effect of various reaction conditions such as amount of the catalyst, reaction time and temperature on the copolymerization.

Sebastian and Srinivas [51] studied DMC catalysts prepared by different methods and their influence on catalytic activity for CHO-CO_2 copolymerization. They reported that even with moderate crystallinity and without co-complexing agents the catalyst are high active for copolymerization, also, CO_2 adsorption studies revealed that higher the guest-host interaction higher would be the catalytic activity [52].

Developing a highly active catalyst system capable of producing high-molecular-weight poly(propylene carbonate) (PPC) and low amount of cyclic polycarbonate (PC, byproduct) is fundamental; under the control of the percentage of CO_2 incorporation [47].

In this research made at the University of Valladolid it is shown the effect of different Zn/Co initial ratio in the preparation of five DMC catalysts by testing the catalytic activity in the copolymerization process, the cyclic polycarbonate (PC) production and CO_2 coupling.

A comprehensive study of all the catalysts, physical and chemical characterization has been performed using a number of different analytical techniques.

Activation of the Double Metal Cyanide catalysts

Chapter 3 is in charge of studying the activation process before each copolymerization reaction.

Since Inoue first disclosed the ring-opening copolymerization (ROP) of CO_2 with 1,2-epoxypropane by $ZnEt_2$-H_2O [23], much attention and progress had been made within the past decades to explore various relating catalyst to ensure the copolymerization and afford to synthesize a range of aliphatic polycarbonates [43].

The copolymerization process of CO_2 is strongly dependent on the selection of the catalyst and various heterogeneous and homogeneous catalysts have been studied [20].

Homogeneous catalysts are generally suitable for research, since their chemical structure can be well defined, and some homogeneous catalysts show high activity and product selectivity . Among them, typical homogeneous catalysts are metal porphyrins, zinc phenolate, discrete β-diiminate zinc, and binary or single bifunctional catalyst systems based on metal-salen complexes. Prominent among them are β-diiminate zinc complexes and metal salen complexes [36, 53-56].

Dinuclear or bimetallic catalysts comprising metal(II/III) complexes such as Co(III), Cr(III), Mn(III) or Al(III) [40] used with co-catalysts.

The co-catalysts are typically ionic compounds such as bis(triphenylphosphine)iminium (PPN) chloride (PPNCl), or Lewis bases. This catalysts are coordinated by ligands such as salens or porphyrins [20].

It was noteworthy that Salen Co complexes showed excellent effects [36].

The most effective catalysts for epoxide/CO_2 copolymerization proved to be chiral salen Co (III) complexes in combination with strong Lewis acids and nucleophilic co-catalysts [57, 58].

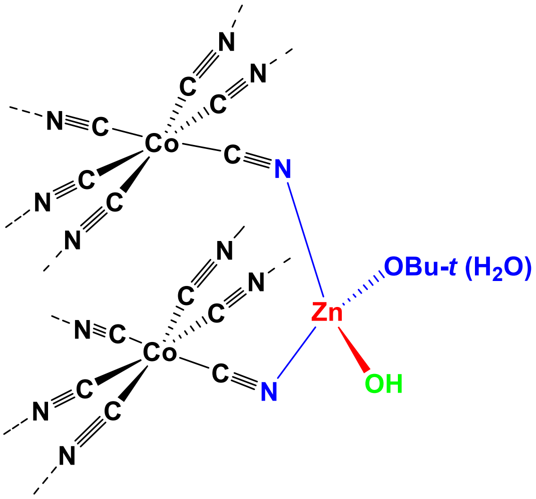

Figure 2. Proposed ground-state structure of the active site of Zn-Co (III) DMCC catalyst by Wei R.J et al.

Both catalysts monometallic or bimetallic mechanisms show high activity, selectivity to polycarbonate, good stereo-selectivity and in some cases enhanced enantioselectivity [23-25] at mild conditions.

The reactions using metallic catalysts have disadvantages, such as poor solubility of the catalyst, difficulties in catalyst recycling, air sensitive, the need of co-solvent, or the requirement for high temperatures [17, 59, 60].

Although the chemical or crystal structures of heterogeneous catalysts have not been completely elucidated, some of them show good potential in industrial applications [8].

Zinc glutarate (or other carboxylates) and double metal cyanides are the two major classes of heterogeneous catalysts [61].

Double metal cyanide complexes (DMC) are well-known catalysts for the ROP of epoxides [19, 21, 37, 41-43, 45, 46, 49, 51, 52, 58, 62-76].

Generally, the DMC catalysts are obtained by reacting a selected metal salt with a cyanide derivative of another metal in the presence of an electrodonor organic complexing ligand [49, 77]. The most commonly studied double metal cyanide catalyst is $Zn_3[Co(CN)_6]_2$ [20, 41, 46] and have been identified as the most active for copolymerization [52].

Besides, a variety of transition metal elements such as Ni, Co, Fe, Mn have also been studied [64].

The incorporation of DMC in the copolymerization of epoxides and CO_2 have some disadvantages. One of the disadvantages is the low CO_2 insertion in the polymer chain.

While DMC catalysts offer significant advantages for the ROP of epoxides, few reports have been published on the copolymerization of epoxides with CO_2 thereby [19, 21, 37, 41-43, 45, 46, 49, 51, 52, 58, 62-76, 78, 79]. The catalysts are highly active and give polyether polyols with low unsaturation and narrow molecular weight distribution compared with similar polyols synthesized using conventional KOH catalysis, resulting in high performance polyurethane products [80].

In this chapter, we show a high active DMC catalyst prepared with potassium hexacyanocobaltate and zinc chloride, as well as a catalysis activation study where the amounts of PO and DMC used for copolymerization has been changed to elucidate the best conditions [45, 64, 66, 70, 81-84].
As far as we know, there are practically no reports of a catalyst activation study in different conditions where the amount of DMC used is crucial to obtain the maximum efficiency for the copolymerization process.

This reaction can be the base of a future chemistry to obtain polymers based also in bio-alcohols, determining if new green polyurethanes and polycarbonates can be synthesized with an industrial application such as biodegradable thermoplastics and biomedical polymers.

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OBJECTIVES

There has been a will of starting up this new research branch in both laboratories: Reaction Engineering and Industrial Chemistry Laboratory of the Process Chemistry Centre (PCC) at Åbo Akademi University (Turku, Finland) and Chemical Engineering and Environmental Technology Department from the University of Valladolid (Valladolid, Spain).

The main objective of this research consists on producing CO_2/propylene oxide copolymers through the Ring Opening Polymerization process in batch and subcritical conditions.

To reach this goal the first step is to build the system in both facilities; this means design and start up both experimental systems. The working conditions are at subcritical pressure but they could be working also at supercritical conditions, making up several parts of the equipment.

Once both systems are ready, the next step implies the synthesis of both catalysts which are going to be used for the copolymerization reactions. Two types of heterogeneous catalysts are going to be used for these copolymerization reactions. The synthesis procedure, their morphologies and their behaviour are completely different.

Each chapter of this thesis is in charge of different studies involving both catalysts: the best conditions for copolymerization reactions, the most active catalyst, the best conditions for activation processes, differences in the catalyst behaviour in order to get the final copolymer with or without by-product after the reaction…

Dividing all this studies into three chapters and two annexes, the specific objectives for each one are the following:

Chapter 1. Heterogeneous Zinc glutarate catalyst study in copolymerization reactions among propylene oxide and carbon dioxide in batch and subcritical conditions. Specific objectives:

- Establish a correct synthesis procedure for this catalyst. Synthesis conditions like temperature, pressure, time and amount of reagents. Steps needed to get the catalyst. Reproducible method and result.
- Characterization of the catalyst by several techniques such as Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).
- Study of Zinc glutarate catalyst in copolymerization reactions using propylene oxide and carbon dioxide as reagents. Obtain the best subcritical conditions in batch mode for the reactions: amount of catalyst, reaction temperature, reaction pressure, final copolymer molecular weight and reaction time.
- Characterization of the copolymers by Fourier transform infrared spectroscopy (FTIR) and Size Exclusion Chromatography (SEC) techniques.

Chapter 2. Effect of Zn/Co initial preparation ratio in the activity of a Double Metal Cyanide catalyst for propylene oxide and carbon dioxide copolymerization. Specific objectives of this chapter:

- Study of the ratio among metals (Zn/Co) in the synthesis procedure of this heterogeneous Double Metal Cyanide catalyst (DMC).
- Catalyst characterization by techniques such as Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Nitrogen-Physisorption, Scanning Electron Microscopy (SEM) and X-ray powder diffraction (XRPD).
- Study of the activation of these DMC catalysts in copolymerization reactions using propylene oxide and carbon dioxide as reagents.
- Study the stirring influence in copolymerization reactions.
- Characterization of the copolymers by Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR) and Size Exclusion Chromatography (SEC) techniques.

Chapter 3. Activation study of DMC catalysts in copolymerization reactions with CO_2.

- Study the activation process varying the amount of catalyst in each experiment.
- Characterization of the most active Double Metal Cyanide catalyst from Chapter 2 by Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Nitrogen-Physisorption, Nuclear magnetic resonance (NMR), Scanning Electron Microscopy (SEM) and X-ray powder diffraction (XRPD) techniques.

- Determine the best reagents and catalyst amounts in order to improve the copolymer production.
- Determine the effect of the stirring system during the copolymerization reactions.
- Characterization of the final copolymer obtained at different reaction conditions by Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR) and Size Exclusion Chromatography (SEC) techniques.

Appendix 1. Solubility of CO_2 in several polypropylene carbonates at different conditions

- Determine the maximum amount of CO_2 in the liquid phase during the copolymerization reactions by understanding CO_2 solubility in the polymers

CHAPTER 1

Heterogeneous Zinc glutarate catalyst study in copolymerization reactions among propylene oxide and carbon dioxide in batch and subcritical conditions

ABSTRACT

A huge variety of heterogeneous catalysts has been used for polymerization processes. In this case, Zinc glutarate (ZnGA) was selected and prepared for copolymerization reactions.

Carbon dioxide (CO_2) acted not only as the pressurized medium to drive the reaction but also as a monomer for the reaction since it was used by purpose as a C1 feedstock. The other monomer that was involved in the reaction was propylene oxide. Through the mechanism of Ring Opening Polymerization or Copolymerization (ROP or ROCOP), the incorporation of CO_2 in the polymer chain can be possible.

In this chapter, a comprehensive characterization of this heterogeneous catalyst was done and a complete study of its behaviour in copolymerization reactions was carried out, to determine if new green polycarbonates as a base for polyurethanes can be synthesized with an industrial application.

Several reactions were taken place changing the amount of ZnGA (0.3, 0.6, 1.0, 1.5 g), the temperature of reaction (60, 80 ºC), the pressure of CO_2 (6, 25 barg) in the reactor, final expected molecular weight of the polymer (725, 3000 g/mol) and the reaction time (20, 40 h).

Through these results, firstly it was possible to determine which the best amount of catalyst was for the reaction (1.5 g) and the effect in the polymerization reaction was increasing it.

Secondly, once the best amount of catalyst was determined, it was set and the temperature of the copolymerization reaction was studied. It was possible to determine that an increase in temperature provided better final copolymers.

Third, about the pressure in the reactor, thermodynamics and kinetics sentenced the impact on the polymerization reactions. It was possible to determine that in subcritical conditions of CO_2, pressure has not a decisive effect as a variable of study in copolymerization reactions.

Finally, two more variables were studied: molecular weight of the final copolymer, which showed a considerable impact in the viscosity of the final copolymer when it was increased, and the reaction time. This last variable showed if the process could be done in less time with the same quality.

Several techniques were used to analyse the synthesized catalyst and the polymers gotten after the reaction. Techniques such as Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Size Exclusion Chromatography (SEC), Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).

1. INTRODUCTION

In this chapter, a comprehensive study (synthesis and characterization) of the use of zinc glutarate (ZnGA) in copolymerization reaction is presented. This catalyst is known to work for achieving high molecular weights but it usually needs long reaction times.

A complete study of the catalyst is shown herein besides the characterization of the polycarbonates synthesized from it.

These reactions are copolymerization reactions, which mean that two monomers are involved: one is propylene oxide and the other is carbon dioxide.

Carbon dioxide (CO_2) is one of the main gases that cause the Greenhouse Effect. Several sources like anthropogenic actions as burning coal or other fuels are increasing the concentration of CO_2 in the atmosphere, methane (CH_4) and also nitrous oxide (N_2O). Several regulations are established to control the emissions, like Montreal Protocol or Kyoto Protocol. In fact, at the Paris climate conference (COP21) in December 2015, 195 countries adopted the first-ever universal, legally binding global climate deal. This agreement has been signed by 175 countries on the 22nd April 2016 [1].

About 40% of all the emissions remained in the atmosphere while the rest are on lands and oceans (causing acidification on them). Just from burning coal in 2013, 2.9 ppmv were added to the environment. In 2015 the concentration in the atmosphere raised 400 ppm of CO_2 while it was less than 320 ppm of CO_2 in 1962 (National Oceanic & Atmospheric Administration, 2015) [2, 3].

Developing new biorenewable resources instead of continuing using this petroleum consumption rate are needed [3].

Heede affirmed that 63 % from the total of fuel fossils consumed in the period 1750-2010 had been produced, with technology and financial support, by a total of 70 companies and 8 government-run industries [4].

Heede and Oreskes suggested that an important part of fossil fuel reserves must be not consumed to maintain this climate change below 2 °C preventing dangerous anthropogenic interference (DAI) with the environment [5]. The International Energy Agency (IEA) remarked to consume less than 1/3 of the fossil fuel reserves to 2050 to achieve it [6]. They conclude that several actions from stated-owned companies, investor-owned companies and governments are urgently needed.

As a way of attenuate this damage, CO_2 (a chemical environmentally friendly, low cost, high purity, nontoxic and non-flammable chemical) has been captured and storage and used in copolymerization reactions as a C1 feedstock [7].

The idea behind using CO_2 as a monomer is not to save the world from climate change by adding CO_2 to polymers, as the total amount of CO_2 for this task is minimal compared to the total CO_2 emitted; that is obvious. The target pursued in this chapter is not only because of the green point of view of using a reaction by-product as a monomer (CO_2) but because of the economical aspect, that is involved here. Using CO_2 as a C1 feedstock assures lower OPEX in carbon sources from other chemicals, as in epoxides in this case [8].

The incorporation of CO_2 in the polymer chain can be possible by means of the Ring Opening Polymerization (ROP**)** mechanism that epoxide exhibits.

One of the pioneers of this type of copolymerization reactions was Inoue back in the 60's [9]. Epoxides had not been used before as a monomer in alternating copolymerization until they used them with carbon dioxide to get polycarbonates using an organometallic compound. First, the metal alkoxide reacts with the carbon dioxide and then, the epoxide with the metal carbonate bond. Propylene oxide was studied with acid anhydride or with α-amino acid N-carboxy anhydride, such as diethylzinc and ethanol. With IR, NMR and an elemental analysis, the polymer was characterized. Other epoxides were also copolymerized and characterized such as epiclorohydrin, ethylene oxide and styrene oxide with carbon dioxide.

Hino et al. studied also copolymerization reactions involving carbon dioxide and propylene oxide, using catalysts such as diethylsinc-benzenediaceboxylic acid or zinc-benzenedicarboxylic acid systems [10]. More recently, Ree and Kim et al made several copolymerizations between propylene oxide and carbon dioxide studying the influence of several heterogeneous catalysts [11, 12]. They proposed a procedure for the synthesis of zinc glutarate catalyst (experimental procedure followed in this chapter with some negligible differences). Several catalysts were synthesized and tested in copolymerization reactions (using eleven different glutaric acid derivatives, they obtained different zinc dicarboxylate catalysts such as zinc 3.3-dimethylglutarate (ZnO/3.3-DMGA), zinc 2-methylglutarate (ZnO/2-MGA), zinc 3-ketoglutarate (ZnO/3-ketoGA), etc.), giving the highest yield of the poly (propylene carbonate) gotten (PPC) using zinc glutarate (ZnO/GA) as the catalyst.

Also, the highest molecular weight was achieved by this heterogeneous catalyst. Infrared spectroscopy gave information about their coordination characteristics: bidentate coordinating bonding mode, unidentate coordination or a mixed coordination mode.

Zinc glutarate belongs to the first group with syn-anti and syn-syn bridging modes.

Wang et al. synthesized high crystalline zinc glutarate catalysts by ultrasonic method and by mechanical stirring methods just to compare, showing higher catalytic efficiency those synthesized via ultrasonic [13]. They analysed both, catalyst and polypropylene carbonate, by techniques as Fourier Transform Infrared Spectroscopy, wide-angle X-ray diffraction technique, differential scanning calorimetry, thermogravimetric analysis and tensile test. Chisholm et al. , explained in detail the structure and conformation of the poly (propylene carbonate) from the reaction among carbon dioxide (CO_2) and propylene oxide (PO) [14]. The catalyst employed was zinc glutarate which has active Zn-OH groups that they synthesized from Ree et al. [15]. They chose zinc oxide and glutaric acid to synthesize it. It was demonstrated that 1g of ZnGA produced only 70 g of PPC in a 40 h of reaction time from PO/CO_2.

From PO they obtained a regioregular polypropylene oxide (PPO) at 60 ºC and with CO_2 (50 bar) they got poly (propylene carbonate) (PPC) with less than 5% of polyether linkages and a small amount of propylene carbonate.

Kim et al. tested several different sources of zinc to get zinc glutarate catalysts appeared [16]. Using solid-state carbon-13 nuclear magnetic resonance spectroscopy and x-ray absorption they determined the structure of the catalysts.

Morphological parameters like the structure of the zinc active site, crystallinity and crystal quality are used for catalyst characterization. They found that the catalyst with the highest crystallinity and crystal quality but with the lowest surface area had the highest catalytic activity in copolymerization reactions.

It was also concluded that the one obtained by using zinc oxide (ZnO) and glutaric acid (GA) was the most active for this type of copolymerization between CO_2 and PO (with a low surface area). For zinc glutarate catalysts surface area has not the relevance that morphological parameters have to improve the catalytic activity. Kim et al., sentenced a fundamental idea about the organometallic catalyst, zinc glutarate [17]. They had been previously sentenced that the catalyst with the highest crystallinity produced the highest yield.

Crystal quality and size are fundamental for the catalytic activity of the catalyst, as it was discussed before, showing a monoclinic structure. Their results explained the network structure of the catalyst showing that the Zn^{2+} centers are the active sites of the catalyst located at the surface. They are coordinated with four oxygen atoms (carboxyl oxygen) in a syn-anti bridge configuration with a tetrahedral geometry.

Ree et al., used various sources for making different zinc glutaric catalysts and derivatives [18]. They prepared monoclinic structure with P2/c space group of sc-ZnGA (single crystals) by hydrothermal reaction between zinc perchlorate hexahydrate and glutaronitrile. They also found in copolymerization reactions that as PO is absorbed easier than CO_2 onto Zn^{2+} from the surface of the catalyst, PO is the monomer that starts the copolymerization being inserted into the Zn-O bonds.

Moreover, they have confirmed that ZnGA from ZnO and GA gives the highest yield (64 g). The activity, as it has been mentioned previously, depends on the zinc source and the morphological parameters (crystallinity and surface area) from the different ZnGA catalysts.

The aim of this chapter is then to study several reactions by varying the amount of ZnGA, the reaction temperature, the pressure of CO_2 in the reactor, molecular weight of the final polymer and the reaction time trying to find the best reaction conditions possible. We start from the idea that ZnGA is not a fast catalyst but will explore the margin of improvement if there is one.

The research has been carried out at Åbo Akademi University (Åbo/Turku, Finland), there has been and there is a willing of starting and continuing this new research line working with CO_2-polymers.

2. OBJECTIVES

There are two main objectives to reach in this chapter.

First, to synthesize and characterize the heterogeneous zinc glutarate catalyst. Zinc glutarate is to be synthesized at the Industrial Chemistry and Reaction Engineering Department of Åbo Akademi (Turku, Finland). Once it is synthesized, the next goal is to characterize it in order to being used as the catalyst of the copolymerization reactions.

Several techniques will be used to characterize this heterogeneous catalyst: Techniques such as Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).

The second main goal is to perform a comprehensive study of the copolymerization reactions at subcritical conditions with this catalyst. In this case, the best conditions for the copolymerization and the behaviour of the catalyst will be defined. The Propylene oxide/CO_2 copolymer will be obtained under subcritical conditions in a batch-wise process. Several specific objectives will be pursued. The molecular weight targeted will be 3000 g/mol and, in any case, below 6000 g/mol to assure the liquid phase (avoiding high viscosity polymers to favour stirring and mass transfer).

Specific goals as design and start up the experimental system, make the polymerization study changing variables like reaction pressure, reaction temperature, amount of catalyst, final molecular weight of the polymer and reaction time.

To characterize the polymer gotten in each experiment, Fourier transform infrared spectroscopy (FTIR) and Size Exclusion Chromatography (SEC) are techniques used for that purpose.

3. MATERIALS AND METHODS

All the work done for the synthesis of zinc glutarate catalyst and all the copolymerization reactions have taken place at the Industrial Chemistry and Reaction Engineering Laboratory at Johan Gadolin Process Chemistry Centre – PCC at Åbo Akademi University (Åbo/Turku).

3.1. MATERIALS

3.1.1. SYNTHESIS OF THE CATALYST

For synthesizing the zinc glutarate catalyst, the chemicals used were zinc oxide (ZnO) (puriss. p.a., ACS reagent, ≥ 99.0% (KT)) from Sigma-Aldrich and glutaric acid (GA) 99% from Aldrich. Both reactants are in solid state. Toluene used (liquid phase) is from J.T. Baker; baker analyzed.

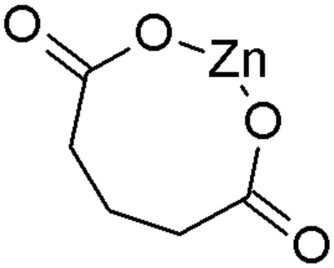


Figure 1. Heterogeneous catalyst ZnGA

3.1.2. COPOLYMERIZATION REACTIONS

After the catalyst was synthesized, it was used for copolymerization reactions among propylene oxide (PO) and carbon dioxide (CO_2).

Therefore, the materials required for these copolymerization reactions were the following: Carbon dioxide was purchased from AGA, the same as Nitrogen (N_2) (5.0), Propylene Oxide (ReagentPlus® ≥ 99%) and Polypropylene glycol (PPG, with an average Mn ~ 425) both were from Aldrich.

3.2. METHODS

3.2.1. SYNTHESIS AND CHARACTERIZATION OF THE CATALYST

The equipment used for the synthesis of the catalyst consists of a Rotavapor from Heidolph, LABOROTA 4000-efficient, with silicon oil as a thermic fluid in a thermic bath with an inert argon atmosphere. The vacuum pump was from Vacuubrand, PC 3001 VARIO CVC 3000.

3.2.1.1. Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine)

FTIR and FTIR with pyridine have been made using the same equipment.

FTIR is used to determine how the structure of the catalyst is. The bonds of the material that it is being used are susceptible for being measured.

Lewis and Brøwnsted acid sites of the catalyst are shown using infrared spectroscopy (ATI Mattson FTIR) with pyridine.

It was necessary to analyse the catalyst via Thermogravimetric analysis-mass spectrometry (TGA-MS), as it is described in section 6.1.8. A complete understanding about the behaviour of the catalyst was acquired with TGA-MS.

3.2.1.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

This technique consists in an elemental analysis which was used to determine the quantity of Zinc in this catalyst.

The samples were exposure to a plasma irradiation. Their emission spectra identified the elements and the quantity of them.

3.2.1.3. Light scattering (with air and distilled water)

Two different models of the same equipment (Mastersizer 2000 and 3000, Malvern) were used to determine the particle size distribution of the catalyst, in air and water medium, respectively. In distilled water, where the zinc glutarate is not soluble, the sample was measured three times [12].

3.2.1.4. Nitrogen-physisorption

By nitrogen (N_2) physisorption, surface area, pore volume and pore size distribution of zinc glutarate catalyst were determined [19-21].

Macro- and microporous of the catalyst can be specified by several methods getting adsorption and desorption isotherms and different parameter values. The N_2 physisorption equipment was a Sorptomatic 1900, Carlo Erba Instrument.

3.2.1.5. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy microanalysis (EDX)

Catalytic properties of the catalyst are influenced by morphological parameters. Thus, characterize the sample by scanning electron microscopy and energy-dispersive x-ray spectroscopy microanalysis (SEM and EDX) will give very important information about the catalyst (size, shape, surface area, distribution of the crystals and amount of each component). The equipment used for both types of analysis was a Zeiss LEO Gemini 1530.

3.2.1.6. Thermogravimetric analysis-mass spectrometry (TGA-MS)

The thermal stability of the catalytic was determined by thermogravimetric analysis (TGA-MS).

The equipment used was NETZSCH STA 449F1 using argon as inert gas. This equipment belongs to the Organic Chemistry Department at Åbo Akademi University.

3.2.1.7. X-ray photoelectron spectroscopy (XPS)

The oxidation state of the metal (zinc) from the catalyst was determined by a Perkin-Elmer PHI 5400 spectrometer (photoemission spectra) with a monochromatized Mg Kα. X-ray source operated at 14 kV and 200 W. The pass energy of the analyser was 17.9 eV.

3.2.1.8. X-ray powder diffraction (XRPD)

A Philips X'Pert Pro MPD X-ray powder diffractometer was used in the XRD measurements for determine the crystallinity of the sample. The diffractometer was operated in Bragg-Brentano diffraction mode and the monochromatized Cu-Kα radiation (λ = 1.541874 Å) was generated with a voltage of 40 kV and a current of 45 mA. The primary X-ray beam was collimated with a fixed 0.25° divergence slit and a fixed 15 mm mask. A 7.5 mm anti-scatter slit was used in the diffracted beam side prior to the proportional counter. The measured 2θ angle range was 6.6° - 70.0°, with a step size of 0.026° and measurement time of 100 s per step. The sample, zinc glutarate, was measured on a cupper (Cu) sample holder.

3.2.2. COPOLYMERIZATION REACTIONS AND CHARACTERIZATION OF THE PRODUCT

A Parr reactor (Parr Instrument Company, Inc. Moline, Illinois, U.S.A), with a volume of 382 cm3 was used for the polymerization reactions.

The mechanical stirrer was from Parr Instrument Company, Moline, Illinois, U.S.A. A1120HC II55 with a motor from Bodine Electric Company, Chicago 60618, USA, Small Motor, type: 32D3BEPM. This stirrer assures good mass and heat transfer inside the reactor.

The temperature of the reactor was controlled using a Parr 4843 temperature control unit equipped with a J-type thermocouple. Pressure and temperature were also logged and saved on a computer using a PicoLog TC08 logger (Fike ® Corporation).

The system has two inlets: one for carbon dioxide (CO_2) conducted to a Swagelok 304 L stainless steel tank and the other one, for nitrogen (N_2).

The equipment has also two cooling systems: one inside (tap water) and a coil (glycol as a refrigerant) outside of the reactor for unreacted condensed monomers. Besides, the same vacuum pump used in the synthesis of the catalyst assisted to remove easily these unreacted monomers from the reactor.

Two techniques were used to analyse the final polymers: Fourier transform infrared spectroscopy (FTIR, same equipment as Section 3.2.1) and Size Exclusion Chromatography (SEC), that will be explain in Section 6.2.2.

4. EXPERIMENTAL SETUP AND PROCEDURE

4.1. SYNTHESIS OF THE CATALYST

The procedure for the synthesis of zinc glutarate catalyst is similar to the one described by Ree et al. [15].

Using a round flask, 98 mmol of glutaric acid (GA) have been dissolved in 150 mL of toluene. Once the mixture is stirred, 100 mmol of zinc oxide (ZnO) are added to it. A rotary system and a refrigerated coil, with an argon atmosphere, is used to separate and condense any by-product.

The mixture was stirred at 55°C during 4 h. A make-up step for the mixture was necessary. First, it was cooled down to room temperature and then a filtration step, with several washes with acetone, was needed. Zinc glutarate catalyst was the product rejected in the filter.

The powder catalyst was then dried in the same equipment at a vacuum of -18 mbar and a temperature of 100°C during 2 days.

Finally, it was crashed in a mortar and dried again during 3 more days at - 25 mbar and 100°C.

4.2. COPOLYMERIZATION REACTIONS

A Parr reactor (382 ml) was used for the copolymerization reactions.

It was filled with the desired amount of catalyst (the day before the reaction, it was placed under a vacuum pressure of - 25 mbarg inside the reactor to dry it for the copolymerization), starter (polypropylene glycol) and the required amount of propylene oxide.

A mechanical stirrer was used, at any moment, for assuring homogeneous mixture. Once it was closed, nitrogen was passed through the system to check that there were no leaks; three different attempts were made for each reaction at different pressures.

The reactor was heated until reaction temperature and carbon dioxide was added until the desired reaction pressure. Once the reaction conditions were reached and stabilized, the reaction kicked-off and it continued during the next 40 h.

Once the reaction is finished, pressure was slowly released using a go back-pressure valve at the same time that temperature was decreased. Unreacted propylene oxide monomers fully condensed in cold-trap with a round flask before going to the extraction duct. Before opening the reactor, 30 min at a low vacuum pressure (-600 mbarg) were necessary in order to recover all the unreacted monomers from the reactor.

5. DIAGRAMS OF THE SYNTHESIS AND REACTIONS

5.1. BLOCK DIAGRAM OF THE SYNTHESIS OF THE CATALYST

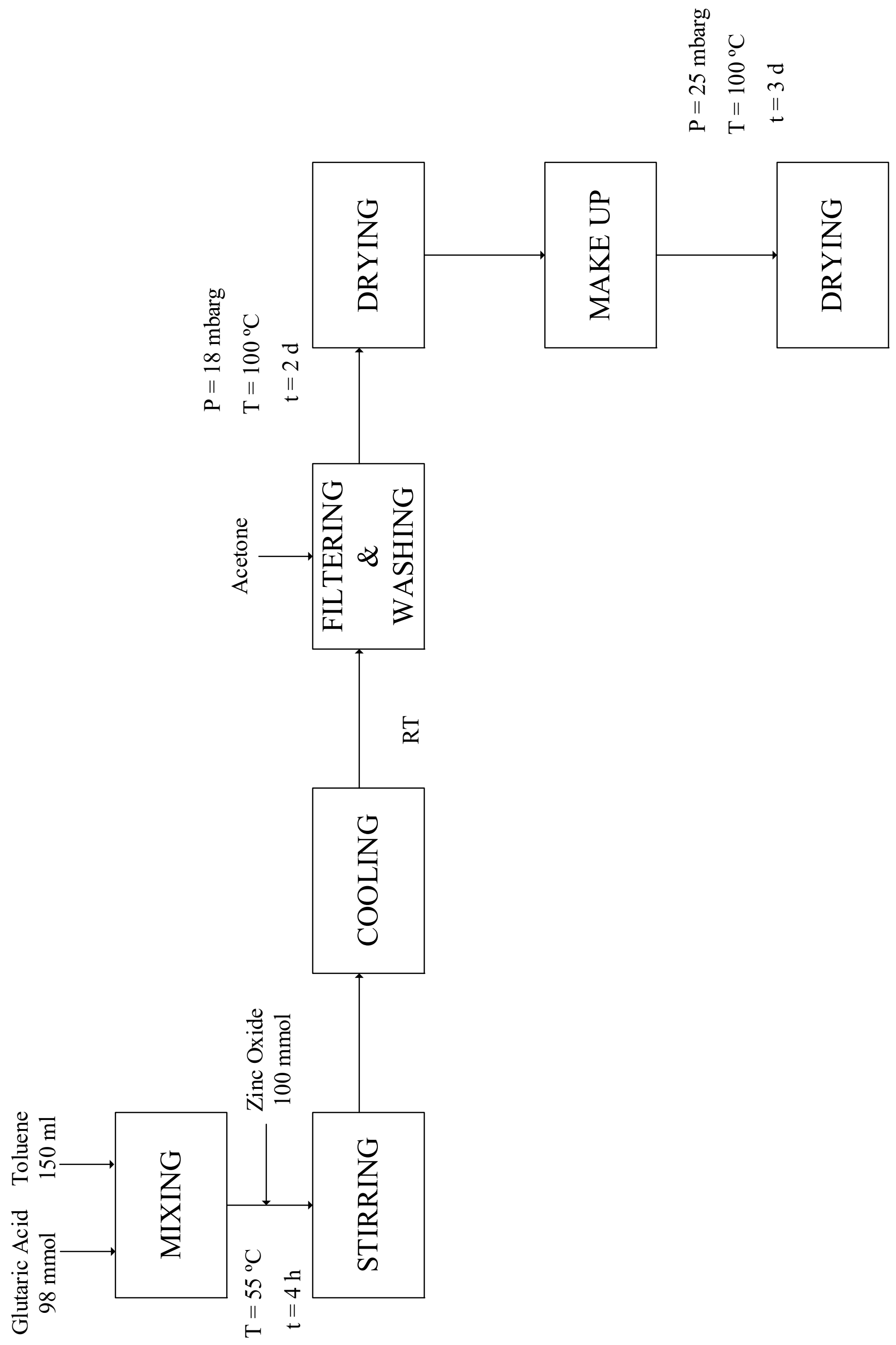


Figure 2. Block diagram of the catalyst ZnGA preparation process

5.2. BLOCK DIAGRAM OF THE COPOLYMERIZATION REACTION

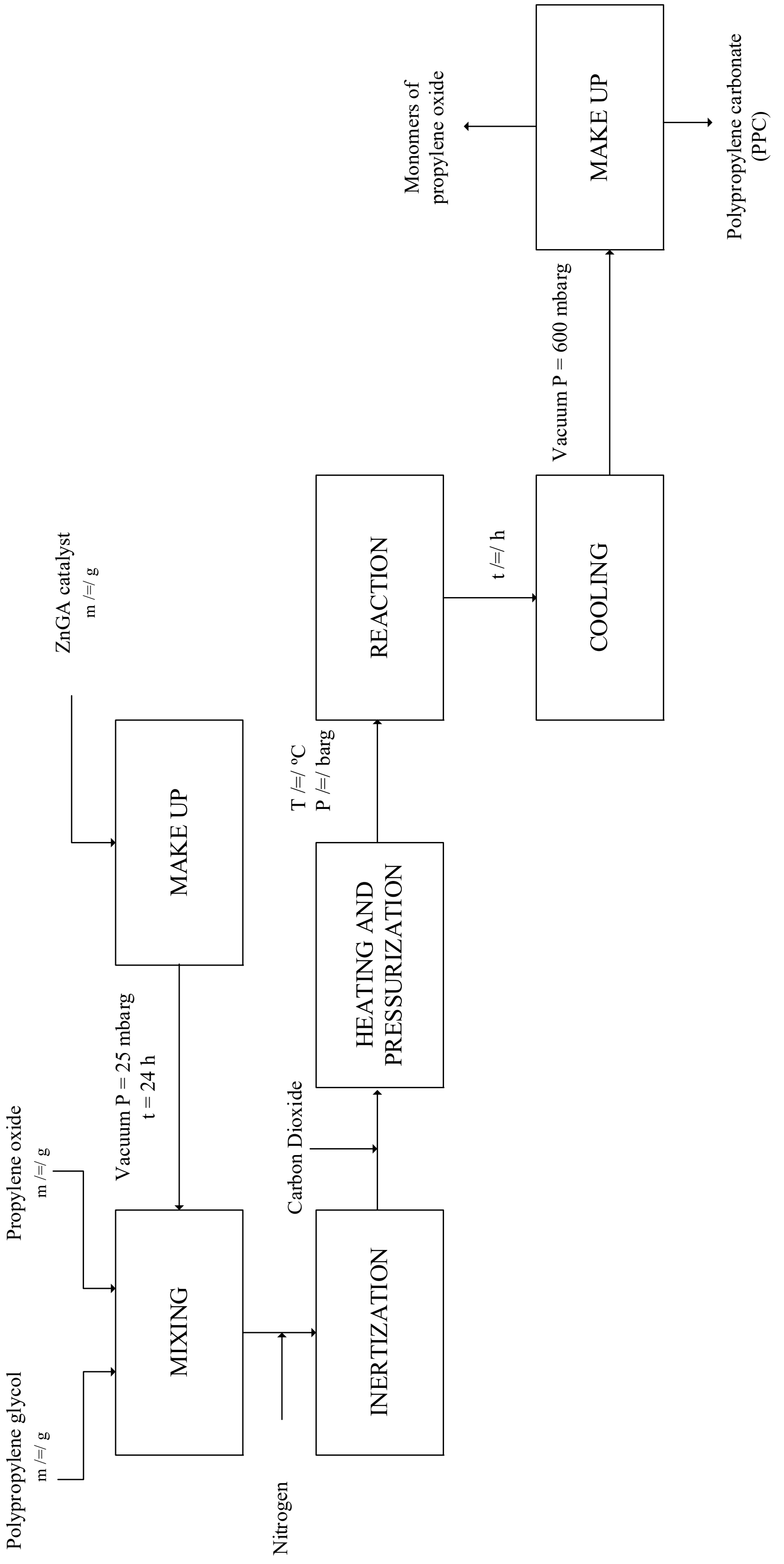


Figure 3. Block diagram of the copolymerization reaction using ZnGA as catalyst

5.3. SYMBOLS DIAGRAM OF THE COPOLYMERIZATION REACTIONS

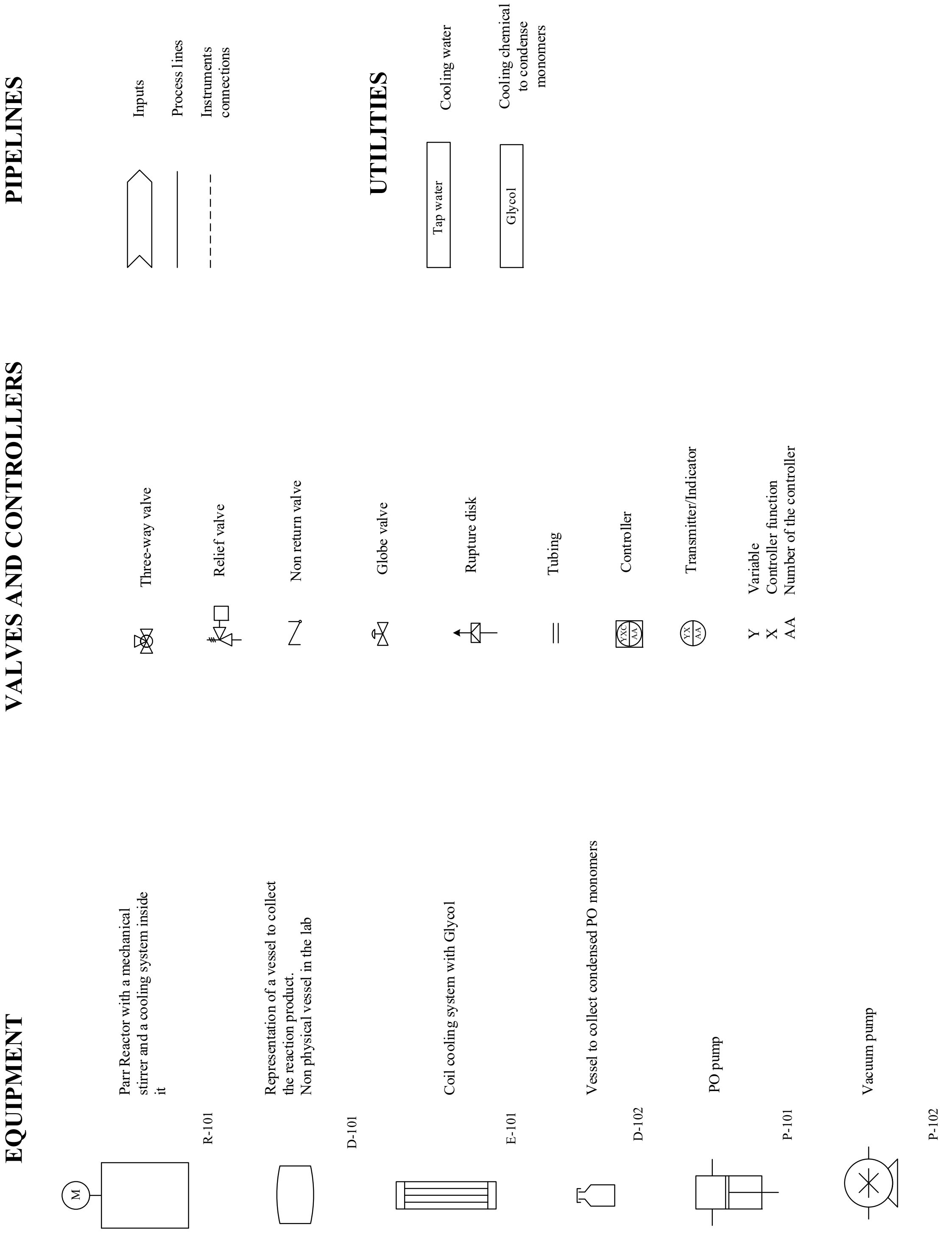


Figure 4. Symbols used in the process block diagram

5.4. PROCESS FLOW DIAGRAM OF THE COPOLYMERIZATION REACTIONS

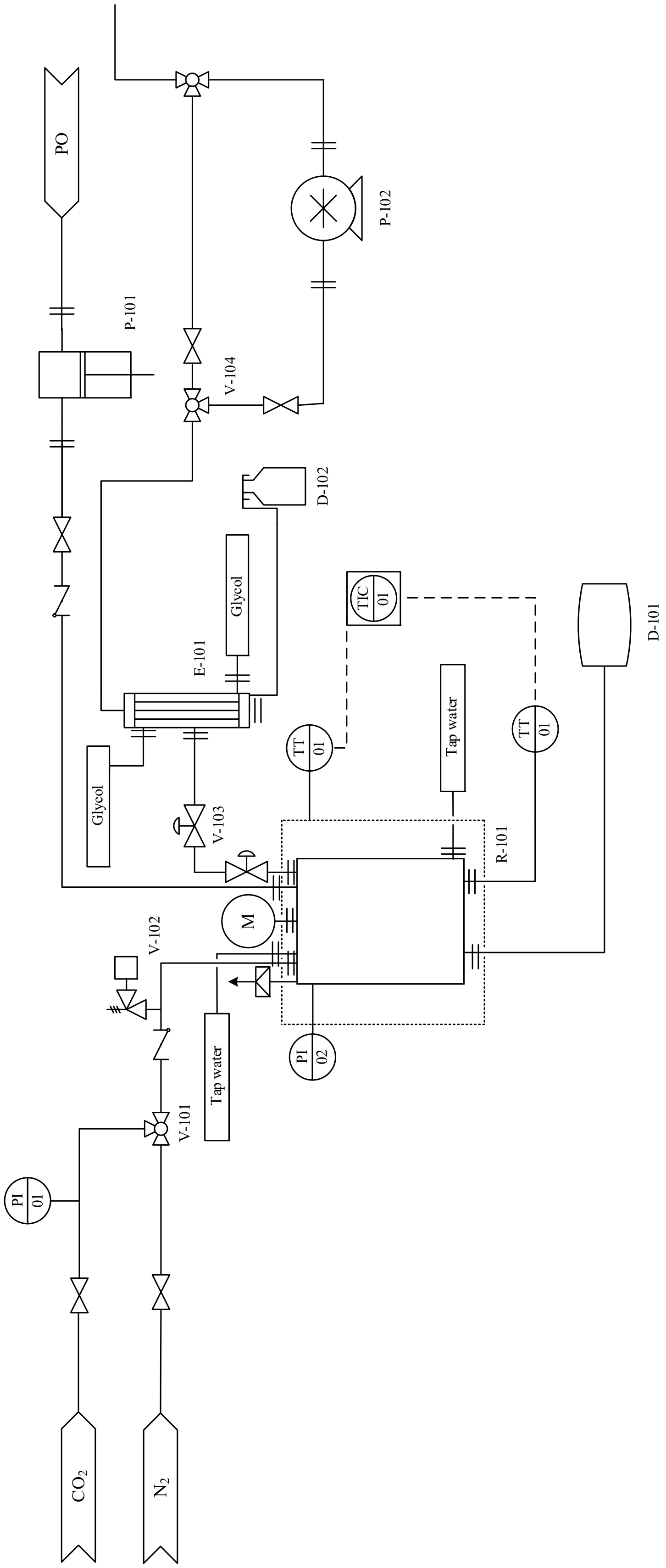


Figure 5. Process flow diagram of the copolymerization reactor for ZnGA

A nitrogen stream is used to inert the reactor (R-101) and, also to check if there are leaks.

Two main stream are going to be driven to the reactor with carbon dioxide (CO_2) and with propylene oxide (PO).

The line with CO_2 has a rupture disk, just for security in the case pressure exceeds the maximum tared value (V-102) and PO has to be pumped (P-101) to the reactor. In order to avoid the evaporation of the PO, its vessel is pressurized with 5 barg of N_2.

The reactor (R-101) has a mechanical agitation and a cooling system inside it with tap water. The temperature can be considered constant at any moment and any point of the reactor. These are very exothermic reactions and the stirring is a very important parameter to avoid hotspots or runaway reactions.

The output current has a cold trap (E-101) to separate the unreacted monomers from the final product.

Pump (P-102) is used at the same time with a N_2 current in order to make vacuum and assure no more unreacted monomers are in the product. Also, it is for a safety operation after being the system with a high pressure.

6. RESULTS AND DISCUSSION

6.1. ZINC GLUTARATE CATALYST

Different studies have determined the synthesis conditions of several zinc carboxylates. Zinc glutarate has been selected as the one with the highest activity and the chosen one for these copolymerization reactions among carbon dioxide and propylene oxide.

Zinc glutarate catalyst has been synthesized following the procedure by Ree et al. as it was explained in the previous section 4.1 [15, 18, 22].

6.1.1. Fourier Transform infrared spectroscopy (FTIR)

The white fine powder zinc glutarate catalyst has been subjected to FTIR technique.

Figure 6 shows the infrared absorption spectra of this catalyst (ZnGA).

Studies, like the one made by Stephan Klaus et al. have determined the IR bands for zinc glutarate [23]. Same spectrum was obtained in the synthesis. Several peaks appeared at different wavelengths which corresponded to the created bonds at 2947 cm^{-1} (Carboxylic acids with high concentration of O-H bonds), 1760 cm^{-1} (Anhydride, C=O), 1589 cm^{-1} (Aromatics, C=C), 1525 cm^{-1} (Carboxylates), 1442 cm^{-1} (Alkane, strong C-H scissoring) and 1402 cm^{-1} (zinc, Zn).

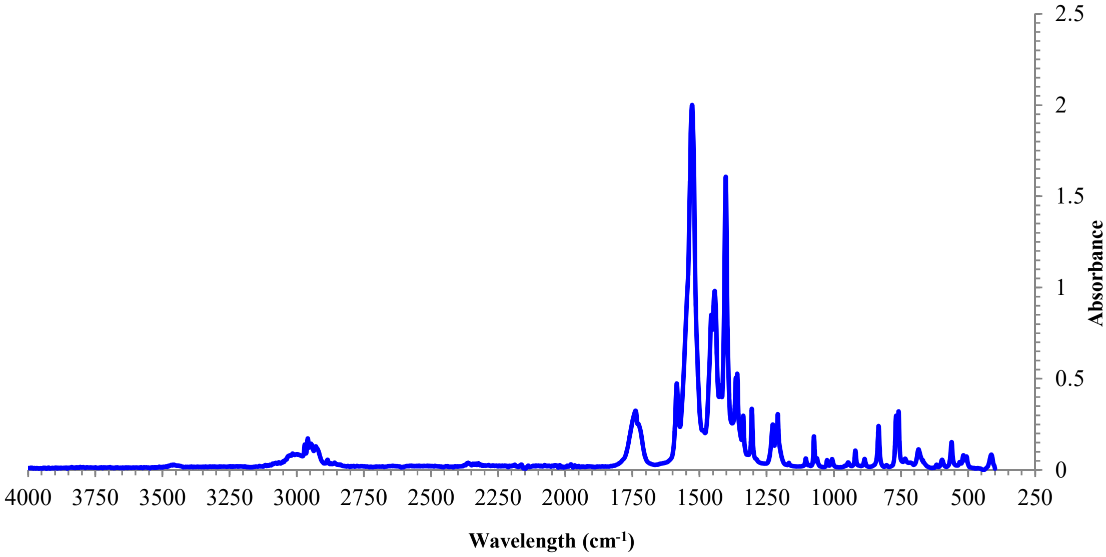


Figure 6. Spectrum of the heterogeneous catalyst, ZnGA

6.1.2. Fourier Transform infrared spectroscopy (FTIR) with pyridine

As it was described in section 3.2.1, the fine powder catalyst was subjected also to FTIR technique with pyridine.

The FTIR with pyridine had been tried three times but the catalyst pellet broke in the first two experiments. After performing the TGA-MS analysis, the conclusion was that this happened because the first ramp of the FTIR with pyridine procedure went to 450 ºC and the catalyst could not stand this temperature.

Once the suitable conditions were determined, the procedure of FTIR with pyridine set the temperature for the variation ramp (ZnGA decomposition temperature is around 400-450 ºC). In an FTIR cell, a thin catalyst wafer was pressed and placed into it. The air in this cell was evacuated and the temperature rose to 300 ºC. After 1 h, the temperature was decreased to 100 ºC.

The background spectra of the sample were recorded. As a probe molecule, pyridine was adsorbed on the sample in conditions of 30 min and 100 ºC.

Desorption at 150 ºC, 250 ºC and 350 ºC during 1 h was the next step. The spectra of the sample were recorded after every change on step-temperature.

The scanning took place under vacuum conditions and a temperature of 100 ºC. Peaks at 1545 cm^{-1} indicate Brøwnsted acid sites (BAS) and peaks at 1450 cm^{-1} identify Lewis acid sites (LAS). Using the constants of Emeis, a quantitative measure of BAS and LAS could be calculated.

The procedure has been described before by Kumar et al. from Abo Akademi but it had been slightly modified for this specific sample [24].

The first attempts (with the initial procedure) were not satisfactory; the sample broke every time, it was not consistent enough. After a thermogravimetric analysis (TGA), temperatures of the protocol were changed in a way that the sample could stand the temperatures and not break itself.

Nevertheless, in the range where Brøwnsted and Lewis acids appear, there was not obtained any spectra.

To conclude, the changes on temperature of the followed method were suitable but the sample does not have Brøwnsted and / or Lewis acid sites.

6.1.3. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

This technique was performed by a microwave digestion (the samples have been digested in Teflon ® and glass) and a quantitative analysis of zinc by using Optical Emission Spectroscopy (ICP-OES) were done, twice.

The results are the following:

Table 1. Several zinc glutarate measurements with ICP-OES

Sample	**Zn (213.857nm) mg/g**
ZnGA_1	320
ZnGA_2	362
ZnGA_3	368
ZnGA_4	362

This technique characterizes the amount of zinc that the sample has in it (an average of 353 mg Zn / g catalyst).

6.1.4. Light Scattering (LS)

As zinc glutarate was not integrated in the library of components from the software, the component chosen for characterizing the sample was just zinc. The refraction index (RI) of the sample, based on zinc, was then impose and maintained at 2.008. To compare with the measurements made at The University of Valladolid, the refraction index was then modified to 1.54.

The liquid level of the beaker was also searched for being equal in each attempt, around 400 ml.

The sample was mixed in distilled water with a vigorous agitation (around 1500 rpm) trying to avoid the creation of air bubbles inside the liquid so the particle distribution would not be disturbing.

Using a pump that is integrated in the equipment, the water with the catalyst particles was driven inside the equipment and also returned to the beaker. Each sample had six single measurements.

All the measurements have been made at least twice, particularly in liquid medium where they were repeated three times.

In the case of the measurement in distillate water, the liquid phase created a non-desirable effect in particle sizes that could be seen from the second measurement.

It is known that zinc glutarate is not soluble in most of the solvents so distillate water was selected as the aqueous phase for the method [12].

6.1.4.1. Light Scattering in aqueous phase

For the first two experiments the mass of the catalyst was 0.59 g, while for the third one, was 0.32 g. The liquid level of the beaker was also searched for being equal in each attempt. This was 450 ml for the first two measurements and 400 ml for the last one.

The sample was mixed in distilled water with a vigorous agitation (around 1500 rpm) trying to avoid the creation of air bubbles inside the liquid so the particle distribution would not be disturbing.

Using a pump that is integrated in the equipment, the water with the suspended catalyst particles was driven inside the equipment and also returned to the beaker.

Each sample had six single measurements.

The next results show the average particle size distribution of the samples made in distillate water.

-First sample-

Zinc glutarate was not part of the chemicals integrated in the library of the equipment (Mastersizer 3000, Malvern) so it was selected just as zinc. The refraction index (RI) of the sample, based on zinc, was then imposed and maintained at 2.008.

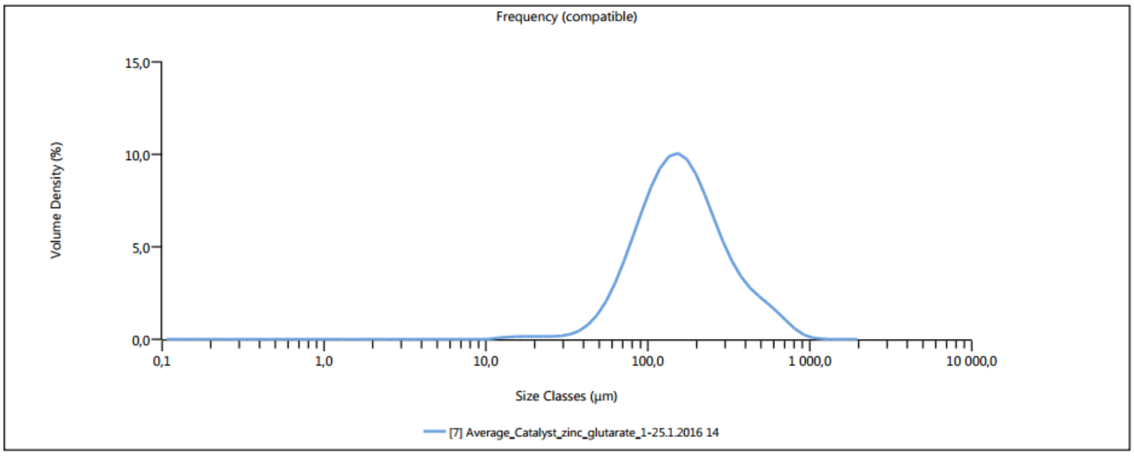


Figure 7. Particle size distribution of zinc glutarate in water. First sample.

Figure 7 shows just one peak what means that the material was not polydisperse and its representation was unimodal.

A quantitative analysis of the size distribution from this first sample is shown in the table below:

Table 2. Particle size distribution from the first sample.

Specific surface area	**Dx10**	**Dx50**	**Dx90**	**Laser obscuracion**	**Residual**
(m^2/kg)	***(µm)***	***(µm)***	***(µm)***	***(%)***	***(%)***
46.74	73	157	378	2.74	12.7

It is remarkable that the 50% of the sample had a size of 157 µm with a specific surface area of the particle of 46.74 m^2/kg.

-Second sample-

For the second sample, taking into account also that the system was going to recognize zinc as the sample, the refraction index selected was the refraction index of the measurements made in University of Valladolid, it was 1.54 (as this parameter can be modified).

This second sample showed a different behaviour from the previous one. This size distribution followed a bimodal representation from a material that seemed to be a polydispersity one.

Some particle agglomeration process was taking place there between catalyst particles and water but not a soluble process. Zinc glutarate is not soluble in water and in other solvents just in acidic solutions (pH < 2) [18, 22].

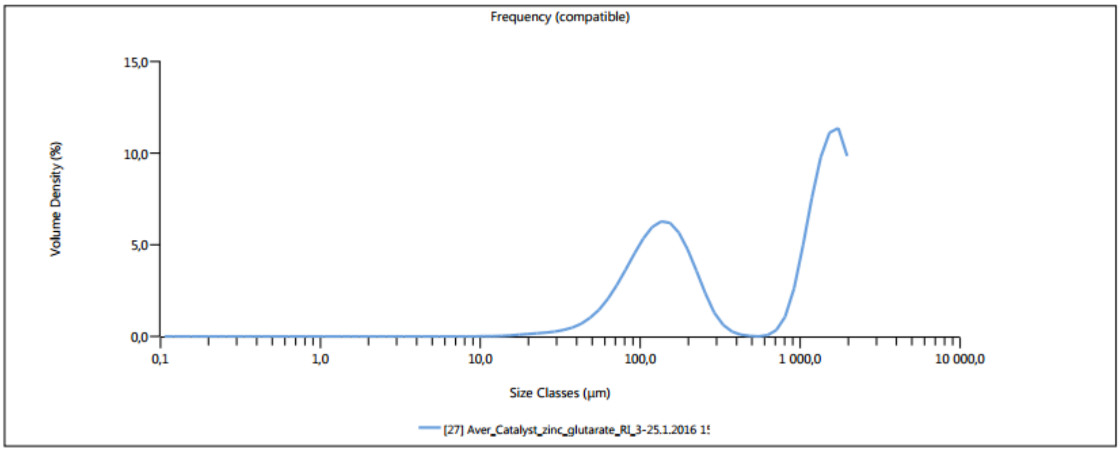


Figure 8. Particle size distribution of zinc glutarate in water. Second sample.

The first peak is not as high as the one obtained in the first sample, where the volume density raised 10 %.

The particle distribution corresponding to the second sample is showing in Table 3:

Table 3. Particle size distribution from the second sample.

Specific surface area	**Dx10**	**Dx50**	**Dx90**	**Laser obscuracion**	**Residual**
(m^2/kg)	***(μm)***	***(μm)***	***(μm)***	***(%)***	***(%)***
30.74	82	350	1821	1.77	6.4

The 50 % of the sample has a size of 350 µm, higher than the previous one, with a specific surface area of the particle of 30.74 m^2 / kg, what means that fewer particles are suspended in the liquid phase (agglomeration process).

-Third sample-

The particle size distribution for the experiment was:

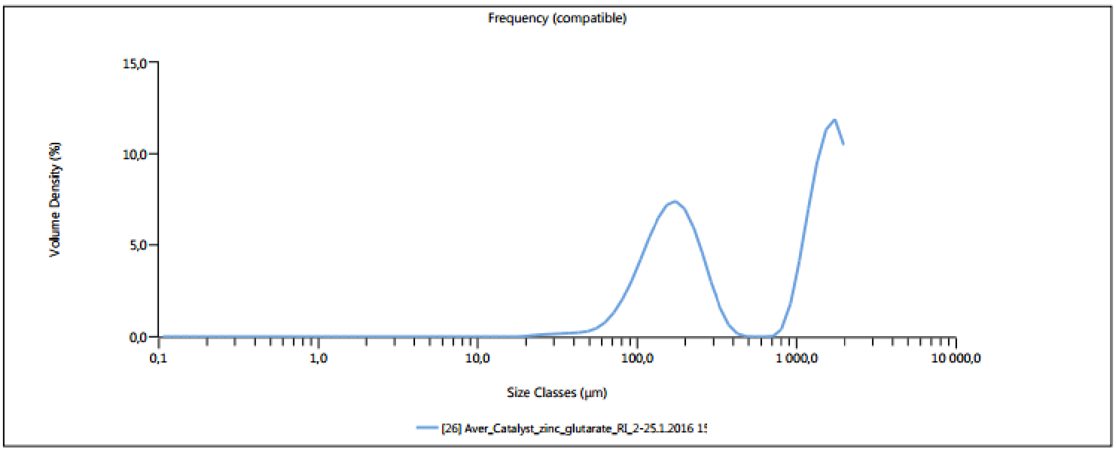


Figure 9. Particle size distribution of zinc glutarate in water. Third sample.

Also in this measurement a second peak appeared. The sample studied was a new one, as in the second sample, but in the system remained particles from the first sample, suspended in the medium; even washing the solution several times.

The results are:

Table 4. Particle size distribution of the third sample.

Specific surface area	**Dx10**	**Dx50**	**Dx90**	**Laser obscuracion**	**Residual**
(m^2 / kg)	*(µm)*	*(µm)*	*(µm)*	*(%)*	*(%)*
24.60	108	307	1836	0.55	21.0

The 50 % of the sample has a size of 307 µm, which is considerable higher than the one before, with a specific surface area of the particle of 24.60 m^2 / kg, what means that fewer particles are suspended in the liquid phase (agglomeration process) from the previous measurements.

Laser obscuration is a parameter which show how opaque is the solution. This parameter decreased in each sample, from 2.74 to 0.55 %.

This means the laser cannot pass through the solution as easy as in the first experiment. Particle agglomeration process became the most certain answer of this phenomenon.

Later, all these results in water will be compared with the ones gotten from air measurements.

6.1.4.2. Light Scattering in air

Light scattering in air was done at the Chemical Engineering and Environmental Technology Department from the University of Valladolid. The equipment was the same as the one used at Åbo Akademi, in Turku but a different model. It was a Mastersizer 2000, Malvern.

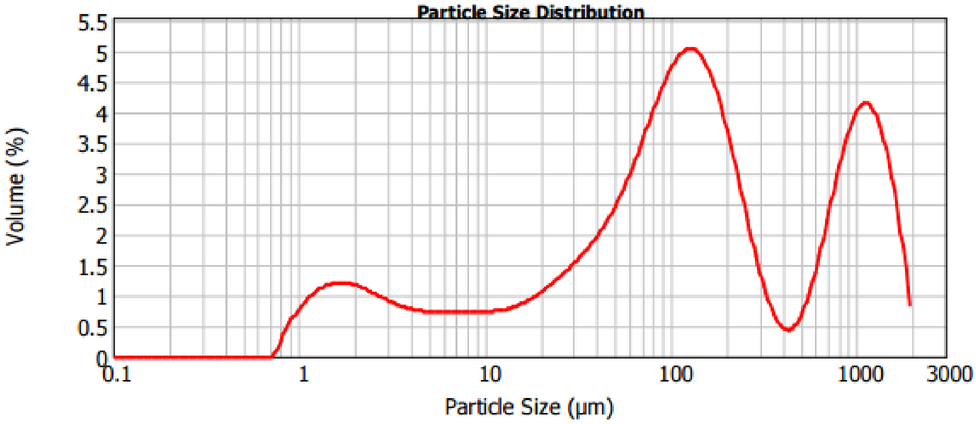


Figure 10. Particle size distribution of zinc glutarate in air.

Three peaks at very different particle sizes were obtained (considering a refraction index of 1.52). Figure 11 shows a multimodal distribution of a catalyst that has a high polydispersity.

Table 1 specify the size distribution of zinc glutarate in air as a medium of analysis.

Table 5. Particle size (μm) of the catalyst

Specific surface area	**Dx10**	**Dx50**	**Dx90**	**Laser obscuracion**	**Residual**
(m^2 / kg)	*(μm)*	*(μm)*	*(μm)*	*(%)*	*(%)*
475	4	118	1167	1.38	0.5

As it can be appreciated, 50% of the material has a diameter of the particle of 118.2 μm. This result is similar as the first experiment made in distilled water (157 μm). However, this distribution is multimodal but not the one showed in Figure 8.

A comparative table is shown below in Table 6.

Table 6. Comparative table of light scattering data.

Medium	**# Sample**	**Specific surface area**	**Dx10**	**Dx50**	**Dx90**	**Laser obscuracion**	**Residual**
		(m^2 / kg)	*(μm)*	*(μm)*	*(μm)*	*(%)*	*(%)*
Water	1	46.74	73	157	378	2.74	12.7
Water	2	30.74	82	350	1821	1.77	6.4
Water	3	24.60	108	307	1836	0.55	21.0
Air	1	475.00	4	118	1167	1.38	0.5

The results are not accurate among them. Samples 2 and 3 in water shows similar size distributions but there were several suspended particles from the first measurement in the equipment so they are not certain values.

The specific surface area in the air measurement is 10 times larger than the first one gotten from water.

As it can be appreciated from the respectively figures, the first peak in the air measurement appears at smaller particle sizes (4 µm) and finishes at higher sizes (1167 µm) what results in a bigger final surface area of the sample. That is the reason of this huge difference between surface areas. Besides, parameter Dx50 in both cases had really near values. So, it is possible to conclude that the results from the first experiment in water and the experiment in air can be considered similar.

Surface area, crystallinity and crystallinity perfectness influence on the catalytic activity of the catalyst [11, 25].

Usually if the catalyst is heterogeneous, larger particles lead to smaller surface area which affects in the activity of the catalyst. Herein (considering sample 1 and sample 4 from Table 6), the average of the particle size is 138 µm. This value is around ten times bigger than the largest one gotten by Kim et al (15.3 µm) and 25 times bigger than the particle size of the zinc glutarate catalyst synthesized from zinc oxide, glutaric acid and toluene (5.7 µm) [11].

According with the arguments presented previously, as the zinc glutarate synthesized here has larger particle sizes, it is completely coherent to have surface area values considerable smaller (shown in Table 2) than those obtained from Kim et al.

However, they have demonstrated that using an amphiphilic block copolymer [Pluronic PE6400: poly (ethylene glycol)-block-poly (propylene glycol)-block poly (ethylene glycol)] in the synthesis of zinc glutarate it is possible to increase the surface area of this catalyst.

6.1.5. Nitrogen - physisorption

The equipment used for nitrogen – physisorption was described in the section 3.2.1.4. After the burette was under outgassing conditions, 0.25 g of the sample was placed inside it. Previously to be analysed, the burette with the catalyst inside was under 0.01 Pa, 150 ºC during an outgassing of 3 h. It was possible to calculate the mass lost after the outgassing. That mass corresponded to the water of the sample (moisture) that had been removed.

It is remarkable that practically not water was lost during the outgassing (4.5 %). No isotherms were found. Microporous with Dubinin surface area calculation method and Horvath-Kawazoe pore size calculation method were chosen to conclude that this material is not porous. The specific surface area in this sample is practically negligible meaning that zinc particles correspond to the active sites of the catalyst.

While in the analysis no results were found about surface area or volume of porous, Kim et al. synthesized different zinc glutarates from several sources and methods and studied the surface area by nitrogen adsorption obtaining values between 19-34 m^2/g [16].

It is known that one catalyst with low surface area but the best crystal properties shows the highest catalytic activity. Nevertheless, morphological parameters are the factors that influence more the catalytic activity than surface area [16, 26].

In the section 6.1.8, crystallinity of the zinc glutarate will be shown and then it will be possible to make a decision about the catalytic activity of the catalyst.

6.1.6. Scanning Electron Microscopy and Energy-Dispersive X-ray analysis (SEM and SEM-EDX)

6.1.6.1. Scanning Electron Microscopy (SEM)

Zinc glutarate obtained has a rectangular plate shape with different thicknesses and sizes. At two scales (µm and nm), it is possible to characterize the catalyst (see Figure 11 and Figure 12).

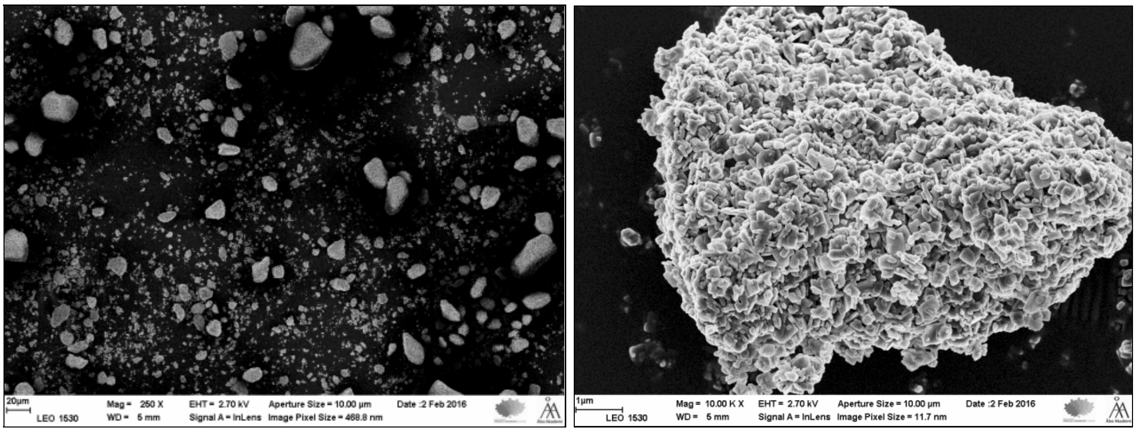


Figure 11. SEM images of zinc glutarate.

Several studies have identified the morphology of zinc glutarate. Depending on the way to synthesis, the size and shape of the particles are different; it is wrinkled petal bundle morphology [18], rectangular plate morphology [11] like in this chapter, agglomerated particles, etc.

In Figure 12, four different SEM images from zinc glutarate catalyst are taken at a zoom of 200 nm.

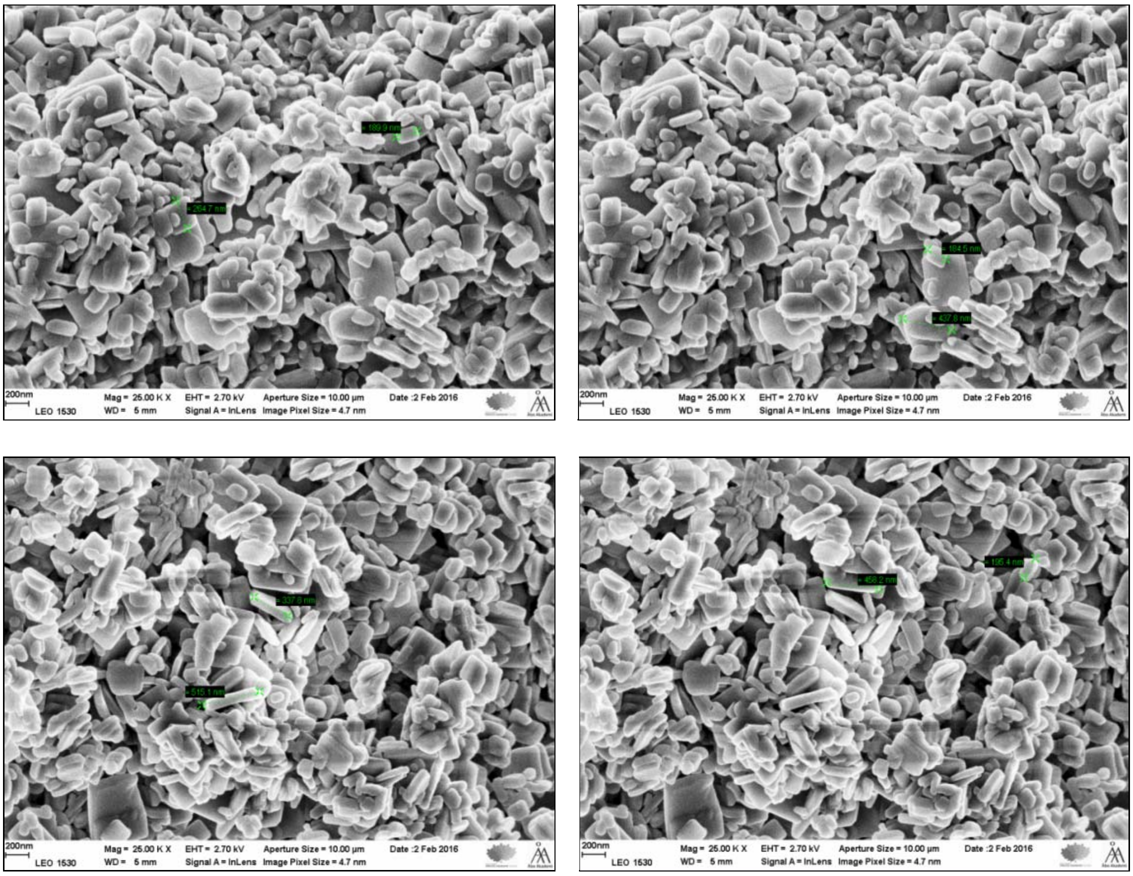


Figure 12. SEM images showing different particles sizes (nm)

Particle sizes goes from 180-520 nm, being the average size 321.6 nm. The sample is really polydispersed, as it has been explained in light scattering results.

Figure 13 shows clearer SEM images at 1µm and 100000 x as magnification of the image:

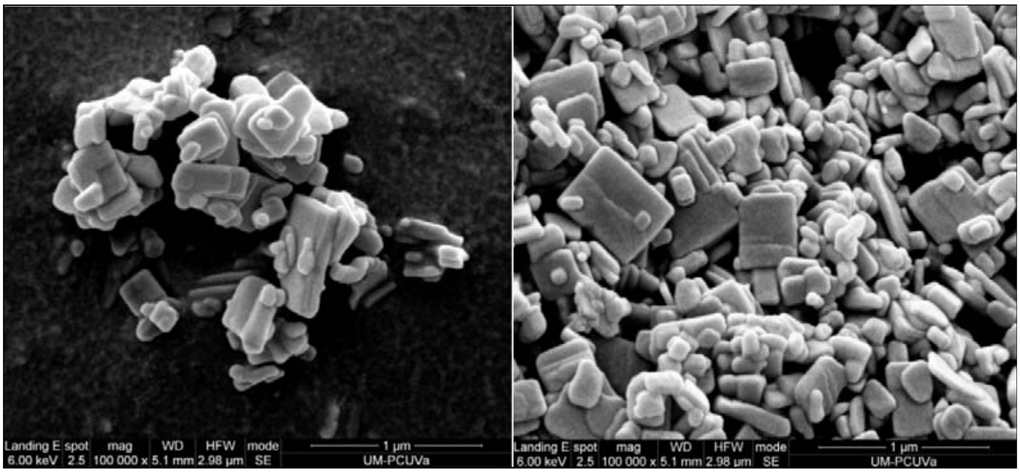


Figure 13. SEM images showing different particles sizes (nm)

6.1.6.2. Scanning Electron Microscopy Energy–dispersive X-ray spectroscopy (*SEM-EDX*)

Through this analysis, the percentage of each component in the sample was defined, which gives important information about the catalyst.

Figure 14 shows the two zones where the analysis has been done. Surface 1 is a wide area while Surface 2 is focus on the surface of one particle. The results from both zones are, logically, not the same.

For this analysis, the equipment gave information about the voltage (15.0 kV), the pixel size of the image (1.18 µm), the magnification of the image (100) and the resolution of the image (1024 by 768).

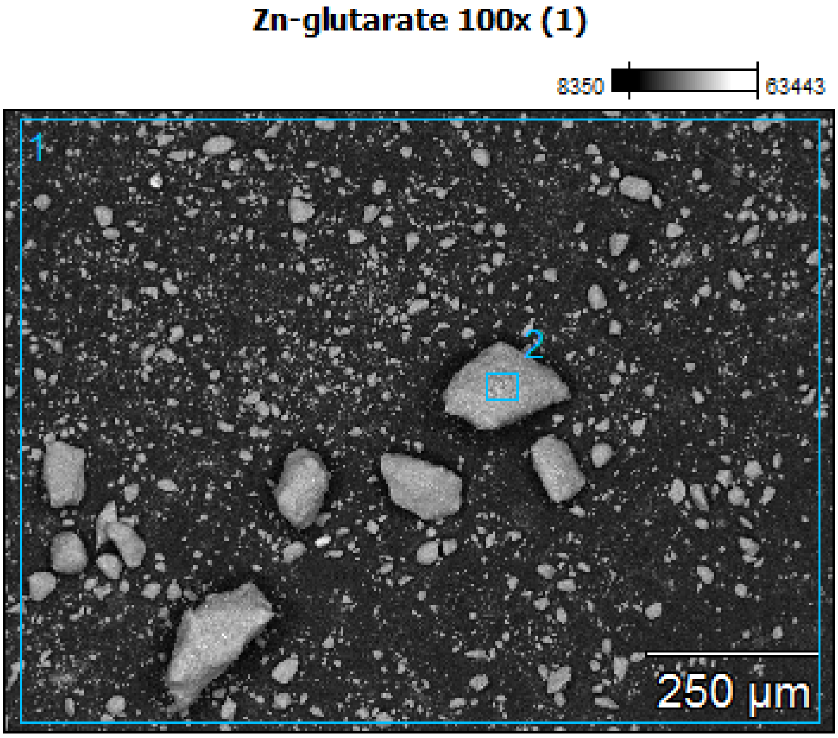


Figure 14. SEM-EDX analysis for ZnGA. Surface 1 and Surface 2 are shown in blue colour.

The results from Surface 1 are the following:

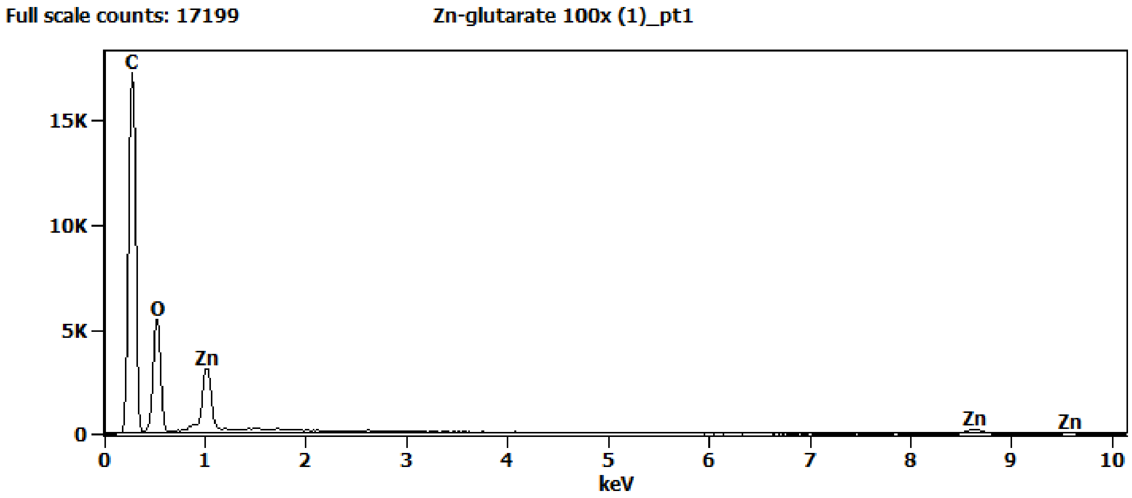


Figure 15. Spectra of the Surface 1.

Here it is demonstrated that if the area is wide, the major component corresponds to carbon followed by oxygen and zinc.

On the other hand, if the analysis is focussed on the surface of one particle, the major component is zinc followed by oxygen and carbon.

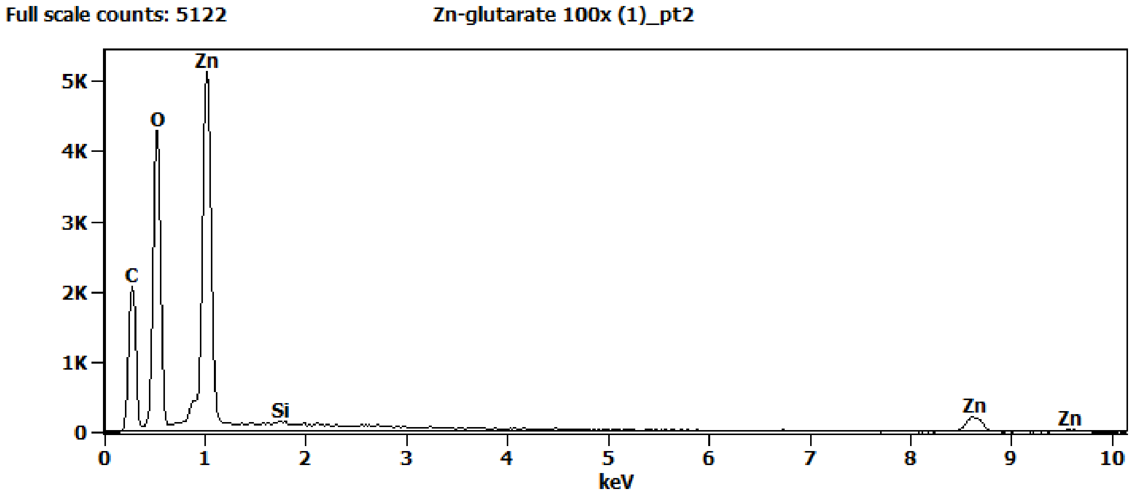


Figure 16. Spectra of the Surface 2

A quantitative analysis is presented in the following tables, Table 7 to Table 10.

Table 7. Weight percentage of the elements from both surfaces

Surface	Sample	O-K	Zn-K	Si-K
1	Zinc glutarate	57.00	43.00	--
2	Zinc glutarate	49.57	50.00	0.43

Oxygen is the component that abundant more in the surface 1 while zinc is the major one in the surface 2, closed value to oxygen one.

In Table 8 it is shown the error (%) of each component in the measurement.

Table 8. Weight % Error (+/- 1 Sigma) of the elements from both surfaces

Surface	Sample	O-K	Zn-K	Si-K
1	Zinc glutarate	± 0.52	± 1.95	--
2	Zinc glutarate	± 0.46	± 1.84	± 0.06

In terms of atom percentage in both surfaces, more atoms of oxygen are presented in surface 1 and in surface 2.

Table 9. Atom % of the elements from both surfaces

Surface	Sample	O-K	Zn-K	Si-K
1	Zinc glutarate	84.42	15.58	--
2	Zinc glutarate	79.89	19.72	0.39

In Table 10 it is shown the error (%) of each atom in the measurement.

Table 10. Atom % error (+/- 1 Sigma) of the elements from both surfaces

Surface	Sample	O-K	Zn-K	Si-K
1	Zinc glutarate	± 0.78	± 0.71	--
2	Zinc glutarate	± 0.74	± 0.72	± 0.06

6.1.7. Transmission electron microscopy (TEM)

Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis.

Results are shown in Figure 17.

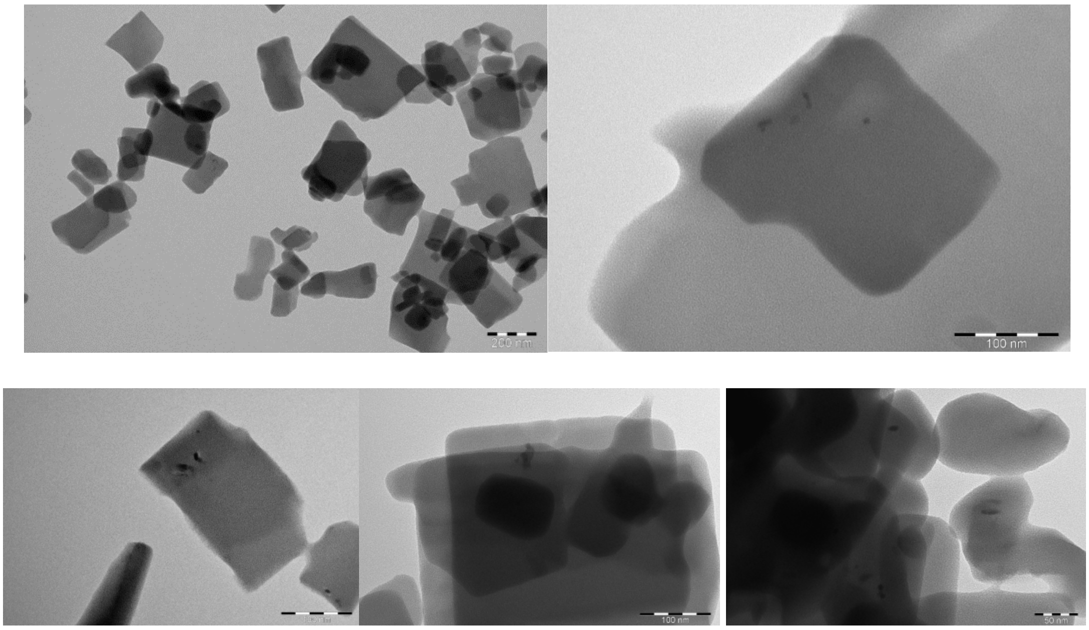


Figure 17. TEM micrographs of ZnGA catalyst.

The darker areas corresponds to zinc particles and the lighter ones corresponds to the glutarate part of the catalyst. Figure 17 settle the same as N_2-physisorption analysis, the surface area of this catalyst is really small because, as it has been explained before, zinc is the active site of the catalyst and it is not located at the outer side of the particles.

6.1.8. TGA / DTA-MS (Thermogravimetric Analysis / Differential Thermal Analysis-Mass Spectrometry)

As it was explained in section 3.2.1.1, analysing the sample by FTIR with pyridine the catalyst wafer broke at every experiment.

The catalyst did not stand the high temperatures of the initial procedure so a TGA / DTA-MS analysis was done to determine the stability of the sample [27].

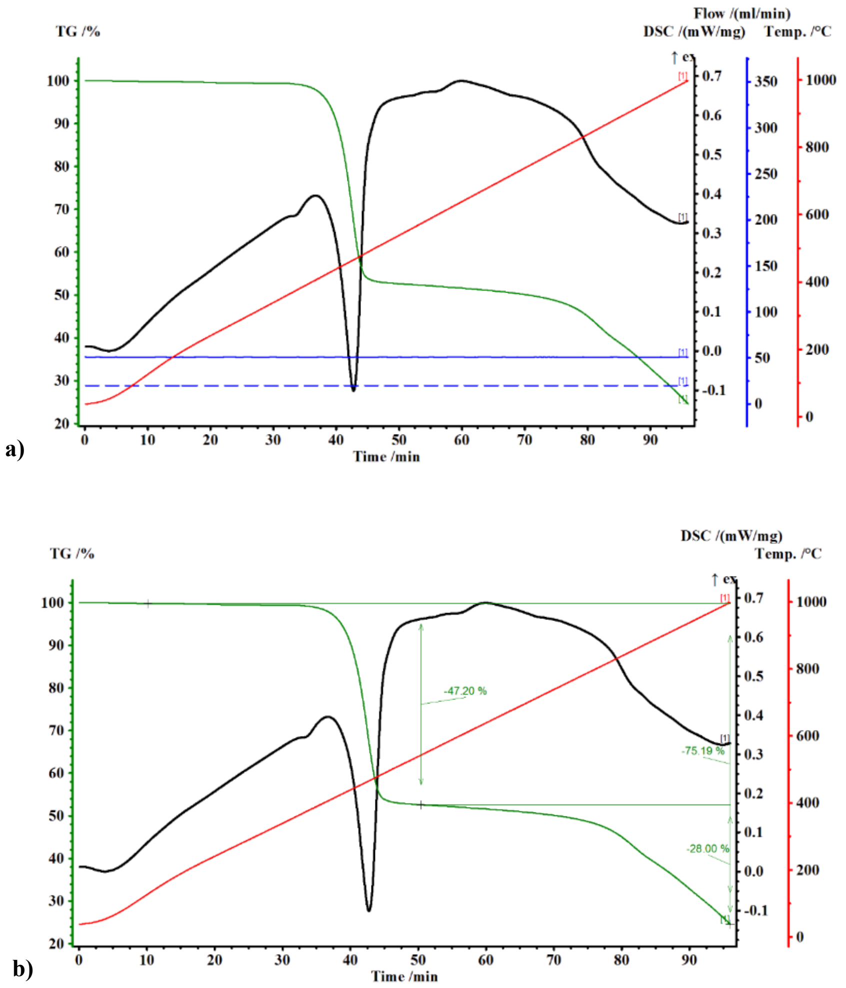


Figure 18 a) and b). TGA diagrams of the ZnGA catalyst.

The red line corresponds to the temperature profile imposed for the analysis. The green line represents the weight loss of the sample due to the slow pyrolysis procedure applied (basis of the TGA), where it can be seen the stability of the ZnGA vs temperature. The black line indicates the numerical estimation of the temperature derivative with time (DTGA).

The maximum of the latter line indicates that clearly the catalyst decomposes at around 400ºC, probably due to the glutarate gasification.

The initial decomposition temperature of the sample is the temperature where the material started to disintegrate and it is the measure of its thermal stability. At 400 ºC the catalyst decomposition started so, because of that, the temperatures of the FTIR with pyridine procedure were modified to lower ones.

The sample is still being decomposed up to 1000 ºC [28, 29], a remaining ash inorganic content of 25% was found.

6.1.9. XPS

Zinc glutarate catalyst was also characterized by XPS by a number of authors [11, 18, 30, 31]. The oxidation of each element was determined by this technique. The results are depicted in Figure 19.

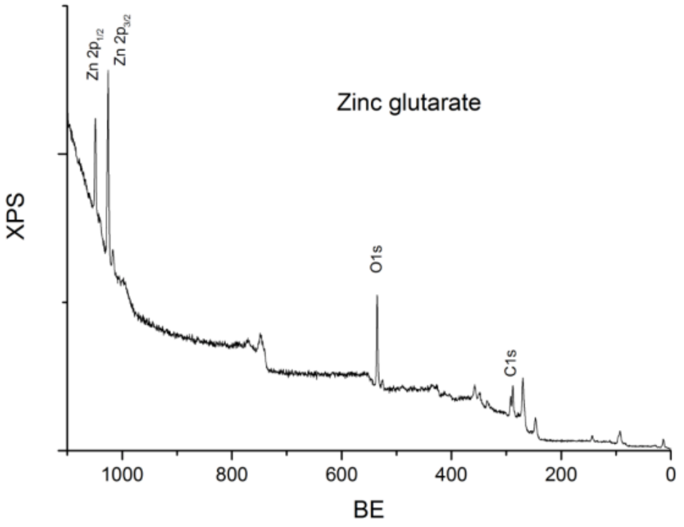


Figure 19. XPS spectrum of zinc glutarate sample.

Here it is shown the spectra of the entire sample. In the next figures, each peak will be explained individually.

1. The **carbon spectrum** was:

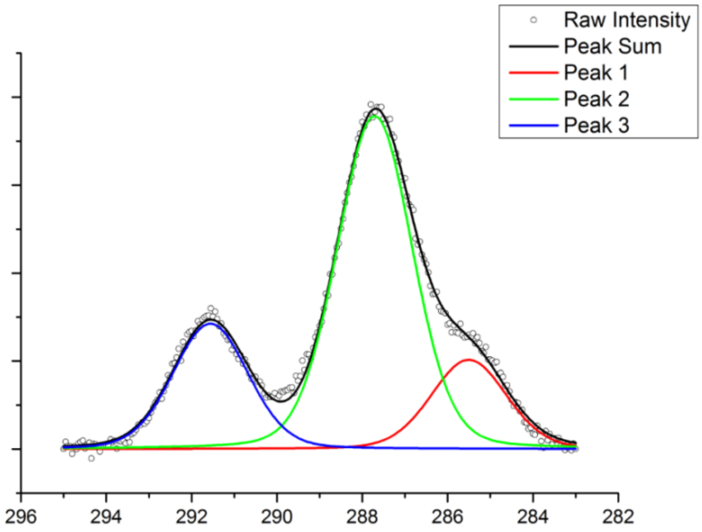


Figure 20. XPS spectrum of carbon with fitted peaks - Carbon

Each peak gives idea about the **carbon bonds** in the catalyst. Considering the binding energy (eV), it is possible to identify the type of compound bond.

This spectrum has to be shift 3 units to the right to adequate it to the correct values of binding energy (the equipment can be charged when it is receiving the beam; normally, the spectrum moves to higher binding energies).

See Figure 1 to review the molecular formula of the catalyst to make easy the identification of the bonds.

From left to the right, the corrected peak 3 (288.8 eV) correspond to a carboxylic bond (C with O), the second corrected one (284.8 eV) correspond to a carbon bond (C with C) and the corrected peak 1 (282.8 eV) corresponds to carbide bond (C-H).

2. The **oxygen spectrum** was:

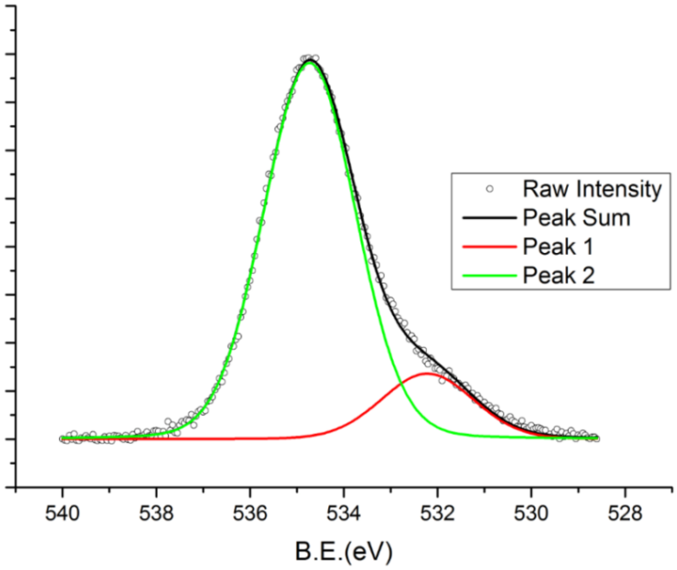


Figure 21. XPS spectrum of carbon with fitted peaks - Oxygen

The oxygen XPS spectrum has also to be shifted to the right scale. Peak 1 (531.5 eV) and in this case, peak 2 (529.2 eV) both shows metal oxide bonds. It has sense because the catalyst was prepared from zinc oxide (ZnO).

3. The **zinc spectrum** was:

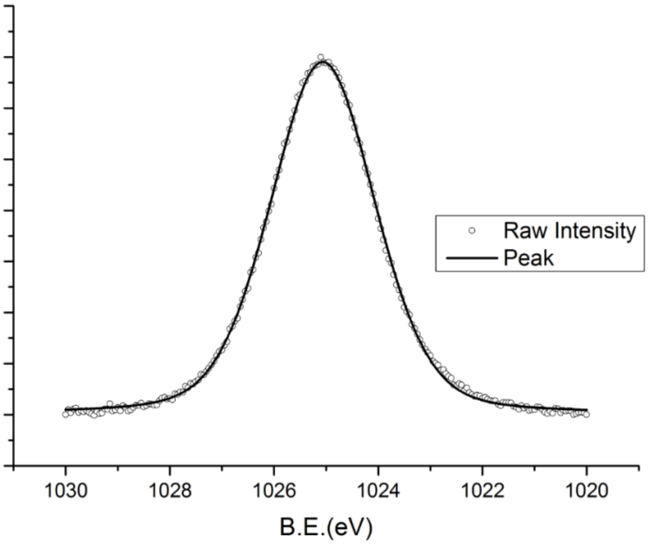


Figure 22. XPS spectrum of zinc with fitted peak - Zinc

Zinc is only appearing in its oxidation state (2+). The corrected peak is located at 1022 eV which corresponds to a ZnO compound type.

6.1.10. X-RAY DIFFRACTION

The measured 2θ angle range was 6.6° - 65.0° with a step size of 0.026° and a measurement time of 100 s per step. The diffractogram obtained is shown in Figure 23. To determine the single crystal structure, peaks appear at the same position as it is shown in literature [18]. That is a measure about no impurities phases are in the sample.

The data quality for the measurement is much better than in that article which means that the peaks are well shaped and there is much less noise. The main peaks are shown in Table 11.

Table 11. Position and angle of every peak of the diffractogram of zinc glutarate catalyst

No.	Position [°2Theta]	No.	Position [°2Theta]
1	12.82	24	41.00
2	18.63	25	41.30
3	19.24	26	42.63
4	19.71	27	43.40
5	20.34	28	44.68
6	20.98	29	45.58
7	21.97	30	46.16
8	22.64	31	46.89
9	23.04	32	47.51
10	23.23	33	48.08
11	25.68	34	50.27
12	26.85	35	51.35
13	28.58	36	52.65
14	29.91	37	53.56
15	31.88	38	55.24
16	32.42	39	56.29
17	33.39	40	57.03
18	34.51	41	59.17
19	36.34	42	59.96
20	37.68	43	61.49
21	38.93	44	62.05
22	39.48	45	63.13
23	39.92	46	64.36

Zinc glutarate catalysts were described elsewhere [11, 18, 22, 32]. Zn^{II} centers of the crystal are coordinated with four carboxyl oxygen atoms on different glutarate ligands via four syn–anti bridges. Ree et al., defined the final geometry obtained as a distorted tetrahedral one.

A monoclinic unit cell with a P2/c space group has been determined for ZnGA [11]. Lattice parameters are define as a = 13.934 (3) Å, b = 4.7842 (11) Å, c = 9.276 (2) Å and β = 90.628 (5) °.

CSD database (Feb 2016, version 5.37), ISCD database and the PDF-2 database were consulted and it was not able to find any crystal structure reference data for zinc glutarate. In some articles, the samples are just compared with a reference ZnGA sample and it is concluded whether the crystal structures match or not (the diffraction peak patterns are simply compared).

So it is almost unavoidable to conclude that this catalyst is not included in any database. One possible reason could be that there is no agreement on the indexing of the structure (reference quality is insufficient to make an appearance in the database).

Ang et al. suggested that among three different zinc glutarates synthesized from several zinc sources, the crystal structure is almost identical [33]. However, the overall crystallinity shows that the one synthesized by zinc oxide (ZnO) and glutaric acid (GA) is the most crystalline (which furthermore, is the one which achieved the highest yield in polymerization reactions with CO_2 [11, 34]); the chosen ones for synthesize the catalyst in this chapter.

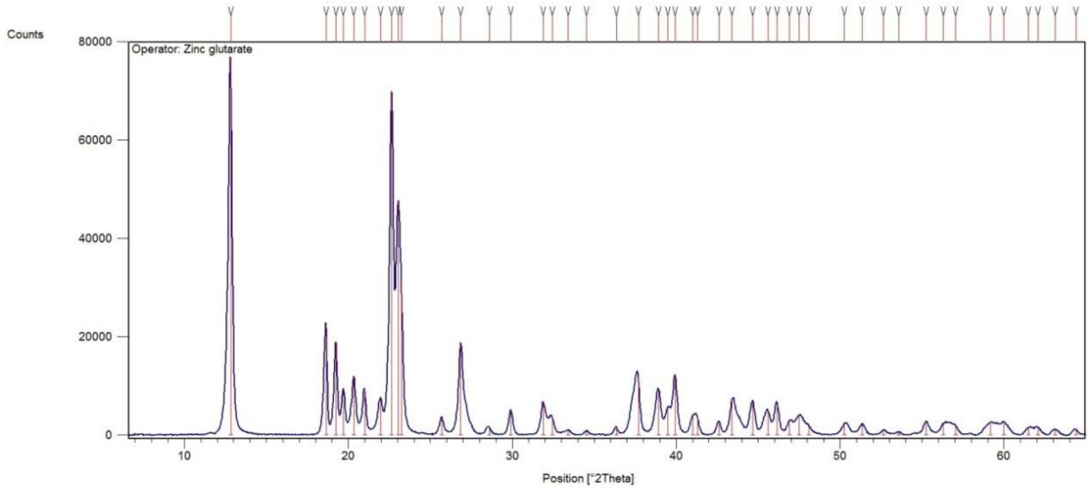


Figure 23. Measured and background corrected diffractogram of zinc glutarate catalyst. Detected diffraction peaks are represented by red lines.

The measured and background corrected zinc glutarate diffractogram is presented in Figure 19. The Cu sample holder may partially contribute to the peaks detected at **2θ = 43.4° and 50.3°**, as the peak positions coincide with the Cu (111) and Cu (200) peak positions.

6.2. POLY (PROPYLENE CARBONATE)

To analyse the polymers from the copolymerization reactions, several techniques have been employed.

The samples analysed had no post-treatment, so the results are directly representing what there was inside the reactor.

It is possible to separate the polymer by first, adding 400 ml of methylene chloride. After it, the catalyst can be removed using 400 ml of a solution of hydrochloric acid diluted and washing it with the same amount of distilled water [22]. Using a rotavapor the product is concentrated, mixed with an excess of methanol and finally, a make-up step is needed to get the polymer.

As it was described in section 5, one of the goals of this study was to achieve successful copolymerization reactions using zinc glutarate as the catalyst.

Using FTIR and SEC, it was possible to determine if the copolymerization reactions had taken place. Variables such as mass of catalyst, reaction temperature, reaction pressure, molecular weight of the final polymer and reaction time were studied to define the optimal reaction conditions.

6.2.1. Fourier Transform infrared spectroscopy (FTIR)

Several studies have been done to characterize the final polymers. All the experiments have been done for a polymer with an expected final molecular weight of 3000 Da.

6.2.1.1. Effect of the amount of catalyst (g)

The first experiments were done varying the mass of catalyst but maintaining the rest of variables set.

As it is shown in *Table 7*, four different masses of catalyst have been considered. Each condition was repeated twice.

The spectra that are going to be presented in this section gives information corresponded to the main bonds created during the polymerization reactions.

At a wavelength around 1742 cm $^{-1}$, the peak corresponds to the carbonate bond, which is desired to be as higher as possible (PPC).

At around 1800 cm^{-1}, the peak corresponds to the formation of the by-product of this reaction, the cyclic carbonate (CC).

Finally, the last main peak corresponds to the possible free bonds (-OH) belong to the propylene glycol (PPG, starter of the reaction) at around 3400 cm^{-1}. As smaller it is, more amount of carbonate bonds have been created during the reaction, meaning it has been a successful one.

Table 12. Reaction conditions of mass variation experiments

# Experiment	Sample	$m_{CATALYST}$ (g)	m_{PPG} (g)	m_{PO} (g)	P (barg)	T (°C)
1	S1	**0.3**	10.0	55.4	7.5	61
2	S2	**0.3**	10.1	55.3	6.2	61
3	S3	**0.6**	10.1	55.7	6.2	61
4	S4	**0.6**	10.0	55.3	6.2	61
5	S5	**1.0**	10.2	56.3	6.2	61
6	S6	**1.0**	10.0	55.1	6.2	61
7	S7	**1.5**	9.9	54.8	6.2	61
8	S8	**1.5**	10.1	55.9	6.5	61

The FTIR of these samples is showed in Figure 24.

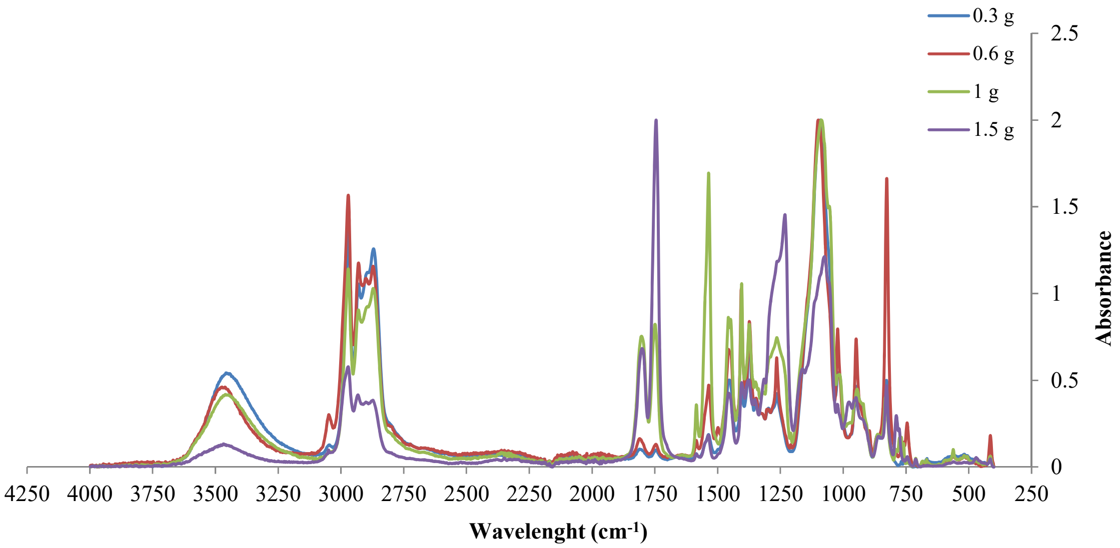


Figure 24. FTIR of the final polymer changing the amount of catalyst

Using 1.5 g of the catalyst, the highest amount of carbonate (~1742 cm^{-1}) and the less amount of possible free bonds belong from propylene glycol (~3456 cm^{-1}) were achieved. It was reasonable to obtain higher the peak corresponded to the amount of cyclic carbonate (~1800 cm^{-1}) at 1.5 g of catalyst than with less amount of ZnGA at the same time that the amount of free bonds are lower.

It can be concluded that the best condition of reaction corresponds at 1.5 g of catalyst.

6.2.1.2. Effect of the reaction pressure (barg)

Once, the optimal amount of catalyst has been determined, the variable to be studied was the pressure.

The experiments have been run at 5 and 25 barg.

Table 13. Reaction conditions of pressure variation experiments

# Experiment	Sample	$m_{CATALYST}$ (g)	m_{PPG} (g)	m_{PO} (g)	P (barg)	T (°C)
8	S8	1.5	10.1	55.9	**6.5**	61
10	S10	1.5	10.1	55.6	**25**	61

The FTIR of the samples correspond to Table 13 is showed in Figure 25.

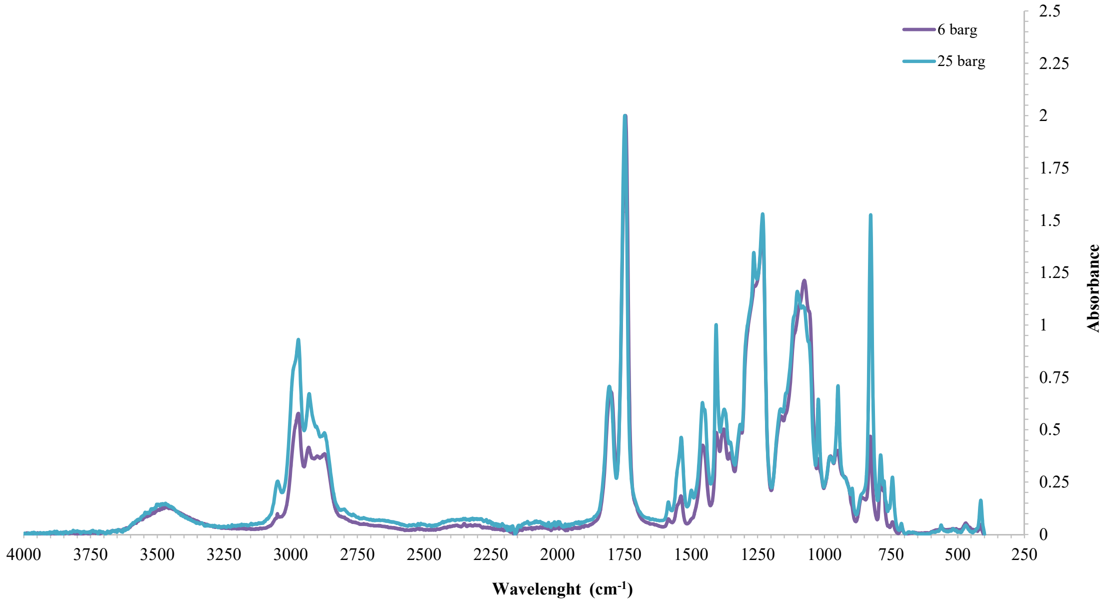


Figure 25. FTIR of the final polymer changing the reaction pressure.

Pressure is related with the CO_2 dissolved on the sample and with the carbonate formed.

As it can be appreciated, the effect of pressure is not completely negligible but the production of carbonate and cyclic carbonate is not really affected by it.

Part of the PO and CO_2 is soluble in PPG but part of this PO change the phase and remains in vapour phase and part of the CO_2 remains in gas phase.

The pressure of 5 barg is the minimum pressure for copolymerization reactions, so the decision was to select 25 barg as desired pressure, what let us a margin of temperatures to check.

6.2.1.3. Effect of reaction temperature (ºC)

So far, the conditions were 1.5 g of catalyst and a pressure of 25 barg. All those experiments were carried out at 61 ºC.

For the study of reaction temperature, two different temperatures were selected, 61 ºC and 81 ºC.

Table 14. Reaction conditions of reaction temperature variation experiments

# Experiment	Sample	$m_{CATALYST}$ (g)	m_{PPG} (g)	m_{PO} (g)	P (barg)	T (°C)
10	S10	1.5	10.1	55.6	25	**61**
11	S11	1.5	10.0	55.3	25	**81**
12	S12	1.5	10.0	55.5	25	**81**

Figure 26 shows the FTIR corresponded for the variation on temperature.

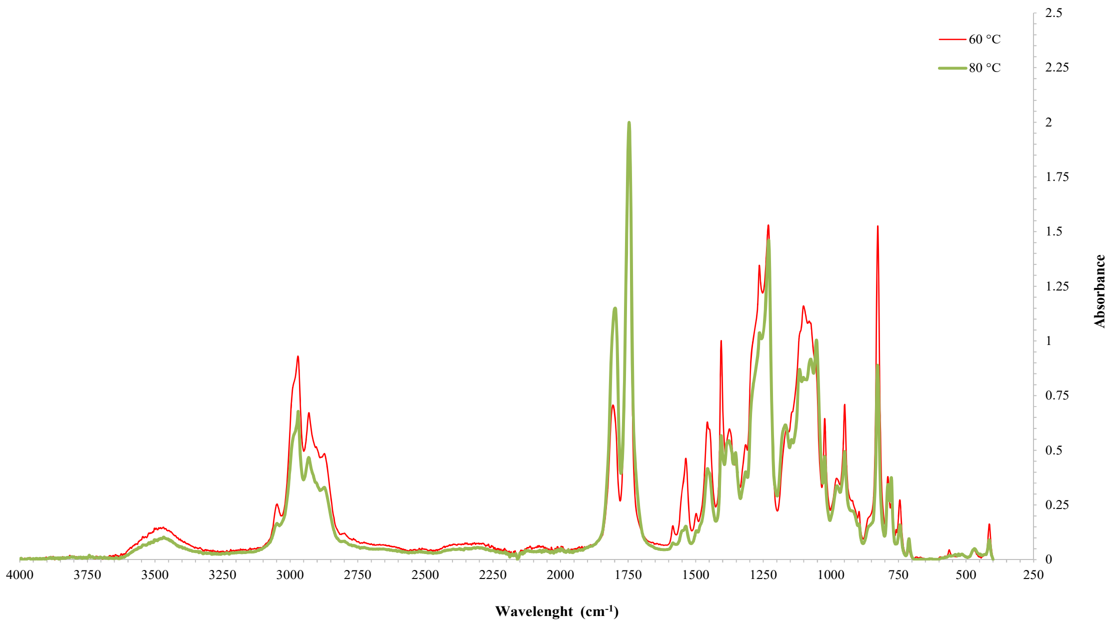


Figure 26. FTIR of the final polymer changing the reaction temperature.

This reaction was really slow so the differences between both temperatures were not significant in terms of carbonate production. Indeed, the production of polypropylene carbonate was practically the same in both cases. More byproduct was obtained as the temperature was increased but less possible alcohol bonds and less carboxylic and alkene bonds are obtained.

In any case, as kinetics is more favourable with temperature, the chosen one for the rest of the experiments was 80 ºC.

6.2.1.4. Variation of the expected final molecular weight (Da)

Until this moment, all the experiments were run considering a final polymer molecular weight of 3000 Da.

For the next experiment, this was the variable to be modified. The final molecular weight wanted was 725 Da.

In this case, only one experiment was done to get a polymer of 725 Da.

Table 15 and Figure 27, show the differences between this experiment (725 Da) and one previous (3000 Da) under the same conditions.

Table 15. Reaction conditions of the expected molecular weight variation experiments

MW (Da)	# Experiment	Sample	$m_{CATALYST}$ (g)	m_{PPG} (g)	m_{PO} (g)	P (barg)	T (°C)
3000	12	S12	1.5	10.0	55.5	25	81
725	13	S13	1.5	10.0	6.2	25	81

The amount of propylene oxide change depends on the final molecular weight of the polymer.

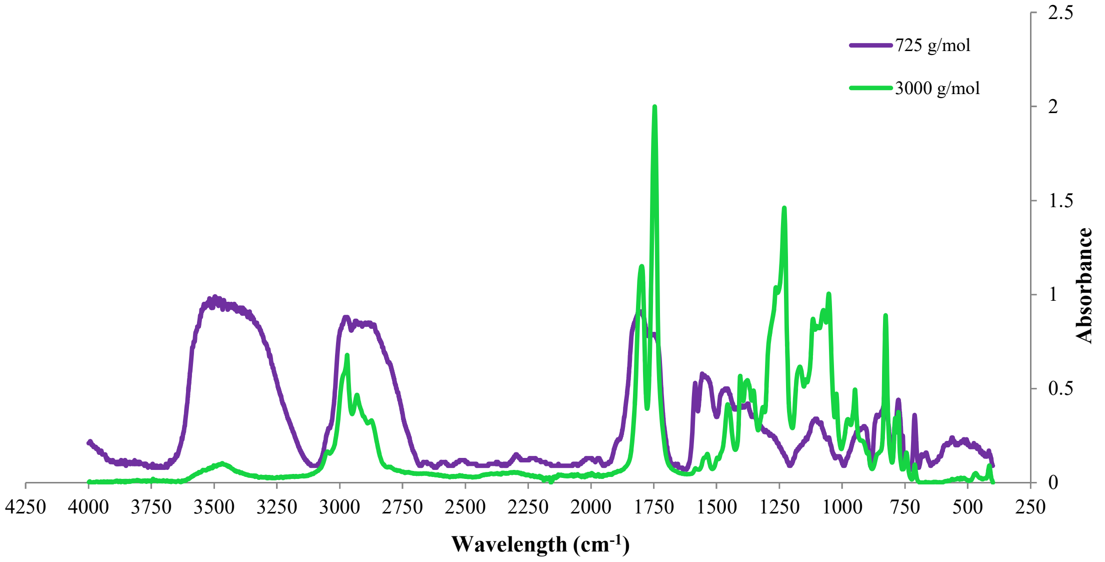


Figure 27. FTIR of the final polymer changing the expected final molecular weight.

The comparison of both spectra shows very clearly the differences if the reaction was taken place with less amount of reactants (PO and CO_2).

Practically, no reaction took place when the desired polymer has 725 Da. The green spectrum corresponds to a 3000 Da polymer. As it is shown in *Figure 25*, if the final molecular weight was 725 Da under the same reaction conditions (purple spectrum), there was a significant amount of –OH bonds unreacted and there was more cyclic carbonate than polypropylene carbonate.

6.2.1.5. Effect of the total reaction time (h)

Four experiments were carried out varying the reaction time from 40 h to 20 h as shown in *Table 11* and *Figure 26.*

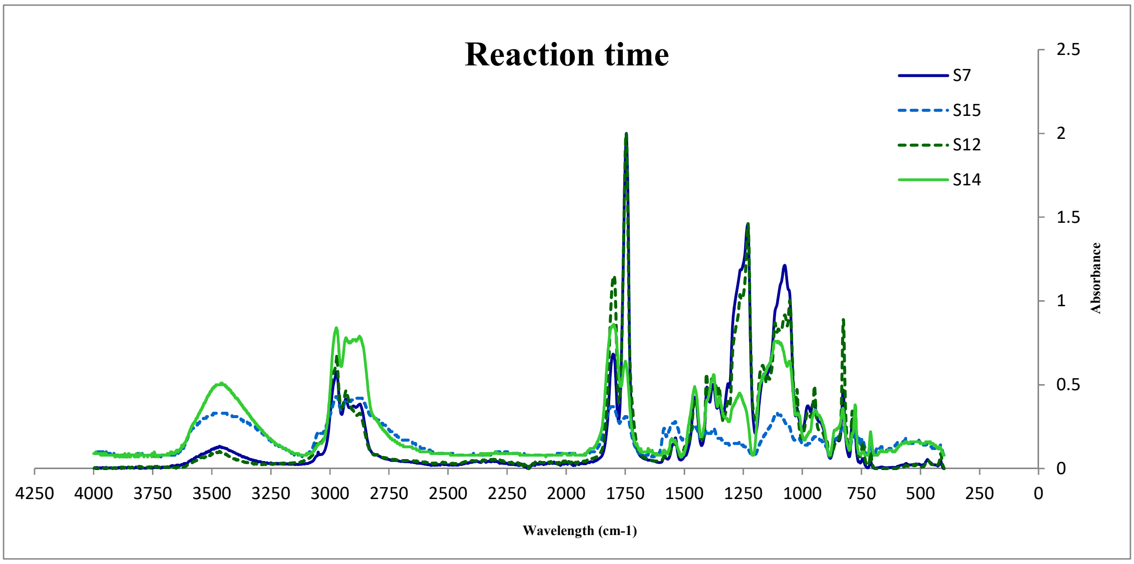
Experiments 7 and 15 were done under the same initial conditions (6 barg and 61 ºC) except the reaction time (40 and 20 h, respectively).

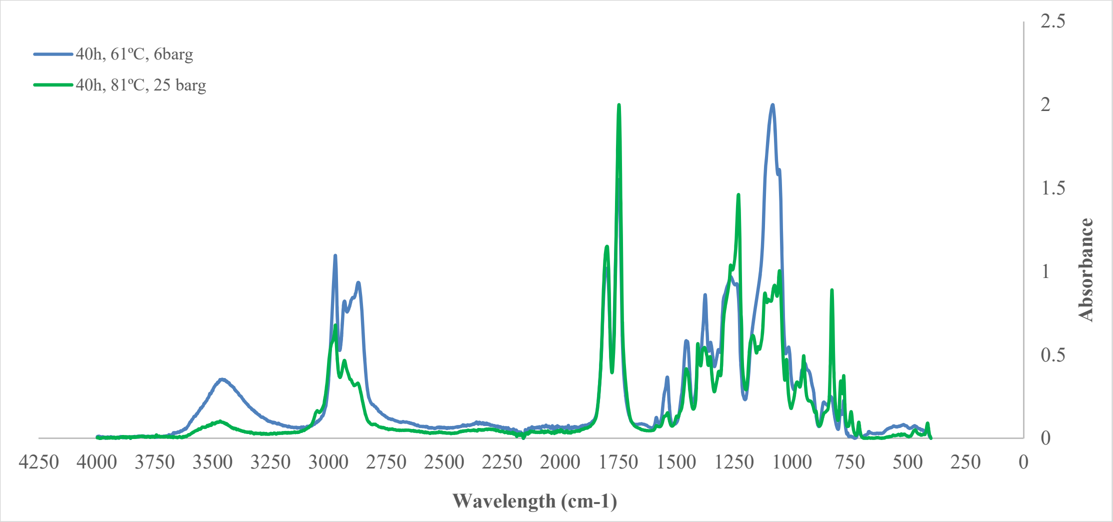
Experiments 12 and 14 (25 barg of reaction pressure and 81 ºC of reaction temperature) were run under the best conditions changing just the reaction time (40 and 20 h, respectively).

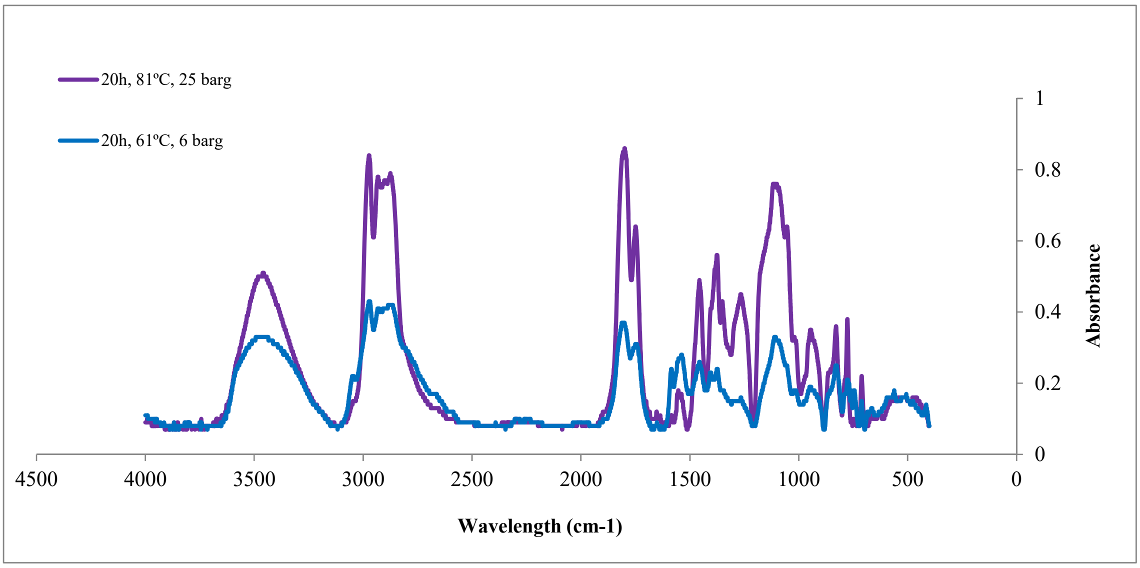
Table 16. Variation of reaction time.

MW (Da)	# Experiment	Sample	$m_{CATALYST}$ (g)	m_{PPG} (g)	m_{PO} (g)	P (barg)	T (°C)	$t_{reaction}$ (h)
3000	7	S7	1.5	9.9	54.8	6.2	61	**40**
3000	12	S12	1.5	10.0	55.5	25	81	**40**
3000	14	S14	1.5	10.1	55.6	25	81	**20**
3000	15	S15	1.5	10.2	56.4	6.0	61	**20**

The spectrum was the following:







Figures 28-30. FTIR comparison of final polymers changing the reaction time.

As the last figures showed, experiment 7 was run successfully comparing with experiment 15. A very high peak of polycarbonate was obtained in the experiment 7 while the peak correspond to the cyclic carbonate was smaller than in the conditions of the experiment 15.

Comparing experiments 12 and 14, it is clear than with less reaction time (exp.14) the product obtained is cyclic carbonate as a major component and not the poly (propylene carbonate).

This means that, considering only the same reaction time, it is possible to evaluate the influence of the rest variables in the final product. The more pressure, the most successful reaction product. If the reaction time is decreased, no successful product is obtained, independently of changes on the rest of variables.

6.2.2. Size Exclusion Chromatography (SEC)

Every product of each reaction was analysed by size-exclusion chromatography (SEC). The samples were not easily analysed by SEC because they were not completely soluble in THF, common solvent. A polystyrene calibration has been done and it determined that part of the sample was soluble in THF but that part just represented the lower molar mass material (< 1000 Da).

Figure a and 31 b show the calibration curves made by MW standards of polyethylene glycol. Figure a and 32 *b* show the normalized and overlaid SEC chromatograms.

For comparison, a polymer with a molecular weight around 3000 Da would elute at around 18 minutes.

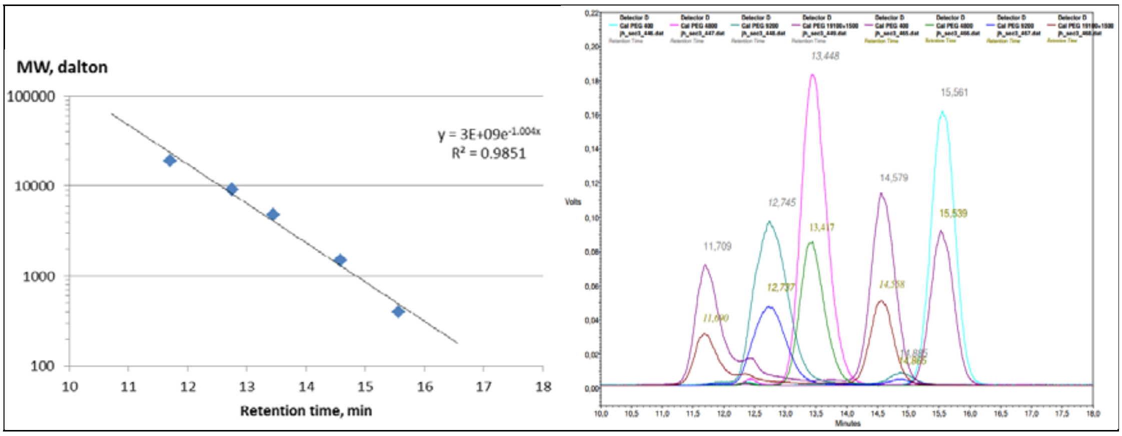


Figure 31 a and b. Calibration curve made with polyethylene glycol and HPSEC runs with molecular weight standards of polyethylene glycol

The calibration was made using a Jordi X-stream 50x10 mm + 300x10 mm column, the eluent was AcOH-MeOH-H2O 50:40:10, 1 ml/min and the detector was ELSD, Gain 3.

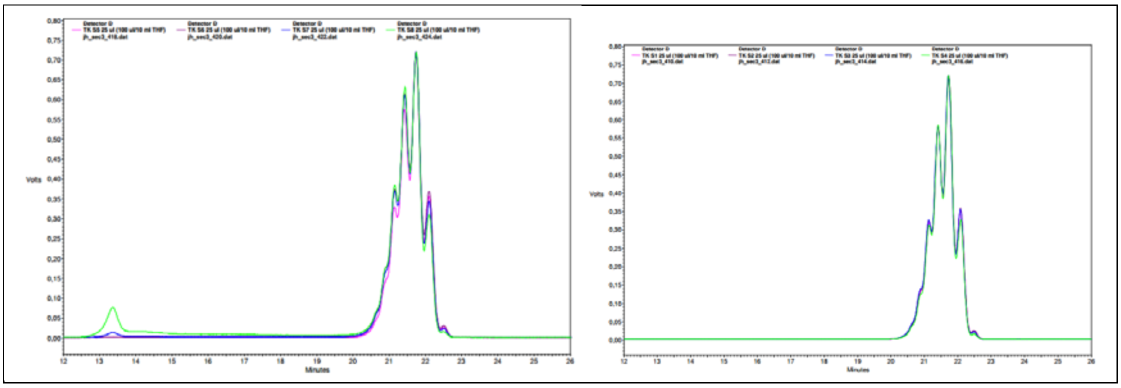


Figure 32 a and b. Normalized and overlaid SEC chromatograms

The samples were analysed in Wood and Paper Chemistry Department from Åbo Akademi University and they were discussed previously to writing this chapter, due to the difficulty of analysis since the first attempts.

Following the nomenclature in Table 17, samples S1-S6 seemed to be soluble in acetic acid or acetic acid-methanol but samples S7 and S8 were not soluble in acetic acid-methanol. Several solvents had been tried before.

These last samples, S7 and S8, were not stable over time; they changed from a smooth suspension into a semi-solid "gel" that could not be easily resuspended.

The analysis was repeated with another column and a using a different eluent solvent mixture. Previous columns and eluent used were 2 x Jordi Gel DVB 500Å with THF but the new column and the new eluent were Jordi X-stream H_2O 1000Å with acetic acid-methanol-water 5:4:1.

Several comments have to been mentioned in this moment. The new column gave lower resolution. The oligomer group eluted as only one peak instead of as a group of partly overlapping peaks. Retention times were not very stable (not reflective of real differences in molecular weights

The Area Percent value might be of interest for comparing the ratio between polymer and oligomer(s).

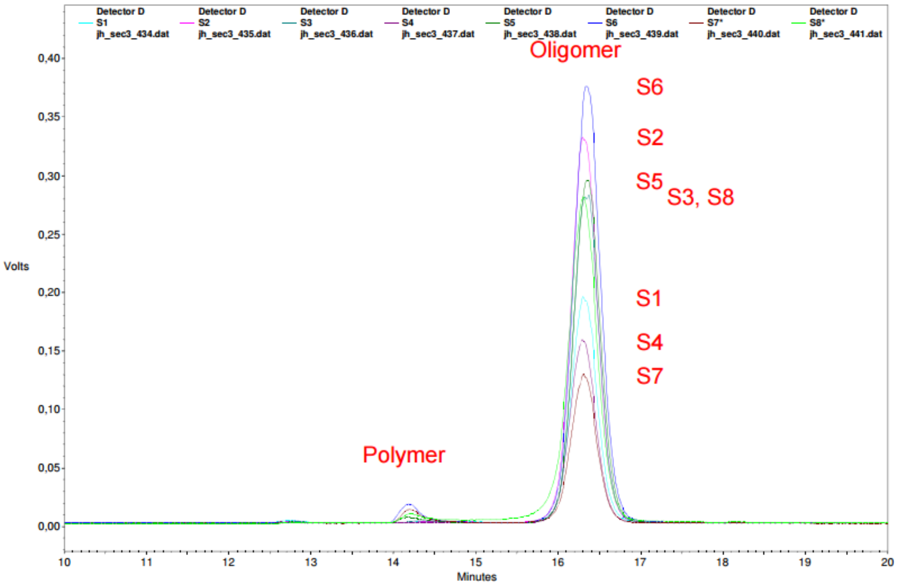


Figure 33. Polymer and by-product (oligomer) chromatogram.

Figure 33 shows that the peak corresponding to the polymer retention time (confirmed that was around 3000 Da) was in 14.1-15.1 min and the oligomer one (by-product) was in 16.2-17.1 min.

Table 17 summarizes the experiments made with zinc glutarate as a catalyst.

Table 17. Copolymerization reactions. In bold, first experiments to discuss.

Sample (amount_P_T)	Main Characteristics
S1_0.3_6_60	**m cat = 0.3 g**
S2_0.3_6_60	**m cat = 0.3 g**
S3_0.6_6_60	**m cat = 0.6 g**
S4_0.6_6_60	**m cat = 0.6 g**
S5_1.0_6_60	**m cat = 1.0 g**
S6_1.0_6_60	**m cat = 1.0 g**
S7_1.5_6_60	**m cat = 1.5 g**
S8_1.5_6_60	**m cat = 1.5 g**
S9_1.5_10_60	**P = 10 barg**
S10_1.5_25_60	P = 25 barg
S11_1.5_25_80	T = 81°C
S12_1.5_25_80	T = 81°C
S13_1.5_25_80	MW = 725 g/mol
S14_1.5_25_80	P = 25 barg. reaction time = 20h
S15_1.5_06_60	P = 6 barg. reaction time = 20h

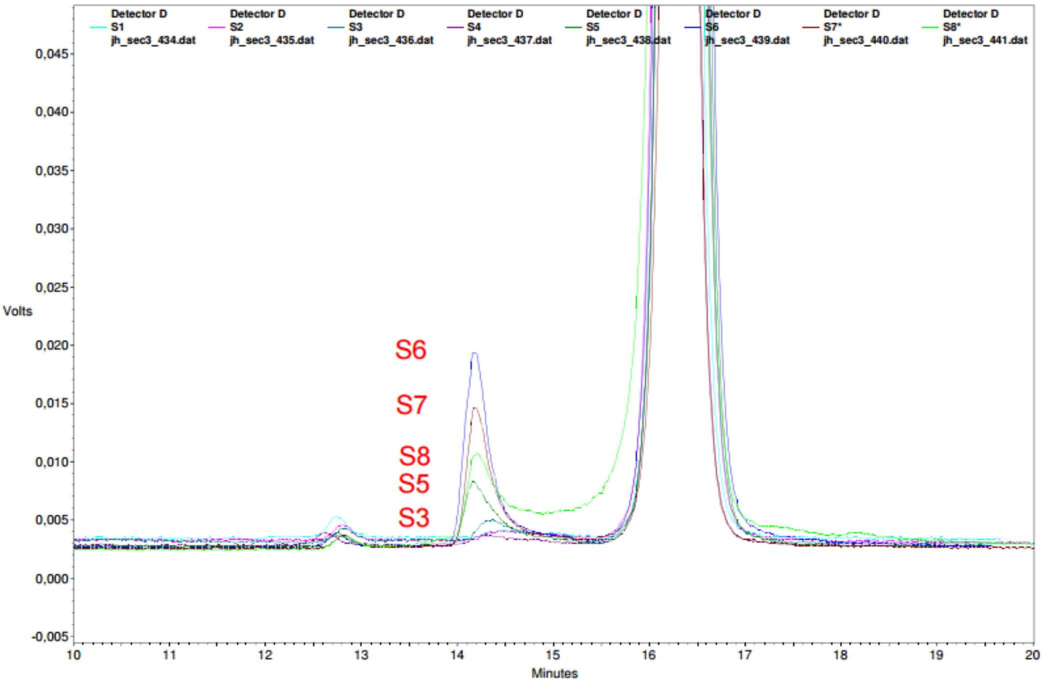


Figure 34. Polymer chromatogram for each sample. S1-S8 modifying mass of catalyst.

The reactions which gave more polymer were S6, S7 and S8. As it can be seen in Figure 34, S6 and S8 gave more by-product but S7 was the one that produced less amount of it. So, the copolymerization reaction in the experiment S7 was more successful that in the rest of experiments.

It is possible to conclude that S7 shows the best amount of catalyst to continue with the reactions.

This means that the rest of the reactions were done with 1.5 g of catalyst.

Figure 35. Samples from S1-S8 modifying mass of catalyst.

Table 18. Copolymerization reactions. In bold, latest experiments to discuss.

Sample (amount_P_T)	Main Characteristics
S1_0.3_6_60	m cat = 0.3 g
S2_0.3_6_60	m cat = 0.3 g
S3_0.6_6_60	m cat = 0.6 g
S4_0.6_6_60	m cat = 0.6 g
S5_1.0_6_60	m cat = 1.0 g
S6_1.0_6_60	m cat = 1.0 g
S7_1.5_6_60	m cat = 1.5 g
S8_1.5_6_60	m cat = 1.5 g
S9_1.5_10_60	P = 10 barg
S10_1.5_25_60	**P = 25 barg**
S11_1.5_25_80	**T = 81°C**
S12_1.5_25_80	**T = 81°C**
S13_1.5_25_80	**MW = 725 g/mol**
S14_1.5_25_80	**P = 25 barg. reaction time = 20h**
S15_1.5_06_60	**P = 6 barg. reaction time = 20h**

In the following discussion, experiments S10-S15 in which other parameters previously commented were modified, it is shown that most of the samples were not soluble or were just partially soluble in the eluent. Some of these new samples were again difficult to dissolve, especially S11 and S12 (but also S10). Also the unreacted monomers from two samples (distillate sample, D10 and D15) were analysed. These distillate samples were determined that no oligomer and no polymer peak (only an artefact peak from filtering the samples) were on them.

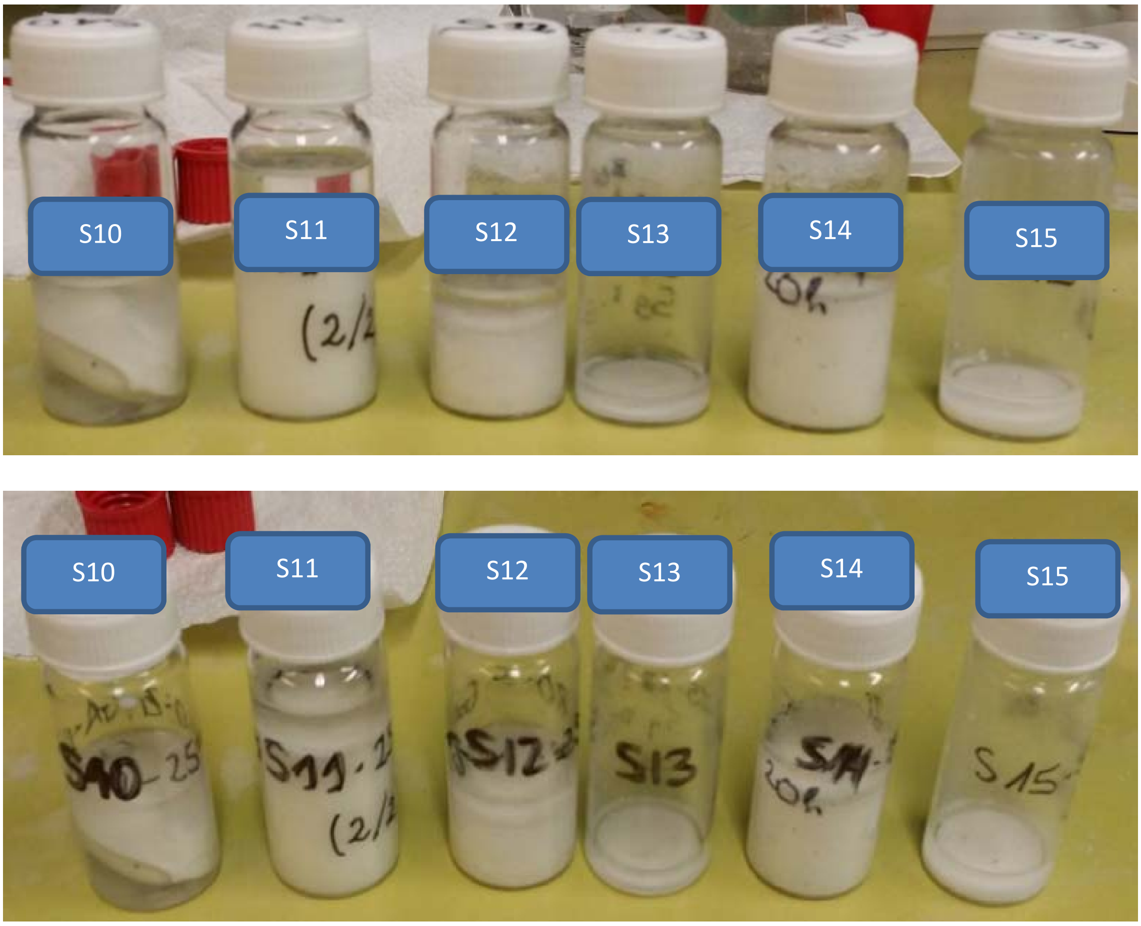


Figure 36. Samples from S1-S8 modifying mass of catalyst.

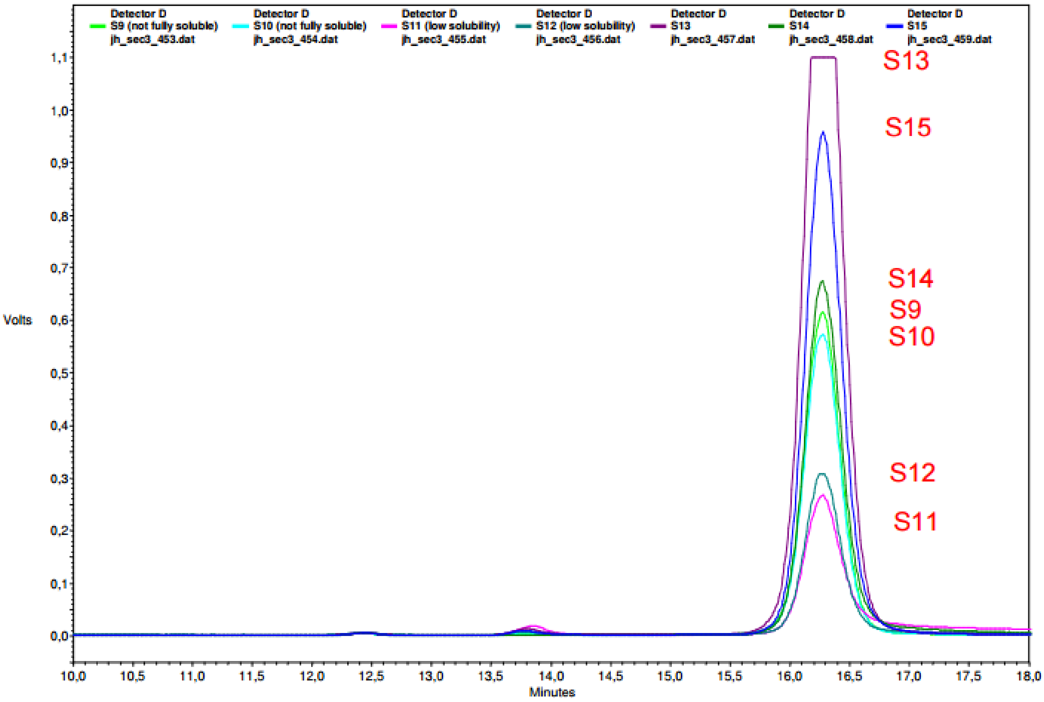


Figure 37. By-product (oligomer) chromatogram for samples S9-S15.

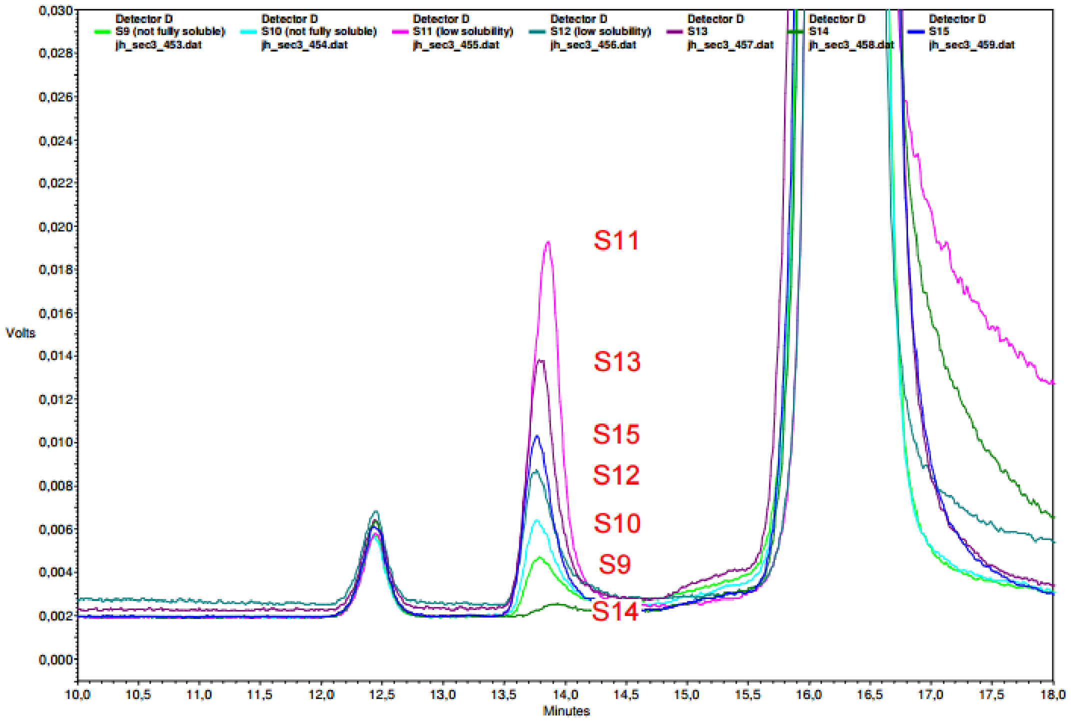


Figure 38. Polymer chromatogram for samples S9-S15.

These results for S9-S15 (where S10 was an unsuccessful sample) are not totally reliable based on the low solubility of the polymer in the eluent. It is seen that S11 had more polymer and less by-product that S13 and S15.

It is not possible to assure that conditions belonging to S11 were the better ones but they seemed to be, taking also into account the results by FTIR technique.

7. CONCLUSIONS

The heterogeneous zinc glutarate catalyst (ZnGA) was successfully synthesized and characterized by several techniques: Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).

Through these techniques it was possible to determine the following:

- The catalyst was stable up to 400 ºC, although the reactions targeted were always below 130ºC.
- The active reaction area of zinc glutarate corresponded to the outer surface area. No pores were found in its structure.
- The catalyst particles had a rectangular plate shape with a d50 between 100-200 μm.
- Zinc glutarate can be used in copolymerization reactions, but it is an extremely slow catalyst. It achieved the ring opening polymerization process that propylene oxide suffers.

Several different reaction conditions were studied for the formation of polypropylene carbonate from propylene oxide, carbon dioxide and propylene glycol (as initiator of 425 g/mol).

Reaction polymers were characterized by Fourier transform infrared spectroscopy (FTIR) and Size Exclusion Chromatography (SEC).

The best conditions corresponded to 1.5 g of catalyst, 25 barg, 80 ºC, 40 h and 3000 Da of initial PO estimation.

Values of turn over number (TON) and turn over frequency (TOF) are certainly small compared with other type of catalysts as they will be shown in Chapter 2 (DMC catalysts). An average value of TON and TOF for the best amount of catalyst corresponded to 1.6 and $2.8*10^{-08}$ h^{-1}, respectively. This demonstrated the slow behaviour of this catalyst.

8. FUTURE WORK

In this work we have tried to produce the PPC using a well-known zinc glutarate catalyst, however the difficulties arising from the use of this catalyst have been evident. Nevertheless a considerable amount of CO_2 is incorporated in the polymer chain, and the viscosity of the resulting polymer is very high. This causes problems with the mass transfer in the reaction, and stops it easily.

Furthermore, the amount of catalyst needed is high (in the order of grams per 100 grams of product), which forces to recover the catalyst afterwards. We have not done this recovery because it involves a lot of time as it requires a complicated number of dilution and extraction steps.

This will be of the future works: to achieve the precipitation of the polymer, recover the catalyst and analyse this spent catalyst.

Other possible option is to study this reaction in supercritical conditions, although the reactivity is too low, the use of CO_2 under supercritical conditions may improve the mass transfer of the bulk polymer phase, and probably will improve the reactionability.

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CHAPTER 2

Effect of Zn/Co initial preparation ratio in the activity of a Double Metal Cyanide catalyst for propylene oxide and carbon dioxide copolymerization

ABSTRACT

Different Zn-Co double metal cyanide (DMC) catalysts have been prepared by varying the initial amounts of $ZnCl_2$ to analyze the influence of method of preparation on the different copolymerization parameters.

Synthesized catalysts were analyzed by different techniques such as, infrared spectrometry, inductively coupled plasma optical emission spectrometry, scanning electron microscopy, N_2-physisorption and X-ray diffraction to determine whether characteristics affect the catalytic activity.

The obtained copolymers were characterized by infrared spectrometry and gel permeation chromatography.

Highly active catalyst (2.5 kg polymer/g catalyst) was synthesized and low amounts of the cyclic carbonate byproduct were produced (0.4 %), even with medium crystallinity catalysts and considerable amounts of K^+ (0.4% to 1.0%wt).

1. INTRODUCTION

The world is confronted with a major crisis of climate change due to the increased evolution of greenhouse gases, with CO_2 being the main contributing [1].

Methane is now also a threat, due to permafrost defrosting and subsequent CH_4 liberation related to global warming.

In addition, as the current rate of petroleum consumption resources are predicted to be exhausted within the next century, there is a growing effort to develop new chemical processes using biorenewable resources [2].

In this way, CO_2 have received much more attention and its gradually utilization have become a topic of intensive study for its environmental concerns and use of this potential carbon resource [3]. Therefore, CO_2 has not only became into an important C1-carbon feedstock because it is an environmentally benign chemical and a safe alternative, but also because it has received the attention from an economical point of view due to its high purity availability at low cost, and simplicity to handle it on an industrial scale (nontoxic and nonflammable) [4, 5].

As a kind of potential approach, one of the most promising areas for CO_2 is its application as a material for polymer synthesis [6].

Without the intention of competing against natural CO_2 fixation in flora, polycarbonates can be synthesized through the technologically viable process of CO_2 fixation by coupling CO_2 and epoxides with the presence of hetero or homogeneous catalysts [7, 8, 9].

These final polycarbonate products have been proposed as low toxicity and biodegradable alternatives for packaging, engineering polymers and elastomers [8], receiving much more attention because they exhibited good mechanical properties [5].

Economic advantages come from the use of CO_2. It is estimated that producing 1 ton of the final polyol polymer (POL) product will consume approximately 758 kg of propylene oxide (PO) (without including CO_2). Otherwise, when CO_2 is included into the formula, polyol carbonate is produced (PPC) and the PO used is notably reduced. Thus, with a proper catalyst, it can be easily included a 15 wt % of CO_2 into the PPC with savings up to 228 kg of PO in the process. As an example, in the Bayer pilot plant located in Leverkusen, Germany, values above the 30 % CO_2 included into the PPC where obtained and this can lead to high OPEX (operational expenditure) savings. Finally, the impact over carbon footprint is estimated to decrease in 11-19 % [10].

In this sense, the past three decades it has attested a great progress in the fixation of CO_2 into polycarbonates.

Since the pioneering work of Inoue in 1969 using $ZnEt_2/H_2O$ as a catalyst [11], many systems have been reported and demonstrated effective utilization of CO_2 where the importance of a catalyst has never been overestimated [12, 13, 6, 7].

To develop further this promising reaction, various catalyst systems have been developed for the synthesis of polycarbonates [8] and many studies have focused on finding new catalysts with improved activity and selectivity [9]. The target is to synthesize a catalyst fast enough to reduce the reaction time to make the process technically feasible, but at the same slow enough in PO incorporation to give CO_2 the opportunity to react and incorporate into the polymer chain.

Thereafter, a number of catalysts were developed to catalyze the copolymerization of CO_2 and epoxide such as cyclohexene oxide (CHO) and propylene oxide (PO) [5]. Nevertheless, they are generally less effective for the copolymerization of propylene oxide (PO) with CO_2, and undesired byproducts like propylene carbonate (PC) are produced [14].

Propylene carbonate is a byproduct that reduces the atom economy of the reaction, although under certain circumstances it might be of help by reducing the polymer viscosity acting as a solvent and fostering mass transfer.

Several research groups have pursued this path on developing both homogeneous and heterogeneous catalysts for CO_2 fixation [2, 4] and one of the successful examples is double metal cyanide (DMC) catalyst [1, 7].

DMC catalyst generally referred to zinc hexacyanometalate prepared by reaction of zinc halide and hexacyanometalate salt [3] and a complexing agent in some cases [5]. These complexes are considered to be effective not only for propylene oxide ring-opening (ROP) but also for CO_2-epoxides copolymerization [6, 7, 9, 13, 14]. The catalysts are highly active and give polyether polyols that have low unsaturation and narrow molecular weight distribution [6], yielding biodegradable polycarbonates with a wide potential for polyurethane applications [15].

Improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [6].

Copolymerization of propylene oxide (PO) and CO_2 using DMC complex based on $Zn_3[Co(CN)_6]_2$ has been successfully carried out by different researchers.

Chen et al., 2004 demonstrated that $Zn_3[Co(CN)_6]_2$ enhances the catalytic activity higher than $Zn_3[Fe(CN)_6]_2$. The study showed that lower temperature and lower amount of catalyst was favorable for CO_2 incorporation but propylene carbonate was produced as co-product [3].

Gao et al. (2012) [13] studied the effect of molecular weights of the initial polypropylene glycols (PPG) on polymerization and the reaction conditions. Results showed that the catalytic activity changed with carbonate unit content and molecular weight, it reached 10.0 kg oligomer/g DMC catalyst, also, the carbonate unit content varied between 15.3 % and 62.5 %, and the weight ratio of PC was controlled to less than 8.0 wt %.

Li et al. (2011) [14] studied the copolymerization process of CO_2 and PO without initiators. The catalytic activity reached 60.6 kg polymer/g DMC after 10 h. The production of the by-product propylene carbonate (PC) was between 0.4 to 4.4 wt %, but very high molecular weight copolymers were obtain, being the maximum in 130000 g/mol, in this sense they confirmed that a severe oxidative degradation occurred for the low-carbonate-content PPC and that air stability could be significantly improved by adding an antioxidant.

Zhang et al. (2011) [9] reported a nanomellar Zn-Co(III) DMCC catalyst with high surface area for copolymerization. Although the molecular weight was so high 31800 g/mol, the resultant copolymer has considerable productivity (6050 g polymer/g Zn), F_{CO2} (72.6%) and low PC (8.5 wt%).

Zhou et al. (2011) [16] reported good results on polymerization with high crystallinity catalysts and studied the effect of various reaction conditions such as amount of the catalyst, reaction time and temperature on the copolymerization. The efficiency of catalysts was high, 7488 g polymer/g catalyst and results shown that insertion of CO_2 into chains is significantly affected by the amount of catalyst and ambient temperature. The PC production was controlled to be less than 5 % while the molar fraction of CO_2 was more than 30 %.

On the contrary, Sebastian and Srinivas [17] studied DMC catalysts prepared by different methods and their influence on catalytic activity for CHO-CO_2 copolymerization.

They reported that even with moderate crystallinity and without co-complexing agents the catalyst are high active for copolymerization, also, CO_2 adsorption studies revealed that higher the guest-host interaction higher would be the catalytic activity, providing polycarbonates with CO_2 incorporation as high as 86 mol %, average molecular weight of 20900 g/mol and polydispersity index of 1.8.

Therefore, as far as the copolymerization of PO and CO_2 is concerned, developing a highly active catalyst system capable of producing high-molecular-weight poly(propylene carbonate) (PPC) and low amount of PC byproduct is fundamental; under the control of the percentage of CO_2 incorporation [14].

In this work, we will address the effect of different Zn/Co initial ratio in the preparation of five DMC catalysts by testing the catalytic activity in the copolymerization process, the cyclic polycarbonate (PC) production and CO_2 coupling. A comprehensive study of all the catalysts, physical and chemical characterization has been performed using a number of different analytical techniques.

2. EXPERIMENTAL

2.1. MATERIALS

Zinc chloride ($ZnCl_2$), potassium hexacyanocobaltate (III) $K_3[Co(CN)_6]_2$, *tert*-BuOH (t-BuOH) and polyethylene glycol (PEG 1000, Mw=1000 g/mol) were used for catalysts without further purification and purchased from Sigma-Aldrich. Propylene oxide (PO, ≥ 99%, Sigma-Aldrich), polypropylene glycol (PPG 725, Mw= 725 g/mol, Sigma-Aldrich) and CO_2 were used as received.

2.2. PREPARATION OF DMC CATALYST

Different amounts of $ZnCl_2$ and $K_3[Co(CN)_6]_2$ were used for the DMC's preparation in order to determine the effect of including one or the other reagent in excess. The different weighted amounts of both reagents can be seen in Table 1, 1.77 g of PEG 1000 were added and used as co-complexing agent.

Although the stoichiometry of the reaction is 1.5 Zn/Co mol ratio (equation 1), the amounts were changed to determine how can influence the excess of one or another metal on the different catalyst parameters such as, catalytic activity, crystallinity, bounding and copolymerization.

$$2K_3[Co(CN)_3]_2 + 3ZnCl_2 \rightarrow Zn_3[Co(CN)_6]_2 \downarrow + 6KCl \qquad \text{(eq. 1)}$$

Table 1. Amounts of Zn and Co used in the preparation of the different catalysts and experimental Zn/Co mol ratio.

DMC	$ZnCl_2$ (g)	$K_3[Co(CN)_6]_2$ (g)	Zn/Co mol ratio	Catalyst recovered (g)	η (%)
A	0.31	6.94	0.1	0.48	99.9
B	0.79	5.78	0.3	1.20	100.6
C	1.56	3.86	1.0	2.49	96.0
D	2.35	1.93	3.0	1.67	109.0
E	2.81	0.77	8.9	0.78	93.5

The precise $K_3[Co(CN)_6]_2$ amount for each test was dissolved in 80 ml of mili-Q water and $ZnCl_2$ in 210 ml of miliQ water and 50ml of tBuOH. Both solutions were mixed and vigorously stirred 15 min at 50 °C. After 13 min PEG 1000 was added to the mixed solution, the white suspension was centrifugated 6 min at 5000 rpm. The isolated slurry was resuspended with strong stirring during 20 min in 100 ml of a t-BuOH: H_2O (50:50) solution and it was centrifugated as previous. The solid was resuspended in 100 ml of 100% t-BuOH and stirred for 30 minutes, filtered (omnipore PTFE membrane filter, 0.1 µm, Merck Milipore) and dried under vacuum at 50 °C during 30 hours.

2.3. COPOLYMERIZATION PROCESS OF CO_2 AND PROPYLENE OXIDE

Polymerization is a highly exothermic process and a runaway reaction due to a sudden polyol formation may occur if PO concentration in the liquid phase is high (e.g. due to PO accumulation because of an inefficient agitation).

To avoid this situation, completely undesirable that might cause a safety problem indeed and usually leads to overcooked polymers, the PO is often added continuously to the reaction in a batch (semi-batch operation) mode.

Batch copolymerizations of different $Zn_3[Co(CN)_6]_2$ (DMCs) and CO_2 were carried out in a 350 ml reactor.

An initial template polymer was used for catalyst activation and for a better control of the final molecular weight.

PPG 725 was used for that purpose, assuming that the number of moles of polymer was constant during the reaction and that all the –OH branches grew equally. The amounts of the starter PPG 725 and of the catalyst DMC were fixed at 30 g (0.0413 mol) and 40 mg ($6.38 \cdot 10^{-5}$ mol), respectively and placed in the reactor under continuous stirring and homogenous temperature.

Three successive inertizations using N_2 were carried out at different pressures (5, 15 and 20 barg) to remove all O_2 moieties. The reactor is then heated up to 130ºC under vacuum conditions. Once the temperature was raised, the vacuum continued during 30 min to remove moisture in the starting PPG polymer.

First, under vacuum conditions (-0.80 barg) the activity of the catalysts was tested by two sequential activations at 130ºC inserting a fixed amount of PO. The amount of PO added for the activations was estimated to be around 10% of the total PO required if a 3000 g/mol PPC was pursued.

Once the first amount of PO was pumped into the reactor the following criteria was followed to determine if the catalyst was activated properly. The pressure of the reactor increases due to PO vaporization, up to thermodynamic equilibrium. The catalyst takes typically 10 to 30 min to activate, and after that, the reactor pressure decreases due to PO consumption. If a peak of temperature followed by a decrease on pressure occurred before 1 hour of the first addition, the catalyst passed the activation test. Otherwise, if the pressure did not decrease down to the initial vacuum conditions, the catalyst did not activate properly and the experiment was stopped. The second activation was carried out under the same conditions as the first one. Finally, a third PO addition was performed with CO_2 at copolymerization pressure (10 barg) only when the catalyst behaved properly in the two previous additions.

After the PO batch additions, once the system was stationary, the temperature was decreased down to the copolymerization temperature of 105 ºC and PO was pumped in a continuous way (0.35 ml/min). This PO flowrate must consider the maximum heat that the equipment is able to remove by the cooling system, to avoid runaway reactions and hotspots. After this stage, a continuous flow of CO_2 was fed into the system during 2 h to keep the pressure constant.

Finally, the pressure was slowly released and the system was kept under a vacuum current of N_2 to eliminate the unreacted monomers of PO during 1 hour. Then, the reactor was cooled down and the final copolymerization product was weighted and prepared for further analyses.

2.4. CHARACTERIZATION OF THE CATALYST

Elemental analyses of Zn (213.857 nm), Co (238.892 nm) and K (766.491 nm) were performed by optical emission ICP (Varian 725-ES), after a previous microwave digestion of samples (ETHOS SEL Milestone). Infrared spectra from 400 to 4000 cm^{-1} were recorded using a Fourier transform infrared spectrometer (FT-IR) from Bruker ALPHA at a resolution of 2 cm^{-1} and data were taken after 64 scans.

An environmental scanning electron microscope (ESEM) was taken by ESEM-FEI-Quanta 200F after coating with 10 nm gold layer. X-ray diffraction (XRD) patterns and crystallinity results were obtained on Bruker D8 Discover A25 diffactometer using Cu ceramic tube at 2.2 kW and LynxEye detector.

Microporous and mesoporous of the catalyst were analyzed by nitrogen-physisorption (Sorptomatic 1900, Carlo Erba Instrument). The sample preparation was as follow, first an outgassed burette was weighted, and then 0.25 g of DMC A was added to the burette in outgassing conditions during 3h at 150ºC and 0.01 Pa, after that the burette was weighed to determine the moisture of the sample and the specific surface area of the catalyst (m^2/g) were analysed

2.5. CHARACTERIZATION OF COPOLYMER

Spectroscopic analysis of the polymers were performed using FT-IR (Bruker ALPHA) at a resolution of 2 cm^{-1} and the data was taken after 64 scans.

The amount by weight of CO_2 incorporated in the polymer chain was determined by means of 1 H-NRM (Bruker AV III HD 500, 500 MHz, pulse program zg30, waiting time d1:1s, 120 scans). The sample was dissolved in deuterated chloroform. The relevant resonances in the 1 H-NMR spectra (based on TMS = 0 ppm) used for integration were: 1.05–1.25 (methyl group of polyether moieties, area of the resonance corresponds to three H atoms); 1.25– 1.35 (methyl group of carbonate moieties in polyether carbonate, area of the resonance corresponds to three H atoms); 1.50 (methyl group of cyclic carbonate, area of the resonance corresponds to three H atoms). Taking into account the intensities, the relative concentrations as well as the weight fractions were calculated.

Number average molecular weight (Mn) and polydispersity index (PDI) of polymer products were calculated from the obtained curves in a Waters 1515 size exclusion chromatograph (SEC) with 2 AGILENT PLGel 5 µm mixed D (300x7.5) columns, the temperature of which was set at 35°C using THF as solvent. Detection was performed with a refractive index detector, solvent flow was 1 mL/min, and calibration was performed with PS standards.

3. RESULTS AND DISCUSSION

3.1. ANALYSIS AND CHARACTERIZATION OF THE CO-ZN BASED CATALYSTS

The method of preparation including temperature, purity of feedstock, complexing agent and the mode of reagents addition has significant effects on the catalytic activity of the final DMC [5, 17]. As the DMC catalysts were prepared by mixing $K_3[Co(CN)_6]_2$ and $ZnCl_2$, $KZn[Co(CN)_6]$ or K^+ can be also formed. The presence of potassium ions could result in a drastic decrease of activity of the DMC [5].

In order to examine the effects of how different initial metal concentrations in the DMC can influence its chemical and morphological characteristics and therefore their catalytic activity, five catalysts were prepared by changing the concentration of $ZnCl_2$ and used for polymerization reactions. tert-Butanol (tBuOH) was used as complexing agent (CA) to help the retention of $ZnCl_2$ in the catalyst [5] and the co-complexing agent (co-CA) PEG 1000 ,according to Guo et al., (2014) was used to decrease crystallinity and increase the catalytic activity [7]. Thus, they play an important role in DMC catalyst and ring opening polymerization (ROP) [13]. All samples were analyzed to determine the differences based on the amounts of K, Co and Zn (Table 2).

Table 2. Final composition of the different prepared catalysts analyzed by ICP.

Samples	Zn (% mol/mol)	Co (% mol/mol)	Zn/Co mol ratio	K (mol/g)	Co (mol/g)	Zn (mol/g)
A	60%	40%	1.47	0.0008	0.0022	0.0033
B	58%	42%	1.39	0.0007	0.0022	0.0031
C	59%	41%	1.45	0.0004	0.0028	0.0040
D	60%	40%	1.50	0.0003	0.0028	0.0042
E	61%	39%	1.58	0.0001	0.0026	0.0042

FT-IR spectroscopy was used to identify the coordination and bounding in metal complexes. Differences on the DMCs can be seen on the vibration bands that reveal differences in bonding characteristics. The band that vibes at 2192 cm^{-1} correspond to the –C≡N stretch of the DMC complex $Zn_3[Co(CN)_6]_2 \cdot xH_2O(x = 0 \sim 12)$ in the presence of CA and co-CA. According to other researchers [12, 17], the main characteristic vibration bands that appear in all DMC (**Fig 1**) are: at 470 cm^{-1} the Co-C stretching vibration indicates the presence of a coordinated tBuOH in different amounts, 642 cm^{-1} correspond to Co-C bounding, 1199 cm^{-1} to 3º-C-O stretch, 1372 cm^{-1} to -OH bending from tBuOH, 1473 to -CH scissoring, 1615 to –OH bending form water, 1738 correspond to the PEG incorporation into the catalyst, 2981 to –C-H stretch and the –OH stretch in all DMCs vibes from 3661 to 3296 cm^{-1}.

The main difference on the FT-IR analysis correspond to the synthesized catalysts with higher amounts of $K_3[Co(CN)_6]_2$. Catalysts A and B showed one more vibration band at 2129 cm^{-1} (Figure 1). This band may be mainly caused by the –CN group from the excess of $K_3[Co(CN)_6]_2$ added to the catalyst (AIST spectra database).

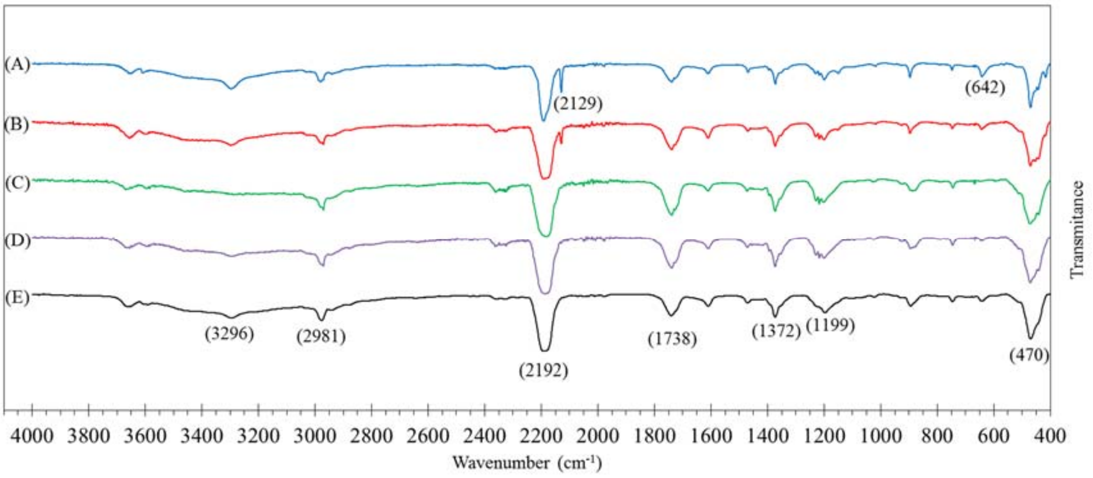

Figure 1. FT-IR spectra of the Co-Zn catalysts.

Selected ESEM images showed that the amount of reagents affects particle size and morphology (Figure 2) of the catalyst. The DMCs prepared showed lamellar, spherical and cubical distributions. Lamellar structures thickness changed from approximately 125nm for A sample to lowers sizes while $ZnCl_2$ was increased in the synthesis. E sample exhibited lamellar structures with thickness of approximately 33 nm together with more spherical agglomerates. It is interesting to note that more agglomerates and spherical structures were formed when Zn^{2+} was increased in the catalyst recipe; although the final Zn/Co ratio was almost the same (see Table 2).

In agreement to Lee et al. (2009) [12] this fact could lead to an aggregation of DMC particles as well as co-CA acts as protecting agent. As can be seen in Fig. 2, catalyst A and B present mostly lamellar and cubical structures while in C catalyst more agglomerates are formed and cubical structures change to spherical, finally in D and E catalyst, the excess of Zn^{2+} could lead to thin lamellar structures surrounded by spherical agglomerates which could mean that the aggregation process is completed in these cases (Figure 2).

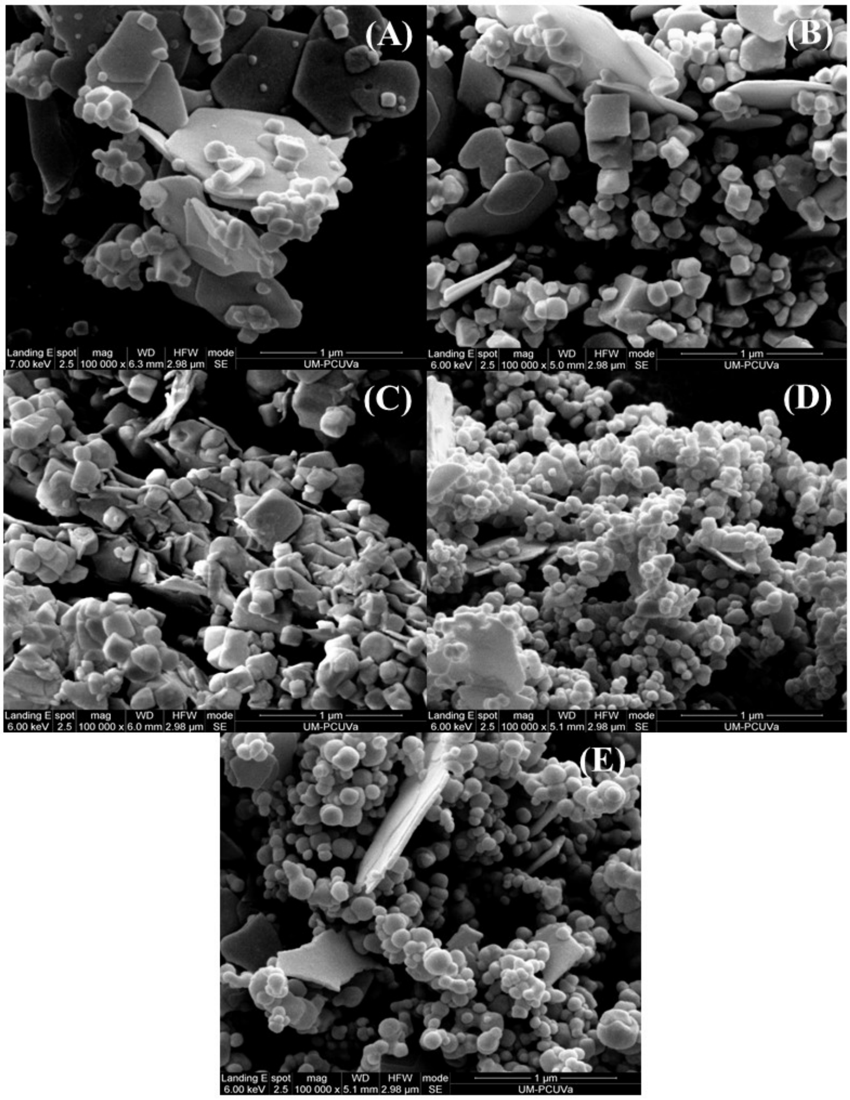

Figure 2. SEM images of DMC catalysts prepared with different initial concentrations of Zn and Co.

The surface properties, crystal structure and crystallinity values of the synthesized catalysts were examined by X-ray diffraction. All of them were identified as Prussian blue analogues (characteristic reflections of $Zn_3[Co(CN)_6]_2$ * 12 H_2O are marked with lines in Figure 3) [12]. Sample A was characterized by cubic (14.9, 17.3, 24.5, 34.8, 39.2º) and monoclinic structures (14.5, 20.7, 23.5, 24.9º) [17, 18]. This sample presented an amorphous structure, as it had a pronounced intensity reflection at 23.7º [7]. Sample B presented a mixture of cubic and in a lesser extent monocyclic structures, the monoclinic phase characteristic peaks at 20.7 and 23.5º [18] had low intensity. Particularly, sample C showed a cubic lattice structure with no monocyclic phase together with the highest crystallinity (50.3%). On the other hand, samples D and E presented also a mixture of cubic and monoclinic structures, being the monoclinic structure more intense in sample E. The extent of the monoclinic structures was more intense at Zn/Co ratios away from the stoichiometric value.

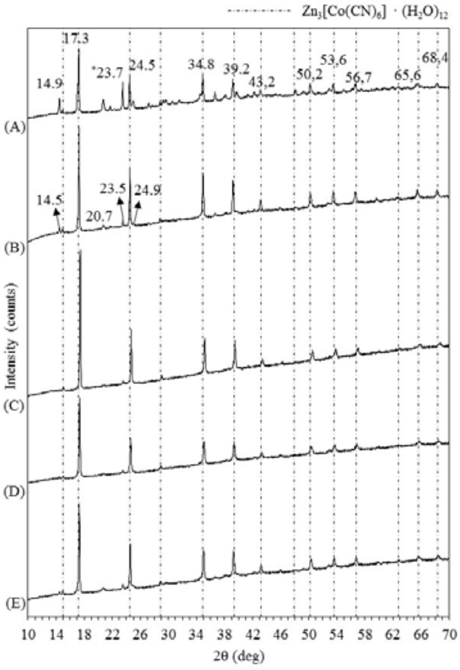

Figure 3. X-ray diffraction of the different Co-Zn catalysts. *characteristic peak of an amorphous state.

3.2 CATALYTIC TEST

From our results we can conclude that a proper activation of the catalysts only occurred when $ZnCl_2$ was in excess on the DMC preparation. This fact leads to changes on the catalyst structure, thus is according with other researches [1, 7, 13, 18, 19, Gao, 2012 #8].

In our case, samples D and E activated well. Differences on the activation are exclusively due to the method of preparation.

Catalyst D with a molar starting mixture of Zn:Co:tBuOH:PEG formulae 1.0:0.3:30.6:0.1, finished its first activation after 40 min with 7.2 gr of PO added and its second activation was carried out with 2.2 gr of PO and finished after 80 min. A quicker activation was carried out by catalyst E with a molar starting mixture of 1.0:0.1:25.6:0.1 that activated much faster, the first activation finished after 28 min with 7.4 gr of PO and its second activation finished after 52 min with 2.3 gr of PO added (Figure 4). The catalyst yield is 1.4 kg polymer/g catalyst for D sample and 2.5 kg polymer/g catalyst for E. Compared to other studies, this value is high for 10 barg (working pressure), other studies have similar catalytic activities working at higher pressures [17, 20], as an example Chen et al. (2004) [3] obtained catalytic activities from 1.5 to 2.1 working at pressures of 20 to 45 bar. Recently Gao et al. (2012) [13] obtained a yield of 3.8 (kg/g) working at 40 bar.

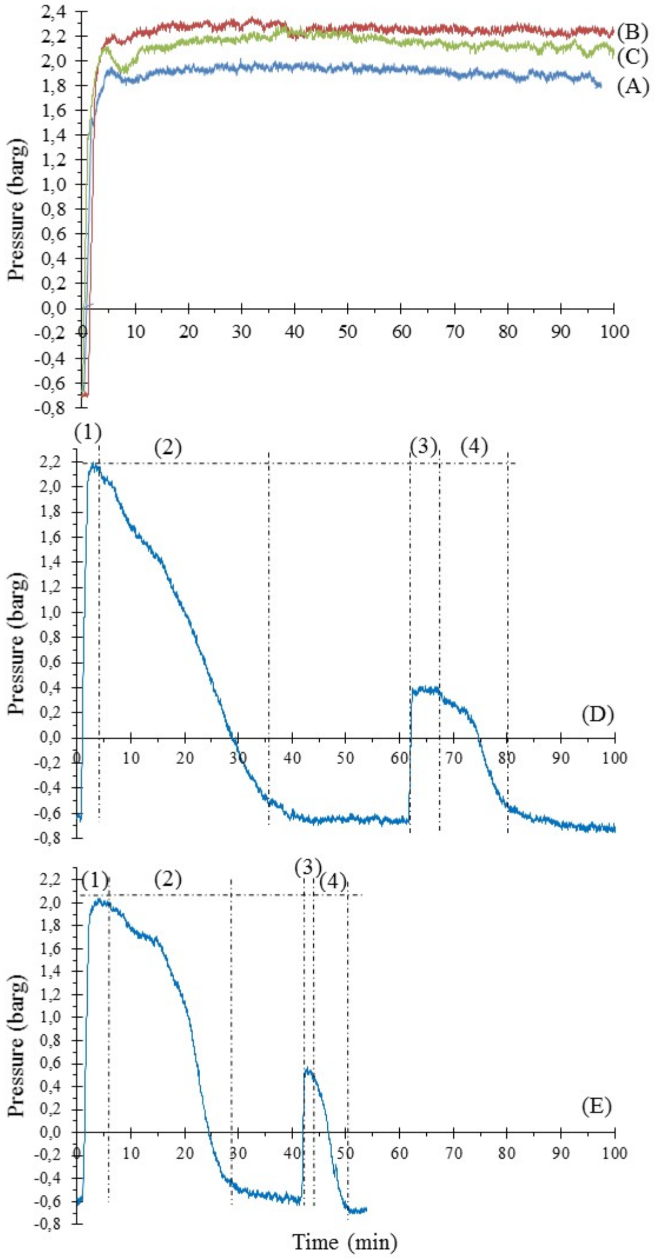

Figure 4. Catalyst activation. A, B and C no active catalyst, D and E active catalysts. (1) First catalyst activation, (2) PO consuming period, (3) second catalyst activation, (4) second PO consuming period.

Therefore, we suggest that the proper catalyst for DMC polymerization should be one with the characteristics of the catalyst D/E.

GPC figures (Figure 5) showed that E sample has consumed half of the starter peak while D sample has consumed almost all that peak. This means that D catalyst is more reactive than E, but lacks of activity to decrease the PDI on the final product. In this sense, specific surface area analysis was performed in both active catalyst to evaluate the pore volume and relate it to the catalytic activity and polymerization process. As can be seen in Table 3, the specific surface area of both catalysts is high (846 m^2/g D sample, 743 m^2/g E sample for microporous analysis and 533 m^2/g D sample, 515 m^2/g E sample for mesoporous analysis). Sample D had less amount of water than E and the highest value of mesoporous volume (0.51 cm^3/g).

Both catalysts D and E are porous however, the values of specific surface area and eliminated water % are different (Table 3). Authors suggest that once the reagent molecule gets inside the pore, some of them are not able to release that molecule. This fact also avoids the release of water content in the pore, obtaining long polymer chains which mean high PDI values. This phenomena occurs in catalyst D (Table 4). Nevertheless, when the pore allows the incorporation as well as the subsequent release of water and polymer molecules, it results in shorter polymer chains. In this case, PDI value decreases as it can be seeing in catalyst E (Table 4).

Specific surface area follows the previous assumption (Table 3). In terms of pore volume, smaller pore values (catalyst E) allow the polymer molecule remain less hold inside the pore. This enables a higher number of short polymer chains, a decrease on PDI value and higher water % elimination.

By optimizing the agitation system, this effect is less pronounced due to the improvement in mass transfer and internal and external diffusion processes.

Table 3. Microporous, mesoporous and surface area of the active catalysts D and E analyzed by N_2-physisorption

Sample	**Water**	**Specific surface area**	**Pore volumen**
	%	**m^2/g**	**cm^3/g**
D_microporous	18.15	846.80	0.30
D_mesoporous	12.86	533.12	0.51
E_microporous	21.43	743.07	0.26
E_mesoporous	21.80	515.24	0.35

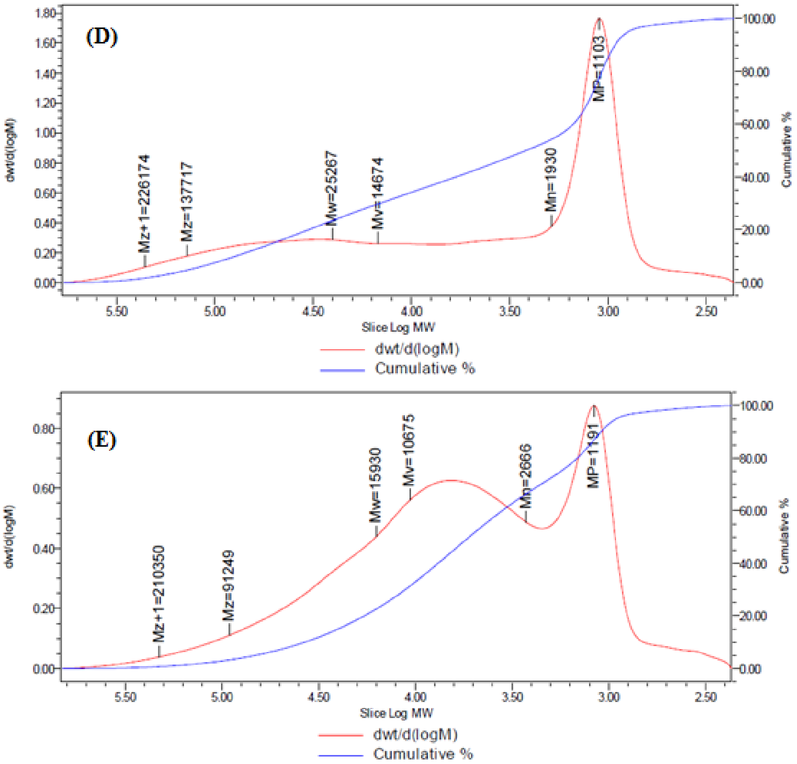

Figure 5. GPC analysis of active catalyst samples D and E

Moreover, we state that thorough washing to eliminate all K^+ of the catalyst is not strictly necessary for a proper working of the catalyst due to with 4000 ppm for E (0.4%WT) or even 10000 ppm for D (1.0%wt) of K^+ in the DMC the activation and polymerization reactions exhibit good results (vide infra).

Although it was reported in other studies that DMC with lower crystallinity are more active for copolymerization and the DMC exhibited high catalytic activity only when crystallinity degree was ≤ 30% our results as the ones reported by Zhou et al. (2011) [16] or Sebastian et al. (2014) [17] showed significant differences provided D and E are active catalysts with medium crystallinity (> 40%).

Rather, is consistent with the theory reported by Peeters et al. (2013) [18] that the influence on the catalytic activity is based on the structure properties of the Zn^{2+} ion. At the surface of cavity generated by a block vacancy, Zn atoms with an incomplete coordination sphere are found [21] so higher activity can be achieved by more vacancies around Zn [7]. Also, coordinated CA and disperse Cl- in the structure activates Zn^{2+} ions that are critical for high activity of catalysts [17].

3.3 PPC COPOLYMER CHARACTERIZATION

For the copolymerization reaction, the total amounts required of catalyst, PO and PPG were estimated depending on the desired molecular weight for the final copolymer, in this case approximately 3000 g/mol.

Considering this value, the amounts of PO and PPG to be used in the reaction were calculated.

FT-IR spectrum of the obtained copolymers is shown in **Fig. 6**. A sharp C=O asymmetric vibration absorption at 1744 cm^{-1} and a C-O stretching vibration at 1260 cm^{-1} was found, providing the evidence of the incorporation of CO_2 into the polymer chain [3, 7].

At the same time, it can be seen low intensity peaks at 1790 and 790 cm^{-1} which are characteristics of cyclic carbonate (PC).

The copolymerization reaction resulted in the main product, polypropylene carbonate (PPC) and the byproduct, cyclic polycarbonate (PC). Before the reaction is carried out it is recommendable to estimate the $\%CO_2$ that could be incorporated as well as the amount that is going to be formed of PC, in order to predict the PO amount needed for the PPC synthesis reaction.

The more incorporation of CO_2, the less PO will be necessary for the reaction, for a similar final molecular weight. On the contrary, when a higher the amount of PC be generated by reaction, the higher the amount needed of PO.

Comparing the calculated data to the experimental analyzed by NMR (Table 4), data showed that the incorporated CO_2 values are similar that the estimated values, 5.6% for D and 6.7% for E.

The benefit of these DMCs was that the cyclic carbonate produced in the reaction was very low, 0.4% for D and 0.3% for E (Figure 6).

Thus, these DMCs were more selective catalysts regarding to the main product PPC, also the production of high amount of the byproduct PC leads to a lesser production of PPC. In this way, we have achieved a high selective DMC that can be used at high temperatures (105ºC) on the contrast to the study of Darensbourg et al. (2003) [22] where the tendency to produce large quantities of PC increased with elevated temperatures.

Table 4. Data of copolymerization of CO_2 and PO for the active catalysts [(a)]

Catalyst	PPG/DMC (g/mg)	t (h)	Yield[(b)]	TON[(c)]	TOF[(c)]	W_{PC}[(d)] (%wt)	CTR[(d)] (%wt)	PPC product Mw	PPC product Mn	PDI
D	30/42	6.5	1.4	34	7	0.3	5.6	25267	1930	13.09
E	30/41	6.0	2.5	99	14	0.4	6.7	15930	2660	5.97

(a) All copolymerization were carried out at 105ºC, 10 barg with 30 gr of PPG (725 g/mol) and 90 gr of PO.

(b) Calculated by kg polymer/g catalyst

(c) TON calculated as mol PPC/mol catalyst, TOF calculated as TON/h

(d) Carbonate content unit (CTR) and ratio of PC in the product (W_{PC}) was determined by NMR

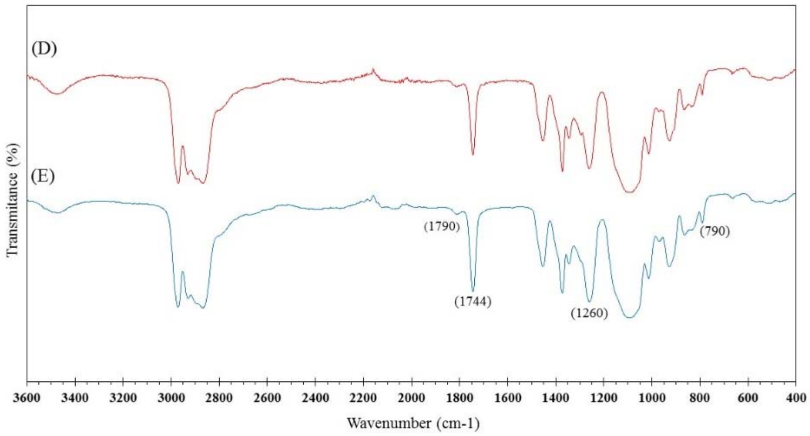

Figure 6. FT-IR spectra of the copolymer obtained with catalysts D and E

The copolymers obtained were of high and low molecular weights that implied a high polydispersity (PDI), this fact was due to a lesser agitation on the reactor during copolymerization process.

The increased viscosity of the polymer caused mass transfer limitations due to the agitation, as the magnetic stirring was insufficient and therefore ineffective. PO dripping always in the same area and such inefficiency of the agitation led to formed molecules with a long carbon chain in that area, and other molecules with shorter chain, in more remote PO feeding areas. This resulted in an unexpectedly high polydispersity value, as can be seen in Table 4.

The increase on the viscosity may be due to low formation of the cyclic polycarbonate, however, this is a characteristic result and one of the objectives to achieve, because it avoids the need of further purification processes to remove the cyclic polycarbonate. A low PDI is essential for optimum properties of the polyol in its subsequent use for the synthesis of polyurethanes.

This could be improved by including a vigorous agitation system or a mechanical stirring, during the copolymerization reaction that will lead to decrease notably the PDI and so the molecular weight. Thus, two more reactions were carried out in a Parr reactor (Parr Instrument Company, Inc. Moline, Illinois, U.S.A), with a volume of 382 cm^3 with a mechanical stirrer (Parr Instrument Company, Moline, Illinois, U.S.A. A1120HC II55 with a motor from Bodine Electric Company, Chicago, USA) to prove this fact. Variables such as temperature, and amount of catalysts used where the same as in the other experiments. The PO amount was changed in order to prove the agitation effect on the PDI of the final polymer. As the final molecular weight is not an influence variable on the PDI value the reaction was performed to 1000 g/mol instead of 3000 g/mol. Results showed a considerable decreased on the PDI. Obtained values for PDI were 1.11 and 1.10 for D and E catalysts, respectively being Mw and Mn 1066 and 960 for catalyst D and 1139 and 1034 for catalyst E. Therefore, both catalysts are appropriate for copolymerization processes because both can decrease the final PDI, producing low amounts of PC.

Finally, the incorporated CO_2 in the chain will be increased while the working pressure also increases. As Guo et al. (2014) [23] reports, higher pressure, lower temperature and longer reaction time increase the speed of ring opening.

It is worth to mention that using these DMC catalysts, low amounts of PC are produced and once this active catalyst is obtained, they can be used for increasing the CO_2 incorporation by varying the temperature and increasing the pressure.

4. CONCLUSIONS

In this study, Zn/Co double metal cyanide catalysts were synthetized by varying the amounts of $ZnCl_2$ on the preparation method.

The main goal was to synthesize active DMC catalysts which lead to produce very low quantities of the byproduct (cyclic carbonate) and a greater production of the main product, polypropylene carbonate.

Different DMC catalysts were tested for that purpose.

Only when Zn was in excess the catalyst was active but a thorough washing to eliminate K^+ until is not detected, it was appreciated that it is not necessary in order to obtained high active catalysts. With amounts between 0.40% and 1.00 %wt ppm K^+ the catalyst exhibited good catalytic activity and only 2 washings were necessary. This fact might help in the reduction of time and solvent costs in the preparation of DMCs.

Active catalysts showed medium crystallinity, which implies that the amorphous state was not override. Thus, it leads to the fact that the catalytic activity was influenced based on the structural properties of the Zn^{2+} ions where Zn-OH group in DMC catalyst is the active center for polymerization.

The study reveals that the preparation method based on initial amounts of Zn^{2+} can affect the copolymerization process. Although the PDI was between 5.97 and 13.09 due to the high viscosity of the polymerization in the bulk fluid (as low amounts of PC were obtained), it could be improved by enhance the stirring system.

To prove it, two more reactions were carried out using a mechanical stirrer, the effect was clear producing a decrease in the PDI value.

The N_2-physisorption and GPC analysis of these catalysts showed that with higher amount of water and similar specific surface area, catalyst E is less reactive but the catalytic activity is higher than for catalyst D.

The specific surface area and pore volume are crucial to characterize the catalytic activity in order to obtain short polymer chains which implies a good value of PDI on the final product.

Highest catalytic activity (2.5 kg polymer/g catalyst), more CO_2 incorporation (6.7%) and less production of PC (0.3%) even at high temperatures (105ºC) were performed by the DMC E, prepared with the highest amount of $ZnCl_2$, although the stoichiometric reaction was similar in all cases.

5. ACKNOWLEDGMENTS

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CHAPTER 3

Double Metal Cyanide catalyst and propylene oxide influence on the activation stage study and copolymerization reaction

ABSTRACT

DMC catalysts activate under certain conditions to polymerize propylene oxide into polyether or propylene polycarbonate (if CO_2 is present). For the activation of the catalyst only PO is used to avoid catalyst poisoning before activation.

In this chapter, we have studied a prepared DMC catalyst during its activation period. Two variables were analyzed, amount of catalyst from 10 to 80 mg and amount of propylene oxide from 4 to 18g (related to reactor pressure).

We have found two different behaviors, a slow activation if PO is in low quantity and a fast activation for higher PO quantities. The amount of catalyst also influenced the behavior, but, while almost any quantity work for the activation, it is recommended not to use very low amounts, as they can be deactivated during the reaction.

1. INTRODUCTION

Since Inoue first disclosed the ring-opening copolymerization (ROP) of CO_2 with 1,2-epoxypropane by $ZnEt_2$-H_2O [1], much attention and progress had been made within the past decades to explore various related catalysts to ensure the copolymerization and afford to synthesize a range of aliphatic polycarbonates [2]. The utilization of CO_2 remains important to reduce emissions, and as an economic driver to support carbon capture [3]. The copolymerization process of CO_2 is strongly dependent on the selection of the catalyst and various heterogeneous and homogeneous catalysts have been studied [3].

Homogeneous catalysts are generally suitable for research, since their chemical structures can be well defined, some homogeneous catalysts showed high activity and product selectivity [4]. Traditional homogenous catalysts systems include porphyrin [5], phenoxide, β-diiminate (BDI), and salen systems. New strategies have come up for these catalysts including dinuclear BDI catalyst, binary linked salen, dinuclear salen and immobilized salen and BDI systems [6]. Bicomponent catalysts comprising metal(II/III) complexes such as Co(III), Cr(III), Mn(III) or Al(III) [7] coordinated by ligands such as salens [8] or porphyrins [9] and, dinuclear or bimetallic catalyst where two metals are coordinated by tethered 'mononucleating' ligands, such as Zn(II) β-diiminates (BDIs) or tethered Co(II)/Cr(III) salens [3] are one of the best options.

Metallic catalysts present some advantages, such as high activity, selectivity to polycarbonate, good stereo-selectivity and in some cases enhanced enantioselectivity at mild conditions [10]. On the other hand, the reactions using metallic catalysts have disadvantages, such as poor solubility of the catalyst, difficulties in catalyst recycling, air sensitive, the need of co-solvent, or the requirement for high temperatures [11].

It was noteworthy that salen Co complexes showed excellent effects [12]. Since 2004, Coates first reported salen Co(III) complex [7]. This complexes showed an excellent selectivity to polypropylene carbonate formation (99% vs. cyclic carbonate) with 99% of carbonate linkages [13]. A significant effort was devoted to the synthesis of more efficient salen Co complexes, which contributed to better understanding of reaction mechanism [8, 10]. The most effective catalysts for epoxide/CO_2 copolymerization proved to be chiral salen Co (III) complexes in combination with strong Lewis acids and nucleophilic co-catalysts [10]

On the other hand, although the chemical or crystal structures of heterogeneous catalysts have not been completely elucidated, some of them show good potential in industrial applications [4]. Zinc glutarate (or other carboxylates) and double metal cyanides are the two major classes of heterogeneous catalysts [14]. Other typical heterogeneous catalyst include $ZnEt_2$/active hydrogen-containing compound systems [4], carboxylic zinc [15], and rare-earth metal coordination ternary catalysts [16]. For copolymerization reactions using carbon dioxide, these heterogeneous catalysts require much more forcing conditions than homogeneous species [3].

In the case of zinc glutarate (ZnGA) to obtain appreciable amounts of polymer, high catalyst loading, high CO_2 pressures and long reaction times are mandatory [17, 18]. High activities have been achieved by using ultrasonication, different supports for ZnGA synthesis and different amounts of catalyst [19-21]. Actually it has been tested for terpolymerization reactions achieving TON of 123 with charging 200 mg of ZnGA and 50ml of PO [14] . ZnGA catalyst has been analyzed by different techniques and exhibits yield of 64 g polymer/g catalyst with loadings of 1 g of catalyst and 100 ml of PO [22, 23].

Double metal cyanide complexes (DMC) are well-known catalysts for the ROP of epoxides [24].

Generally, the DMC catalysts are obtained by reacting a selected metal salt with a cyanide derivative from another metal in the presence of an electrodonor organic complexing ligand [25]. The most commonly studied double metal cyanide catalyst is $Zn_3[Co(CN)_6]_2$ [3, 26, 27] and it has been identified as the most active for copolymerization [28]. Besides, a variety of transition metal elements such as Ni, Co, Fe [29], and Mn have also been studied [28]. DMC complexes has been used for copolymerization of cyclohexene oxide (CHO) and CO_2 [30, 31] and also for copolymerization of propylene oxide (PO) and CO_2 [27, 32, 33]. In addition to the correct selection of the types of salt and the complexing ligand, relatively complex preparatory methods are required to obtain the DMC catalysts, involving several critical factors that determine the resulting catalytic activity, kinetic path, and quality of the resulting polyadducts [25]. Furthermore, the incorporation of DMC in the copolymerization of epoxides and CO_2 has some disadvantages.

One is the low CO_2 insertion in the polymer chain. Besides that, the copolymerization conditions involving DMC catalyst include temperatures in the range of about 80-130°C and pressures usually from 50 to 100 atm. Importantly, the copolymer produced has only moderate molecular weight with wide polydispersity [34].

Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyoxypropylene polyols [12–15]. The catalysts are highly active and give polyether polyols that have low unsaturations and narrow molecular weight distribution compared with similar polyols synthesized using conventional KOH catalyst, resulting in high performance polyurethane products [16].

Furthermore, the amount of catalyst is very small and its influence in the final polymer can be neglected, so there is no need of catalyst recovery after the reaction in such case.

While DMC catalysts offer significant advantages for the ROP of epoxides, just few reports have been published on the copolymerization of epoxides with CO_2 thereby [24].

In this paper, we report the activation tests of a DMC catalyst prepared with potassium hexacyanocobaltate and zinc chloride for polypropylene glycol (PPG) and a copolymerization process with propylene oxide (PO). The aim is to elucidate the best conditions for catalysis productivity in terms of activation. As far as the authors know, there are no reports of a catalyst activation study at different conditions, where the amount of DMC used is crucial to obtain the maximum efficiency for the copolymerization process.

2. EXPERIMENTAL

2.1 MATERIALS

Zinc chloride ($ZnCl_2$), potassium hexacyanocobaltate III ($K_3[Co(CN)_6]_2$), *tert*-BuOH (t-BuOH) and polyethylene glycol (PEG 1000, Mw=1000 g/mol) were used for catalysts synthesis without further purification and purchased from Sigma-Aldrich. Propylene oxide (PO, ≥ 99%, Sigma-Aldrich), polypropylene glycol (PPG 725, Mw= 725 g/mol, Sigma-Aldrich) and CO_2 were used as received.

2.2 PREPARATION OF DMC CATALYST

Highly active catalyst was prepared as follows, 2.128g of $K_3[Co(CN)_6]_2$ were dissolved in 80 ml of mili-Q water and 7.738g of $ZnCl_2$ in 210 ml of miliQ water and 50ml of t-BuOH. Both solutions were mixed and vigorously stirred during 15 min at 50 °C. After 13 min, PEG 1000 was added to the mixed solution, and the white suspension obtained was centrifugated during 6 min at 5000 rpm. The isolated slurry was resuspended with vigorous stirring during 20 min in 100 ml of a t-BuOH:H_2O (50:50) solution and centrifugated as previous. The solid was resuspended in 100 ml of 100% t-BuOH and stirred for 30 minutes, filtered (omnipore PTFE membrane filter, 0.1 µm, Merck Milipore) and dried under vacuum conditions at 50 °C during 30 hours.

2.3 CATALYST ACTIVATION AND COPOLYMERIZATION PROCESS

PPG 725 was used as initial template polymer for catalyst activation trials. Assuming that the number of polymer moles was constant during the reaction and also that all the –OH branches grew equally, the amount of PPG 725 starter was set at 30 g (0.04 mol) and also the activation temperature was set at 130ºC.

Catalyst and PO amounts were changed in order to elucidate the best conditions for catalyst productivity. The amounts used for every experiment are shown in Table 1.

Table 1. Amounts of catalyst and PO used for each activation experiment

Catalyst (g)	**PO (g)**		
	1st activation	**2nd activation**	**Total**
0.010	3.00	1.00	4.00
	6.20	2.00	8.20
	11.90	6.30	18.20
0.020	3.00	1.00	4.00
	6.10	2.10	8.20
	12.00	6.00	18.00
0.040	3.00	1.20	4.20
	6.10	2.00	8.10
	12.00	6.10	18.10
0.080	3.20	1.00	4.20
	6.10	2.10	8.20
	12.00	6.00	18.00

The amount of PPG 725 starter and the selected amount of DMC catalyst were placed in the reactor under continuous stirring and heat. Three successive inertizations using N_2 were carried out at different pressures (5, 15 and 20 barg) to remove all O_2 moieties.

A next step of heating to 130ºC under vacuum conditions was performed during 30 min to remove moisture in the PPG starting polymer.

Under vacuum conditions (-0.80 barg) the activity of the different amounts of catalyst (Table 1) were tested by two sequential activations at 130ºC. The amount of PO fed was also changed to perform the different experiments (Table 1). Usually, the amount of PO added for the activations was estimated to be around 7% of the total PO required if a PPC 2000 g/mol was pursued (6.10 g). Also, a lower (3.0 g) and a higher (12.0 g) amount of PO were tested for the different experiments (Table 1).

Once the first amount of PO (1st activation, Table 1) was pumped into the reactor the pressure increased due to PO vaporization up to thermodynamic equilibrium. The catalyst took typically between 10 to 30 min to activate itself, and after that, the reactor pressure decreased due to PO consumption. If a slightly increase on temperature followed by a decrease of pressure occurred before 1 hour from the first addition, the catalyst is active. Consequently, the second activation was performed in the same way as the first activation with the correspondent PO amount (Table 1, 2nd activation). The activation process experiments were finished at this point.

The experiments of 3.0 g of PO (1st activation) were driven to polymerization by continuing with the reaction as follows: third PO amount was added at the copolymerization pressure (20 bar) with CO_2.

After this PO addition and once the system raised steady stable conditions, the temperature was decreased down to the copolymerization temperature (105 ºC) and a PO was pumped in a continuous flowrate (0.35 ml/min). This PO flowrate must consider the maximum heat that the system can removed by the cooling equipment in order to avoid hotspots and runaway reactions.

After this stage, a continuous flow of CO_2 was fed into the system during 1 h to maintain a constant pressure.

Finally, the pressure was slowly released and the system was kept under vacuum conditions, flushing with N_2 to eliminate the unreacted PO monomers during 1 hour. Then, the reactor was cooled down to room temperature and the final copolymerization product recovered and weighted and saved for further analyses.

2.4 CHARACTERIZATION OF THE CATALYST

Elemental analyses of Zn (213.857 nm), Co (238.892 nm) and K (766.491 nm) were performed by optical emission ICP (Varian 725-ES), after a previous microwave digestion of the samples (ETHOS SEL Milestone). Infrared spectra from 400 to 4000 cm^{-1} were recorded using a Fourier transform infrared spectrometer (FT-IR) from Bruker ALPHA at a resolution of 2 cm^{-1} and data were taken after 64 scans.

An environmental scanning electron microscope (ESEM) was taken by ESEM-FEI-Quanta 200F after coating with 10 nm gold layer.

X-ray diffraction (XRD) patterns and crystallinity results were obtained on Bruker D8 Discover A25 diffractometer using Cu ceramic tube at 2.2 kW and LynxEye detector.

Micropours and mesoporus of the catalyst were analyzed by Nitrogen-Physisorption technique (Sorptomatic 1900, Carlo Erba Instrument). For the sample analysis first an outgassed burette was weighted, and then 0.25 g of DMC A was added to the burette in outgassing conditions during 3h at 150ºC and 0.01 Pa. After that, the burette was weighed to calculate the moisture of the sample and the specific surface area and pore volume of the catalyst (m^2/g) were determined.

2.5 CHARACTERIZATION OF COPOLYMER

Spectroscopic analysis of the polymers was performed using FT-IR (Bruker ALPHA) at a resolution of 2 cm^{-1} and spectrum data was taken after 64 scans.

The amount by weight of CO_2 incorporated in the polymer chain was determined by means of 1 H-NMR (Bruker AV III HD 500, 500 MHz, pulse program zg30, waiting time d1:1s, 120 scans). The sample was dissolved in deuterated chloroform. The relevant resonances in the 1 H-NMR spectra (based on TMS = 0 ppm) used for integration were: 1.05–1.25 (methyl group of polyether moieties, area of the resonance corresponds to three H atoms); 1.25– 1.35 (methyl group of carbonate moieties in polyether carbonate, area of the resonance corresponds to three H atoms); 1.50 (methyl group of cyclic carbonate, area of the resonance corresponds to three H atoms). Taking the intensities into account, the relative concentrations as well as the weight fractions were calculated.

Number average molecular weight (Mn) and polydispersity index (PDI) of polymer products were calculated from the obtained curves in a Waters 1515 size exclusion chromatograph (SEC) with 2 AGILENT PLGel 5 µm mixed D (300x7.5) columns, the temperature of which was set at 35°C using THF as solvent.

Detection was performed with a refractive index detector, solvent flow was 1 ml/min, and calibration was performed with PG standards.

3. RESULTS AND DISCUSSION

3.1 DMC CATALYST CHARACTERIZATION

DMC catalysts are highly efficient PO homopolymerization catalysts [35] and have been developed for decades for the production of high molecular weight and lower unsaturation polyethers [31]. Catalysts based on $Zn_3[Co(CN)_6]_2$ exhibits the highest catalytic activity [36]. It is reported that these active catalysts are a mixture of crystalline (35-70 wt%) and amorphous DMC [37]. Higher catalytic activity could be achieve by adding complex agent (CA) such as t-ButOH which activate Zn^{2+} ions [38]. Also, the excess of $ZnCl_2$ in the preparation is vital for catalytic activity. The retained $ZnCl_2$ enable the catalyst to be active being the active species likely related to $ZnCl_2$ coordinated by cyanide ion [31].

Zn-Co catalysts were prepared with $ZnCl_2$ in excess, complexing and co-complexing agents as described above. Different techniques have been used to describe the chemical properties of the catalyst prepared for the study in order to determine the influence of its characteristics on the activation processes.

ICP analysis was used to determine the amounts of Co, Zn and mainly K on the sample (Table 2). As the DMC catalyst was prepared by mixing $K_3[Co(CN)_6]_2$ and $ZnCl_2$, $KZn[Co(CN)_6]$ or K^+ can be also formed [31]. High amounts of K^+ could lead to decrease the catalytic activity of the DMC. Although in our case the content of K^+ is higher than in other studies [28], less than 100 ppm compared to 7820 ppm, the catalyst remains active for co-polimerization.

Table 2. Amounts of K, Co and Zn on the DMC catalyst analyzed by ICP.

Sample	Zn/Co mol ratio	K mol/g	Co mol/g	Zn mol/g	∑ (Zn+Co) mol/g
A	1,3478	0,0002	0,0027	0,0036	0,0063

FT-IR spectroscopy was used to identify the coordination and bounding in the DMC catalyst (Figure 1). The IR spectra exhibited the characteristic peak at 2189 cm^{-1} attributed to the $-C\equiv N$ stretch of the $K_3[Co(CN)_6]_2$ in the presence of CA and co-CA [30]. More characteristic peaks of the DMC are at 3460 cm^{-1} the –OH stretch, at 2977 cm^{-1} the C-H strech, at 1608 cm^{-1} the -OH bending from water, at 1470 cm^{-1} the –CH scissoring, at 1372 cm^{-1} the –OH bending from t-ButOH, at 1196 cm^{-1} the 3º-C-O stretch, at 642 cm^{-1} the Co-C bounding and at 471 cm^{-1} the Co-C stretching, this peak demonstrate that the main compound of DMC, $Zn_3Co(CN)_6$ was successfully formed [24].

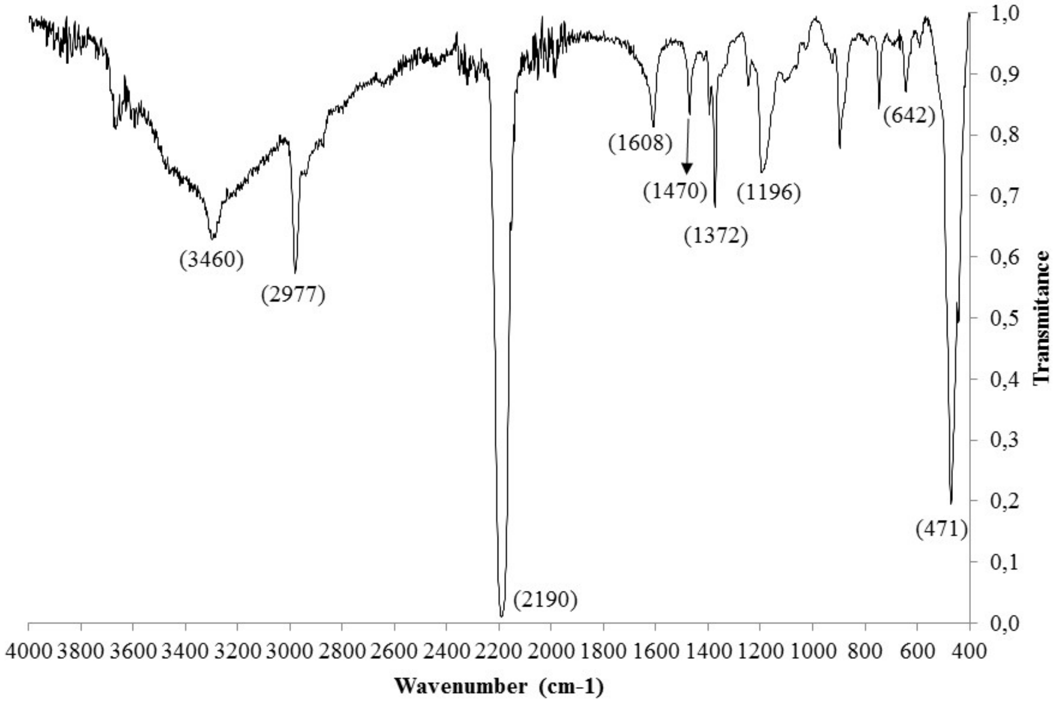

Figure 1.FT-IR spectra of the Zn-Co catalyst

Figure 2 shows the x-ray diffraction pattern of the catalyst being identified as Prussian blue analogue of $Zn_3[CoCN)_6]_2$ * 12 H_2O (lines marked in Figure 2) where most peaks have disappear due to the decrease of crystallinity [30]. The catalyst exhibited sharp lines which are related to a crystalline pattern [39], being the a DMC with high crystallinity (75.2%) besides the addiction of complexing (CA) and co-complexing agents (co-CA). The x-ray pattern is ascribed to cubic and monoclinic phases. Despite the overlap of some of the lines arising from the two different phases, reflections at 17.1°, 24.3° and 39.1° correspond to typical cubic lattice. Reflections at 14.5°, 17.0°, 23.7° and 24.7° are assigned to the monoclinic phase, being the 23.7° angle a clear diagnostic [40].

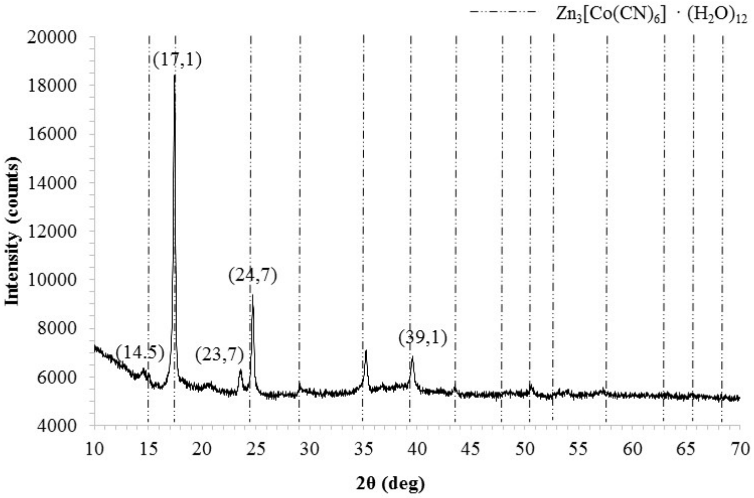

Figure 2. X-ray diffraction of the catalyst

IR band positions correspond to differences in the structure and bonding cyanide groups. As Sebastian et al. (2014) reports, the IR band at 2181 cm^{-1} is ascribed to the cubic structure and the 2190 cm^{-1} band corresponds to the monoclinic structure. Thus, according to the x-ray results, the catalyst is formed by both structures. Bands at 2153 and 2220 cm^{-1} are due to surface cyanide groups [38] (Figure 3).

The presence of this peaks also confirms that the catalyst could contain monoclinic and other phases along with the cubic phase.

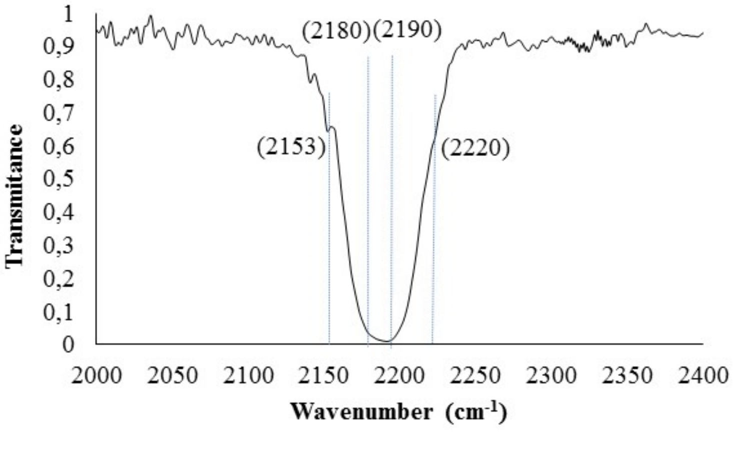

Figure 3. FT-IR spectra of the -C≡N stretch from the $K_3[Co(CN)_6]_2$ amplified

The ESEM images at different magnifications, 100.000x (a) and 50.000x (b) shown the particle size and morphology of the synthetized DMC (Figure 4). This catalyst showed thin lamellar structures with a length approximately of 33 nm surrounded by spherical particle agglomerates.

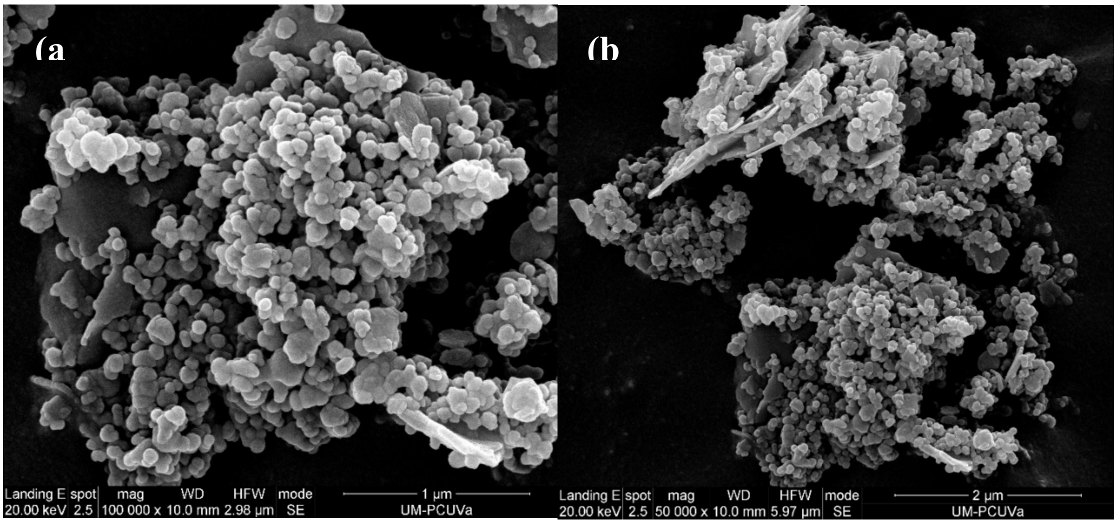

Figure 4.ESEM image of the synthetized catalyst

The N_2-physisorption analysis were carried out by microporous and mesoporous methods. DMC A microporous (21.28 % moisture) were analyzed by Dubinin surface area calculation method (714.12 m^2/g) and Horvath-Kawazoe pore size calculation method (0.254 cm^3/g). DMC A mesoporous (12.87 % moisture) were determined by B.E.T surface area calculation method (393.69 m^2/g) and Dollimore-Heal pore size calculation method (0.364 cm^3/g). The main parameter for the N_2-physisorption technique for the catalyst characterization is the surface area of the sample, and data shown a very high surface area (714.12 m^2/g) compared to other studies 443 m^2/g [41] and 653 m^2/g [36]. The high surface area means that the catalyst presents many active sites for co-polymerization reaction.

3.2 CATALYST ACTIVATION STUDY

Before starting the reaction, the experience shows that the catalyst centers need to be activated properly. The activation is usually carried out using PO alone, avoiding CO_2 that can slow the reaction rate. In this study we have considered two activation steps. First, PO is added to the reactor at the activation temperature and under vacuum conditions. Due to thermodynamic phase equilibria the PO vaporizes as soon as it reaches the reactor, increasing the reactor pressure. The PO is transferred from the gas phase to the liquid phase (initial polymer) and as the catalyst activates it is consumed in the liquid phase. If the activation occurs properly the final pressure nearly reaches the initial vacuum values. From a transport phenomena viewpoint the two in series steps are there: first, mass transfer from the gas to the liquid and second, reaction in the catalyst activate centers. To be completely sure that all the sites are active, a second activation was conducted in all cases. For the second activation the amount of PO pumped into the reactor was slightly lower (Figure 5).

The activation of a small amount of a heterogeneous catalyst suspended in a viscous liquid is not trivial. The study of the catalyst activation was carried out by varying 2 different parameters, the initial amount of DMC used and the PO used for the 2 subsequent activations. The point that we wanted to study was how the centers were activated depending on the quantity of PO available per potential active center and depending on the number of active centers per initial polymer chain.

In this sense, 12 experiments were performed using, 10, 20, 40 and 80 mg of DMC catalyst and 4, 8 and 18 g of OP in total for the activations (Table 1).

This study clearly shows the existence of two different activation mechanisms, depending on the conditions that occur in the time of activation, as shown in Figure 5.

Thus, an activation that we can call "fast" is characterized by an induction time, where a constant pressure, followed by a sudden drop in pressure is maintained. This activation period depends on the initial pressure in the reactor. The curiosity in this case is that at a low amount of catalyst per mol of PO, the consumption rate is extraordinary fast. A second type of activation that we can call "slow" was also found in some of the runs. In that case, once the maximum pressure in the reactor was reached (after the first PO addition) this pressure begins to decrease gradually without observing a proper activation period (that is characterized by a sudden pressure decrease). In this case, the higher amount of catalyst causes a higher PO consumption rate, as it could be expected of a heterogeneous catalyst (more catalyst more reaction rate).

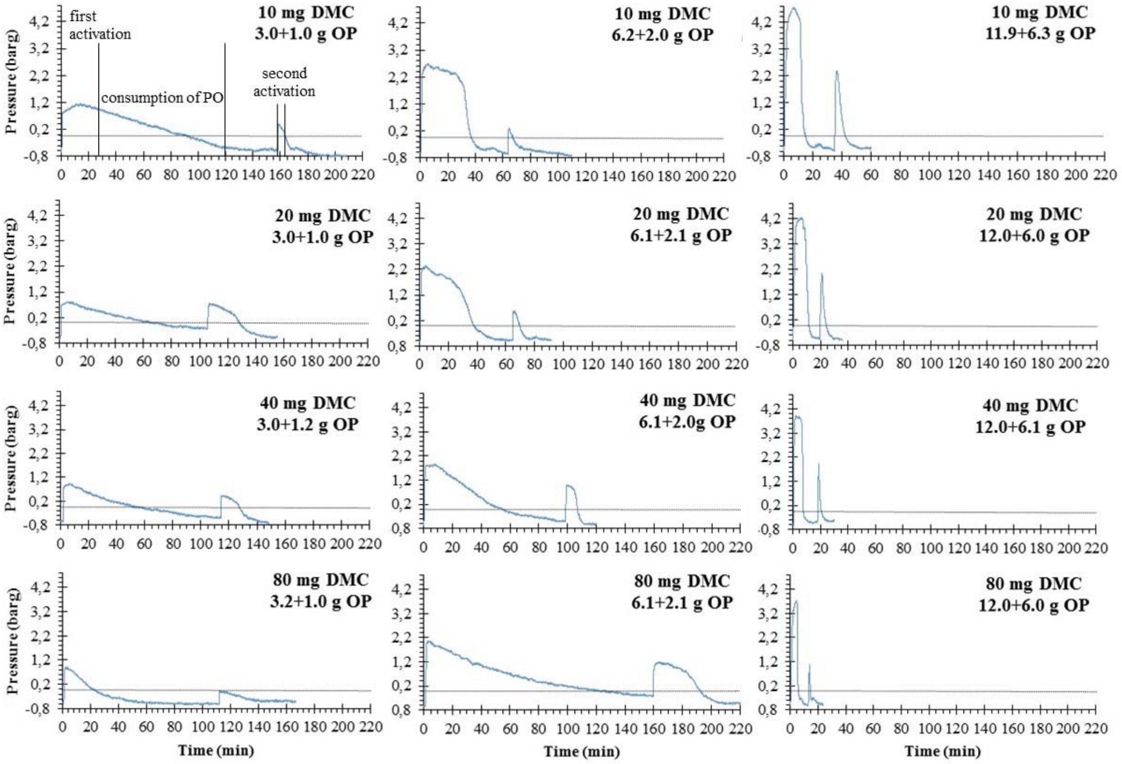

Figure 5. Catalyst activation with different amount of PO and DMC added for the copolymerization reaction.

As shown in the figure 6, the boundary between both types of activation depends on the pressure reached in the reactor after loading the PO, i.e. the number of moles of PO loaded. A hypothetical interpretation of these behaviors could be as follows: when there is an excess of moles with respect to the catalyst (as in the case of introducing 18 g PO giving a maximum pressure of 4.2 barg) rapid equilibration between the free PO in the bulk liquid and OP adsorbed on the catalyst sites, causing all active centers are activated simultaneously resulting in the sudden drop in pressure (by fast PO consumption). On the other hand, when an insufficient amount of PO is fed (as in the case of 4 g of OP giving a maximum pressure of 1.2 barg) the PO diffuses slowly to reach the active site and activation occurs gradually only in certain sites. At intermediate pressures (e.g. the case of 8 g of PO and 2.2 barg pressure), depending on the relative amount of PO both types of activation might occur, and it is not that easy the accurate prediction.

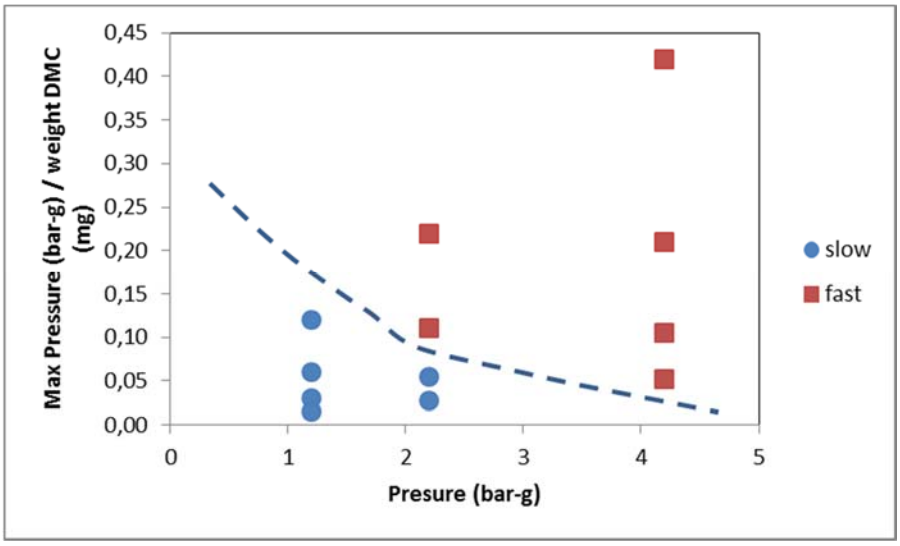

Figure 6. Fast and slow activation types as a function of the initial pressure

As this reaction is highly exothermic, at high PO flowrate inside the reactor or at high consumption rate of PO, it is possible to obtain hotspots or runaway reactions. So, there has to be a good control of the released heat from the reaction.

From the results obtained just taking into account the DMC activation processes, it can be suggested that the best ratio DMC/PO should be the one that assures a complete activation of the catalyst and a moderate reaction rate for the best homogeneous product, which involves a low PDI. This ratio could be improved depending on the corresponded process requirements such as refrigeration system, amount of final product to be obtained and molecular weight of the final product. Furthermore, it can expected that a homogeneous activation of the catalyst may result in improved polymerization and thus the quality of the final product.

3.3 COPOLYMERIZATION STUDY BY VARYING THE INITIAL AMOUNTS OF DMC

FT-IR spectrum of the obtained copolymers is shown in Figure 7. A sharp C=O asymmetric vibration absorption at 1742 cm^{-1} and a C-O stretching vibration at 1252 cm^{-1} was found, providing the evidence of the incorporation of CO_2 into the polymer chain [27, 33] . At the same time, it can be seen low intensity peaks at 1809 and 786 cm^{-1} characteristic of the byproduct, cyclic carbonate (PC).

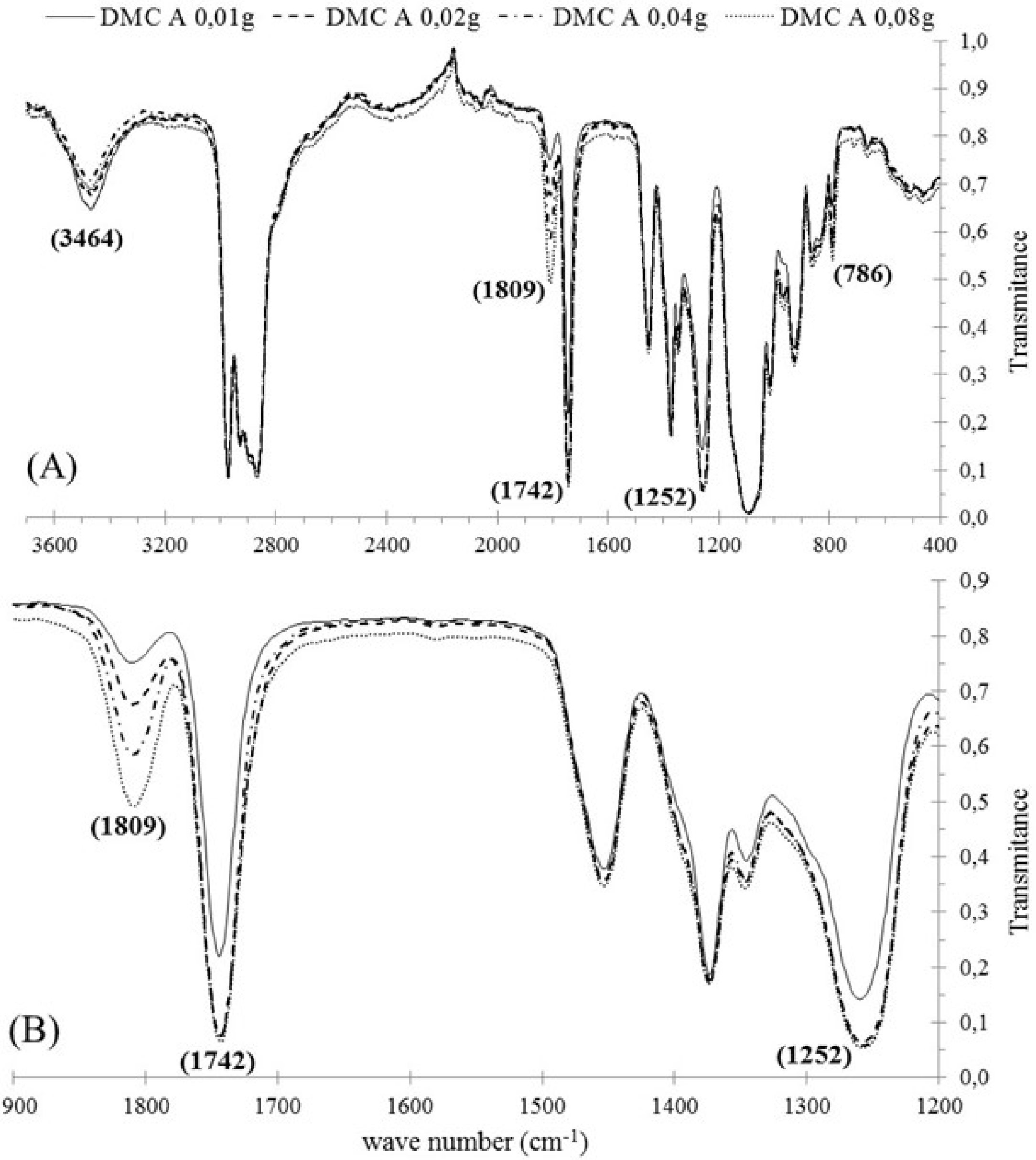

Figure 7. FT-IR of the co-polymer experiments using 3 g of PO for the first activation and the different amounts of DMC. (A) complete FT-IR of the copolymer, (B) figure zoom at the copolymer and by product peaks.

As can be seen in Figure 7, when DMC A 0.01 g is used the vibrational bands that correspond to the PC (cyclic carbonate, 1809 cm^{-1}) and PPC (polycarbonate, 1742 cm^{-1}) are the smallest. When DMC A 0.02 g is used the PC vibrational band area is smaller than for the DMC A 0.04 g and DMC A 0.08 g but the PPC band area is the same.

For the higher amounts of catalyst (0.04 and 0.08 g) the PC vibrational band area is higher respectively while the PPC remains equal than for the 0.02g DMC.

Table 3. Copolymerization data for the DMC A and the different amounts of catalyst used [(a)]

Catalyst	PPG/DMC (g/mg)	t (h)	TON[(b)]	TOF[(b)]	W_{PC}[(c)] (%wt)	CCU[(c)] (%wt)	PPC product		PDI
							Mw	Mn	
A	30/10	6.0	135	22	0.7	5.9	10002	1283	7.79
A	30/20	4.7	146	31	1.1	7.6	7745	1435	5.40
A	30/40	3.7	49	13	2.1	9.4	11048	1779	6.21
A	30/80	2.9	24	8	2.7	8.5	12713	1583	8.03

(a) All copolymerization reactions were carried out at 105ºC, 20 barg with 30 g of PPG (725 g/mol) and 50 g of PO in total.

(b) TON calculated as mol PPC/mol catalyst, TOF calculated as TON/h

(c) Carbonate content unit (CCU) and ratio of PC in the product (W_{PC}) was determined by NMR

As the DMC catalyst is not a selective one, in these experiments both carbonate and byproduct (PC) are obtained. When a higher amount of DMC is used for the experiments, the byproduct production increased maintaining similar incorporation of carbonate into the polymer.

When more catalyst is involved in the reaction there are more active sites to carry out the co-polymerization process. At these operation conditions, the reaction is favorable to get the byproduct instead of PPC production. When only 20 mg of catalyst are used even having less active sites in the medium, the reaction drives to PPC production.

Results showed (Table 3) that the more DMC amount is added into the reaction the less TON and TOF values are obtained, with the exception of 20 mg of DMC. With this amount of DMC, TON and TOF values are the highest, 146 and 31 respectively. Also, it showed the smallest PDI value (5.40), a considerable incorporation of CO_2 (7.6%wt), maintaining a low byproduct production (1.1%wt). These results confirm the ones obtained by the FT-IR technique, where for this operation conditions the best amount of catalyst that can be used is 0.02 g.

4. CONCLUSIONS

DMC catalysts require activation to work properly for polymerization. In this chapter we have demonstrated that the activation period is crucial for the catalyst and it highly depends on the transport phenomena of the propylene oxide to the catalyst sites.

Thus, two different types of activation, namely “slow” and “fast” were encountered. The “slow” activation is the most expected one. A minimum amount of propylene oxide is added, so the mass transfer is slow, not all the centers activate at the same time, indeed only few are activated. Therefore, the PO consumption is extremely slow, although the PO amount was really small. On the other hand, the “fast” activation, works against the expected behavior. A considerable high amount of propylene oxide is added, the ratio of PO per center is high, all the centers have enough PO and all of them activate correctly. This ends in an extremely fast consumption of PO (sudden drop in the reactor pressure). A relation between the pressure in the reactor and the type of activation was envisaged.

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CONCLUSIONS

This research about processing polyalcohols, polycarbonates and polyurethanes in copolymerization reactions is a contribution to the new trend of green technology in every process from laboratory scale to industrial scale.

Two different types of catalysts were studied during this research. Both with a completely different behaviour, have been used for copolymerization reactions among propylene oxide (PO) and carbon dioxide (CO_2).

Several techniques were used for the characterization of the synthesized catalysts and also for the obtained copolymers from each reaction.

This PhD thesis is formed by three papers, all in publication process, that are shown in this document as Chapter 1, Chapter 2 and Chapter 3. Also, it has two annexes with more related work that was developed during these years of researching.

Chapter 1 is focus on Zinc Glutarate catalyst study while, Chapter 2 and Chapter 3 are dedicated to the study of Double Metal Cyanide (DMC) catalysts.

Practically the same analytical techniques were used for the characterization of both types of catalysts, showing differences among them on specific surface area, pore volume, structural configuration, shape and size of the particles and catalytic activity in the copolymerization reactions.

About the study of Zinc Glutarate (ZnGA) catalyst, it has been demonstrated that this catalyst has no pores and no acids sites on it, so all the active surface area corresponds to the outer surface of the catalyst. Zn^{2+} are identified as the active sites of the sample.

The morphology of the particles was described as rectangular plate shape with an average of 321.6 nm on sizes and an amount of zinc of 353 mg Zn / g catalyst.

In terms of the catalyst behaviour in the copolymerization reactions, an exhaustive study was done modifying several process variables.

By this way, the best reaction conditions were determined in order to get a 3000 g/mol polymer. These are 1.5 g of catalyst, 25 barg, 80 ºC and 40 h.

Although ZnGA catalyst can open the epoxide (ROP) and form copolymers, its behaviour is extremely slow with its corresponded low TON and TOF values.

A different behaviour is observed using a Double Metal Cyanide (DMC) catalyst.

Five different Double Metal Cyanide (DMC) catalyst were synthesized changing the metal ratio on them to determine its effect on the catalytic activity.

The main objective was to find a catalyst which produced a low amount of the byproduct (PC) and a high one of the desired product (PPC).

The characterization of these five catalysts showed porous catalysts with a considerable amount of moisture in their pores and specific surface areas around 850 m^2/g. Their morphology showed a lamellar and spherical agglomeration shape of particles. Structural properties determined that Zn-OH groups in these DMC catalysts were the active centers for the polymerization reactions.

Only 2 catalyst were activated of the 5 which were synthesized and used for the copolymerization reactions among PO and CO_2.

The stirring system resulted in a very important variable to consider for these types of reactions.

Previous PDI values were between 5.97 and 13.09 due to the high viscosity of the medium. Improving the magnetic stirring into a mechanical one, the PDI values decreased drastically to value 1-1.1. This value implies getting short and more distributed polymer chains in the bulk fluid.

Among all the catalysts synthesized for this study, DMC E catalyst showed the highest catalytic activity (2.5 kg polymer/g catalyst), the more CO_2 incorporation to the chain (6.7%) and the less production of PC (0.3%).

Once it was known which one of all the synthesized DMC was the best one in order to be reactive and to increase the productivity of the process, the next research was a study about the activation step previously to the reaction one.

This catalyst (DMC A) is exactly the same as DMC E, previously discussed but, in this document particularly in Chapter 3, it appears with the same nomenclature as the corresponding paper.

The activation of the catalyst is a crucial step. We have demonstrated that depending on the quantity of propylene oxide available per potential active center of the catalyst, and depending on the amount of catalyst per initial polymer chain, the activation has two different behaviors. A "slow" activation, when not enough propylene oxide is used and only several potential active centers are certainly activated and a "fast" activation, where all the centers activate at once and they consume the propylene oxide at an unexpectedly high rate.

Different amounts of PO and DMC were used for this research. Twelve experiments were done using 10, 20, 40 y 80 mg of catalyst and 4, 8 and 18 g of PO in total. Results showed that using only 20 mg of catalyst, more PPC was produced and less PC was obtained. Also, TON and TOF values are the highest obtained and the PDI value showed the lowest value of all of them. These results are also confirmed with the FTIR spectrum obtained for 20 mg of catalyst.

The solubility of CO_2 in several different PPC produced at different conditions was measured to be from 0.022 g_CO_2/g_PPC at 4.8 bara and 18ºC to 0.637 g_CO_2/g_PPC at 76.2 bara and 120ºC. The solubility increased along with pressure and temperature

RESUMEN

1. INTRODUCCIÓN

Esta tesis surgió con la idea de producir carbonatos de polipropileno en reacciones de copolimerización utilizando dos tipos diferentes de catalizadores heterogéneos: Glutarato de zinc (ZnGA) y los catalizadores Double Metal Cyanide (DMC).

A lo largo de este trabajo, se ha hecho un estudio completo de ambos catalizadores además de la caracterización de los policarbonatos obtenidos en las reacciones.

Uno de los aspectos más interesantes de este tema y, particularmente, en esta Tesis Doctoral, es el uso del CO_2 no sólo como medio de presurización de la reacción sino también como fuente de alimentación de C1.

Entre otros gases como el gas metano (CH_4) y el óxido nitroso (N_2O), el dióxido de carbono es una de las principales fuentes que causan el efecto invernadero. Las acciones por parte del hombre como la quema de combustible y otros fuel están incrementando la concentración de dicho gas (CO_2) en la atmósfera.

De cara a atacar y solucionar este problema el CO_2, que es un gas amigable con el medio ambiente, con baje coste, alta pureza, no tóxico y no inflamable, ha sido capturado, almacenado y utilizado en reacciones de copolimerización como fuente de alimentación C1.

Utilizar el CO_2 como fuente de carbono C1 no es sólo por su importancia desde el punto de vista de química verde (al eliminar o reducir el empleo de sustancias peligrosas para lograr una sociedad sostenible en un futuro) ya que utiliza un subproducto no deseado de reacción como monómero, sino también por su importancia desde un aspecto económico.

Estas reacciones, las cuales son llevadas a cabo en condiciones subcríticas y en modo batch, son reacciones de copolimerización, reacciones que implican la utilización de dos monómeros como reactivos: óxido de propileno y dióxido de carbono.

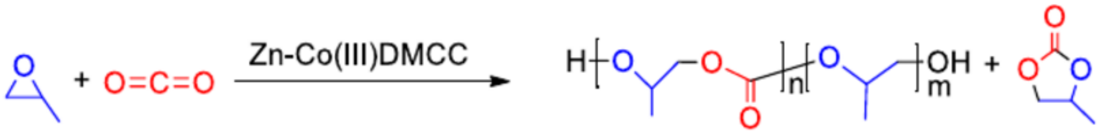

Figura 1. Reacción de copolymerización via catálisis heterogénea con un catalizador Double Metal Cyanide Complex [Zn–Co (III) DMCC] de zinc-cobalto (III).

El hecho de emplear el CO_2 como fuente de carbono C1, asegura menor OPEX en fuentes de carbono provenientes de otros químicos, como en este caso, epóxidos.

A través del mecanismo de Apertura de Anillo en Polimerizaciones (ROP), el epóxido (PO) se abre permitiendo la incorporación de CO_2 en la cadena de polímero.

Se han sintetizado y probado muchos catalizadores para reacciones de copolimerización a lo largo de los años.

De diferentes derivados del ácido glutárico, se han llegado a obtener varios catalizadores dicarboxilatos de zinc, dando el mayor rendimiento en carbonato de polipropileno (PPC) y mayor peso molecular alcanzado utilizando glutarato de zinc (ZnGA) como catalizador heterogéneo (desde ZnO / GA). Para la caracterización del catalizador se tienen en cuenta parámetros morfológicos. Aquel catalizador con elevada cristalinidad y calidad de cristal pero con menor área superficial, mostraba mayor actividad catalítica en reacciones de copolimerización.

El catalizador sintetizado a partir de óxido de zinc (ZnO) y ácido glutárico (GA) resultó ser el más activo para este tipo de copolimerización entre CO_2 y PO.

La investigación realizada con este catalizador se muestra en el Capítulo 1.

El Capítulo 2 y el Capítulo 3 utilizan, para esta reacción de copolimerización, otro tipo de catalizador heterogéneo, Double Metal Cyanide (DMC), en lugar del glutarato de zinc (ZnGA).

Todos los estudios que ha habido relacionados con la síntesis de policarbonatos, han girado en torno a desarrollar nuevos catalizadores que mejoren la actividad y la selectividad del mismo en reacción. Un catalizador que sea suficientemente rápido para reducir el tiempo de reacción pero, a la vez, suficientemente lento a la hora de incorporar PO, dando la oportunidad al CO_2 de reacción y de incorporarse en la cadena del polímero.

Muchos grupos de investigación han llevado a cabo estudios con catalizadores homogéneos y heterogéneos para mejorar la fijación del CO_2 en el polímero. Uno de los catalizadores que han demostrado ser válidos para ello, a la vez que para la apertura del epóxido, son los catalizadores tipo DMC.

Estos catalizadores DMC normalmente son hexacianometalatos de zinc preparados por reacción entre un haluro de zinc y una sal hexacianometalata junto a un agente complejante.

Son altamente activos, producen polioles poliéter con bajas insaturaciones con distribuciones estrechas de pesos moleculares y sirven para obtener policarbonatos biodegradables con un amplio potencial para aplicaciones de poliuretanos.

Muchos estudios han demostrado que se han llevado a cabo reacciones de forma satisfactoria entre el óxido de propileno (PO) y el dióxido de carbono (CO_2), utilizando complejos DMC basados en $Zn_3[Co(CN)_6]_2$ (el catalizador más estudiado de entre todos los complejos). Utilizando en complejo con cobalto, en lugar de con hierro ($Zn_3[Fe(CN)_6]_2$), la actividad catalítica es mayor, es el más activo para reacciones de copolimerización.

En el Capítulo 2 el estudio que se ha llevado a cabo ha consistido en mostrar el efecto que tiene el empleo de diferentes ratios Zn/Co en la preparación de 5 catalizadores DMC, probando su actividad catalítica en reacciones de copolimerización, la producción de subproducto (PC) y la incorporación de CO_2.

El Capítulo 3 estudia el proceso de activación del catalizador DMC que mejores resultados ha mostrado en el Capítulo 2. El proceso de activación de un catalizador DMC es un paso previo a la reacción de copolimerización.

En este capítulo, se muestra un catalizador DMC de elevada actividad, preparado con hexacianocobaltato de potasio y cloruro de zinc. Se muestra un estudio de la activación del catalizador donde las cantidades de PO y de DMC varían para determinar cuáles son las mejores de cara al proceso de copolimerización.

Un estudio de la activación del catalizador en diferentes condiciones donde se varía la cantidad del mismo es crucial para obtener la máxima eficiencia en el proceso.

Esta reacción puede ser la base de una química nueva en el futuro para obtener polímeros basados en el uso de bioalcoholes, determinando si nuevos poliuretanos y policarbonatos verdes pueden sintetizarse con aplicaciones industriales como termoplásticos biodegradables, polímeros con aplicaciones biomédicas…

Además de estos 3 capítulos, el documento presente consta del Anexo I, donde se muestran las experiencias llevadas a cabo para mediciones de solubilidad del CO_2 en diferentes copolímeros desarrollados en el laboratorio.

2. OBJETIVOS

Ha habido un gran interés en establecer esta nueva línea de investigación en ambos laboratorios: Reaction Engineering and Industrial Chemistry Laboratory del Process Chemistry Centre (PCC) perteneciente a Åbo Akademi University (Turku, Finlandia) y el Departamento de Ingeniería Química y Tecnología del Medio Ambiente de la Universidad de Valladolid (Valladolid, España).

El principal objetivo de esta investigación consistió en producir copolímeros de CO_2/óxido de propileno gracias al proceso de apertura de anillo (ROP) en batch y en condiciones subcríticas.

Para alcanzar este objetivo, el primer paso fue construir el sistema experimental en ambos laboratorios.

Las condiciones de trabajo fueron en condiciones subcríticas pero ambos sistemas podrían trabajar también en condiciones supercríticas, simplemente acondicionando ciertas partes del sistema.

Una vez que ambos sistema estaban listos, el siguiente paso implicaba la síntesis de ambos catalizadores heterogéneos que se utilizaron para las reacciones de copolimerización.

El procedimiento de síntesis, sus características morfológicas y su comportamiento son completamente diferentes.

Cada capítulo de esta tesis está a cargo de diferentes estudios con ambos catalizadores: las mejores condiciones para reacciones de copolimerización, el catalizador más activo, las mejores condiciones para el proceso de activación, diferencias en el comportamiento de ambos catalizadores de cara a obtener el copolímero final, con o sin subproducto después de la reacción…

Todos estos estudios están divididos en tres capítulos y dos anexos. Los objetivos específicos para cada uno de ellos son los siguientes:

Capítulo 1. Estudio del catalizador heterogéneo Glutarato de zinc en reacciones de copolimerización entre óxido de propileno y dióxido de carbono en batch y condiciones subcríticas. Los objetivos específicos son:

- Establecer un procedimiento de síntesis para este catalizador. Condiciones de síntesis como temperatura, presión, tiempo y cantidad de reactivos. Etapas necesarias para la obtención del catalizador. Método y resultados reproducibles.
- Caracterizacion del catalizador mediante diversas técnicas como Fourier transform infrared spectroscopy (FTIR and FTIR with pyridine), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), Nitrogen-Physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) y, finalmente, X-ray powder diffraction (XRPD).
- Estudio del catalizador Glutarato de zinc en reacciones de copolimerización utilizando óxido de propileno y dióxido de carbono como reactivos. Obtener las mejores condiciones subcríticas en batch para las reacciones: presión de reacción, temperatura de reacción, cantidad de catalizador, peso molecular final del copolímero y tiempo de reacción.

- Caracterización de los polímeros obtenidos mediante las técnicas Fourier transform infrared spectroscopy (FTIR) y Size Exclusion Chromatography (SEC).

Capítulo 2. Efecto de la relación Zn/Co inicial en la actividad de un catalizador Double Metal Cyanide (DMC) en copolimerizaciones mediante óxido de propileno y dióxido de carbono. Los objetivos asociados a este capítulo son los siguientes:

- Estudio de la relación entre metales (Zn/Co) en el procedimiento de síntesis de este catalizador heterogéneo DMC.
- Caracterización del catalizador mediante técnicas como Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Nitrogen-Physisorption, Scanning Electron Microscopy (SEM) y, por último, X-ray powder diffraction (XRPD).
- Estudio de un correcto protocolo de operación para la reacción de copolimerización.
- Determinación del efecto y la influencia de la agitación como parámetro durante reacciones de copolimerización.
- Caracterización de los copolímeros por Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR) y, finalmente, por Size Exclusion Chromatography (SEC).

Capítulo 3. Estudio de activación de los catalizadores DMC en reacciones de copolimerización. Estudio del proceso de activación variando la cantidad de catalizador en cada experimento.

- Estudio de la activación de los catalizadores DMC en reacciones de copolimerización utilizando óxido de propileno y dióxido de carbono como reactivos.
- Caracterización del catalizador Double Metal Cyanide más activo de los sintetizados en el Capítulo 2. Técnicas empleadas: Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Nitrogen-Physisorption, Nuclear magnetic resonance (NMR), Scanning Electron Microscopy (SEM) y, finalmente, X-ray powder diffraction (XRPD).
- Determinación de las mejores cantidades de reactivos y catalizador de cara a mejorar la producción de copolímero.
- Caracterización del copolímero final obtenido en diferentes condiciones de reacción mediante Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (NMR) y Size Exclusion Chromatography (SEC).

Annexe 1. Solubility study of CO_2 in several polymers at different pressure conditions.

- Determine the effect on the stirring system during the copolymerization reactions.

3. RESULTADOS Y DISCUSIÓN

CAPÍTULO 1. Estudio del catalizador heterogéneo Glutarato de zinc en reacciones de copolimerización entre óxido de propileno y dióxido de carbono en batch y condiciones subcríticas.

El objetivo principal de este capítulo fue realizar un estudio exhaustivo del catalizador Glutarato de zinc (ZnGA). Para ello, el primer objetivo específico a llevar cabo fue la síntesis de este catalizador heterogéneo.

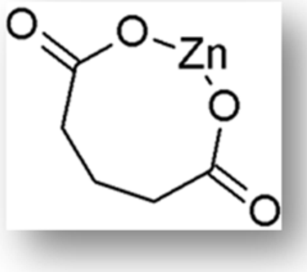

Figura 1. Glutarato de zinc (ZnGA).

El catalizador se ha sintetizado a partir de óxido de zinc, ácido glutárico y tolueno. Numerosas técnicas se han llevado a cabo para caracterizar este catalizador: Fourier transform infrared spectroscopy (FTIR and FTIR con piridina), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Light scattering (with air and distilled water), N_2-physisorption, Scanning Electron Microscopy and Energy–dispersive X-ray spectroscopy (SEM-EDX), Thermogravimetric analysis-mass spectrometry (TGA-MS), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD).

A través de estas técnicas, se ha determinado la ausencia de porosidad de este catalizador, donde la zona activa del catalizador corresponde a la superficie externa del mismo, mostrando que no dispone de ácidos Brøwnsted y/o Lewis.

El contenido medio de zinc en el catalizador es de 353 mg Zn / g catalizador, siendo la muestra muy polidispersa en cuanto a tamaño de partícula mostrando, a su vez, una morfología en forma de placas rectangulares, con un tamaño medio de 321.6 nm (Figura 2).

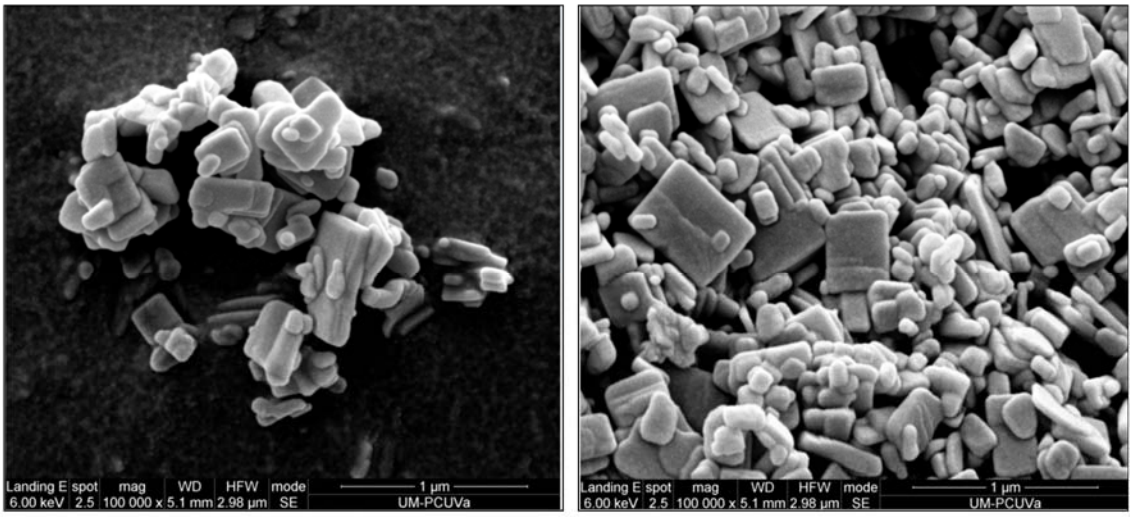

Figura 2. Imágenes SEM correspondientes al catalizador ZnGA

Una vez que este catalizador se obtuvo de forma satisfactoria y reproducible, se utilizó para obtener un copolímero de CO_2 / óxido de propileno; buscando la creación de enlaces policarbonatos (PPC) y tratando de minimizar la producción del carbonato cíclico (PC, subproducto de la reacción de copolimerización).

En estas reacciones, el dióxido de carbono no sólo actúa como medio de presurización para llevar a cabo la reacción, sino que también participa en la copolimerización como monómero, como fuente de carbono, C1. El otro monómero implicado en la reacción es el óxido de propileno.

Gracias al mecanismo de apertura de anillo (Ring Opening Polymerization, ROP), la inserción de CO_2 en la cadena es posible.

A través de Fourier transform infrared spectroscopy (FTIR) y de Size Exclusion Chromatography (SEC), se ha analizado el producto final de cada reacción de copolimerización.

Varias copolimerizaciones se han llevado a cabo variando las condiciones de reacción como la cantidad de catalizador (0.3, 0.6, 1.0, 1.5 g. Ver Figura 3), la temperatura de reacción (60, 80 ºC), la presión de reacción (6, 25 barg), el peso molecular final esperado de cada polímero (725, 3000 g/mol) y el tiempo de reacción (20, 40 h).

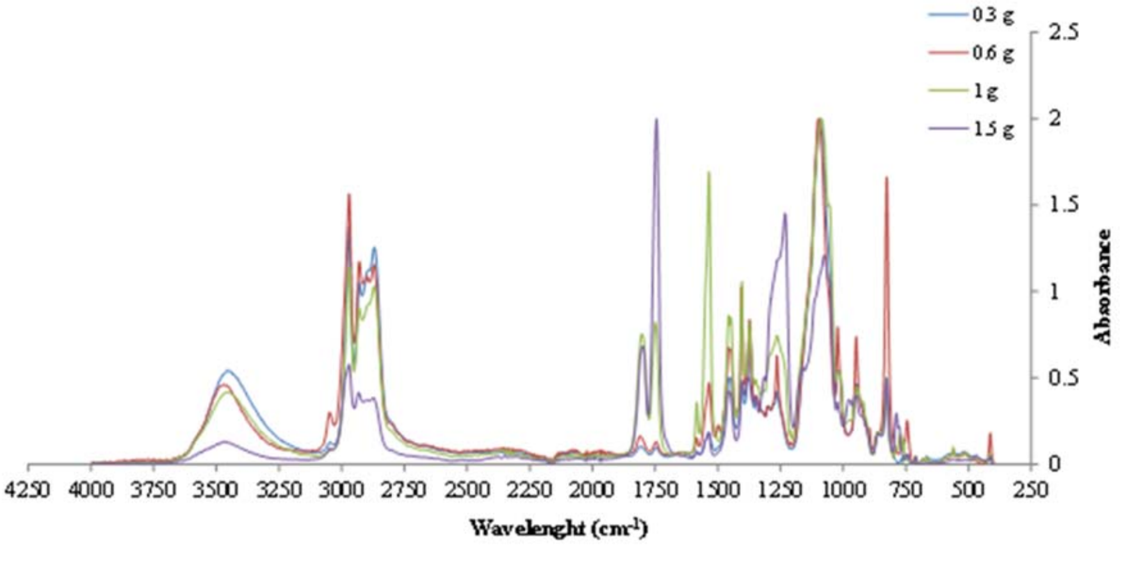

Figura 3. FTIR que representa el estudio de la cantidad de ZnGA en cada reacción.

En la figura 3 se muestra el estudio de cantidad de catalizador donde 1.5 g de catalizador se demostró que era la cantidad idónea para llevar a cabo polimerizaciones a 6 barg y 60 ºC con una cantidad de iniciador de 10 g y de óxido de propileno de 55 g.

En esas condiciones, el pico correspondiente al enlace carbonato (~1742 cm^{-1}) es el mayor de todos (es el producto de reacción que se busca obtener) y el pico que muestra los posibles enlaces libres para reaccionar, es el menor de todos (~3456 cm^{-1}). Esto quiere decir, que la reacción ha sido llevada a cabo de la manera más satisfactoria posible en esas condiciones.

Una vez hecho el estudio de los copolímeros se llegó a la conclusión de que las mejores condiciones de reacción fueron a 25 barg, 80 ºC, 1.5 g de catalizador, buscando un peso molecular final de 3000 g/mol y un tiempo de reacción de 40 h.

CAPÍTULO 2. Efecto de la relación Zn/Co inicial en la actividad de un catalizador Double Metal Cyanide (DMC) en copolimerizaciones mediante óxido de propileno y dióxido de carbono.

En este capítulo, el objetivo principal consiste en establecer cuál de los catalizadores Double Metal Cyanide (DMC) sintetizados es el más activo produciendo mayor cantidad de policarbonato (PPC) y una menor cantidad de subproducto (carbonato cíclico, PC).

Para ello, se ha variado la relación Zn/Co en el método de síntesis; aunque la estequiometría de la reacción es 1.5 Zn/Co (mol), las cantidades de ambos reactivos se han modificado para determinar la influencia de cada metal en exceso en la actividad catalítica en las copolimerizaciones, en la cristalinidad del catalizador, etc.

Estos catalizadores heterogéneos DMC se sintetizan a partir de $ZnCl_2$, $K_3[Co(CN)_6]_2$, tert-butanol (tBuOH, como agente complejante (CA)) y PEG 1000 (como agente co-complejante, (co-CA)).

Una vez establecido tanto el protocolo de síntesis de los catalizadores como el protocolo de reacción, se sintetizaron cinco catalizadores DMC diferentes y se llevaron a cabo las respectivas polimerizaciones entre el óxido de propileno y el CO_2.

Los catalizadores sintetizados se caracterizaron mediante el análisis con técnicas tales como Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP, Tabla 1), Scanning Electron Microscopy (SEM), N_2-physisorption y X-ray powder diffraction (XRPD).

Tabla 1. Composición final de los catalizadores sintetizados analizados por ICP.

Samples	Zn (% mol/mol)	Co (% mol/mol)	Zn/Co mol ratio	K (mol/g)	Co (mol/g)	Zn (mol/g)
A	60%	40%	1.47	0.0008	0.0022	0.0033
B	58%	42%	1.39	0.0007	0.0022	0.0031
C	59%	41%	1.45	0.0004	0.0028	0.0040
D	60%	40%	1.50	0.0003	0.0028	0.0042
E	61%	39%	1.58	0.0001	0.0026	0.0042

La presencia de iones K^+ hace que la actividad del catalizador DMC decrezca drásticamente, mientras que la presencia de iones Zn^{2+} hace que la morfología del catalizador tenga cada vez más aglomerados esféricos (ver catalizador E). A través de los análisis por SEM y N_2-physisorption, estos catalizadores muestran distribuciones tipo laminares, esféricas y cúbicas (Figura 4) con áreas superficiales alrededor de 850 m^2/g. El área superficial y el volumen de poro son parámetros cruciales para determinar la actividad catalítica de cara a obtener cadenas de polímero más cortas, lo que implica un buen valor en el índice de polidispersidad (PDI) en el producto final de reacción. El hecho de implementar un sistema de agitación mecánico, mejoró considerablemente el valor de la PDI, reduciendo su valor drásticamente desde valores comprendidos entre 5.97 y 13.09 hasta 1-1.1. Esto lleva consigo la obtención de cadenas más cortas de polímero, en el producto final, y mejor distribuidas.

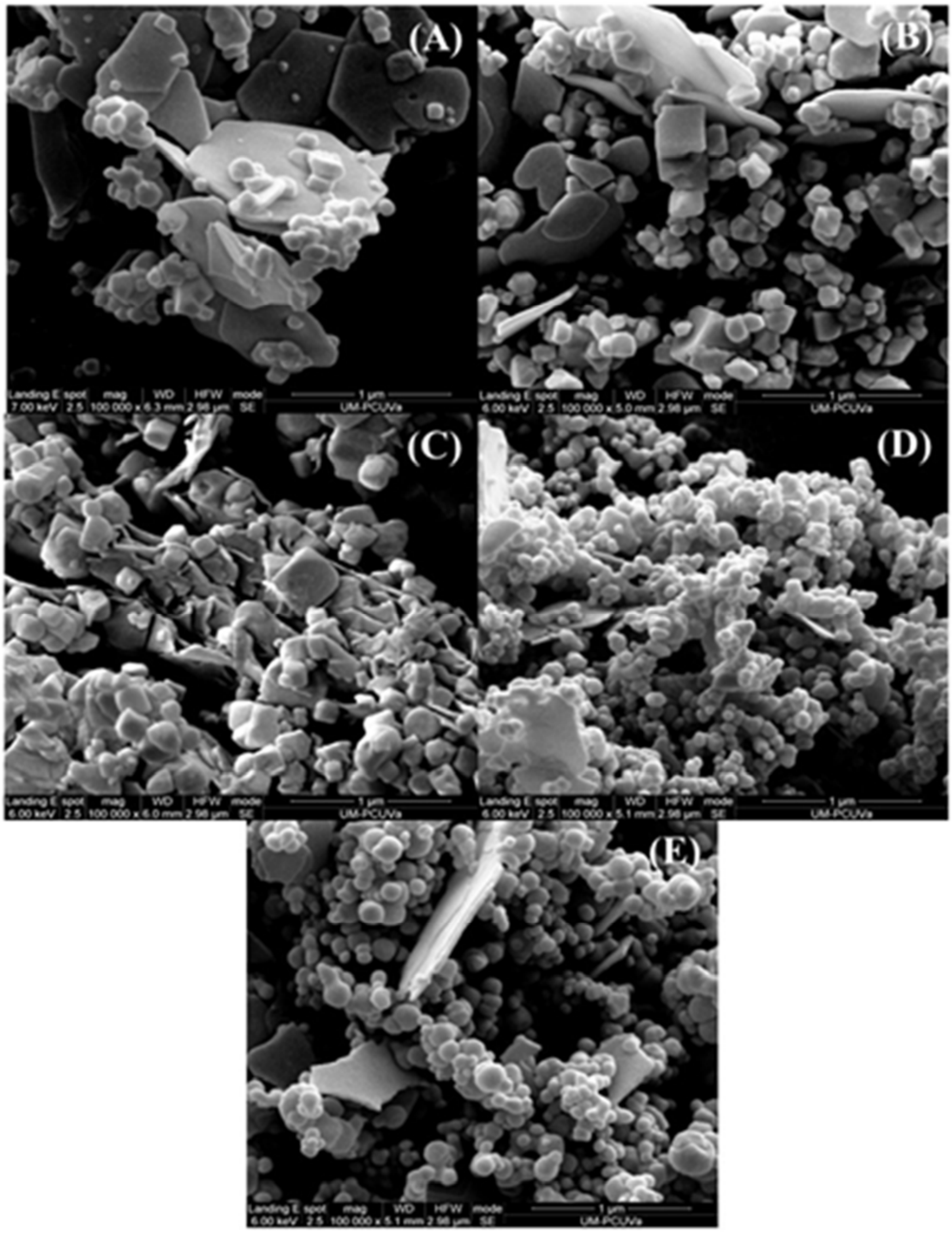

Figura 4. Imágenes SEM de los DMC sintetizados con distinta concentración inicial de Zn y Co.

Tras someter los catalizadores a un test de activación y en concordancia con los argumentos presentados anteriormente, sólo los catalizadores D y el E (ambos con un exceso de Zn^{2+} en su preparación) han llegado a activarse (Figura 5).

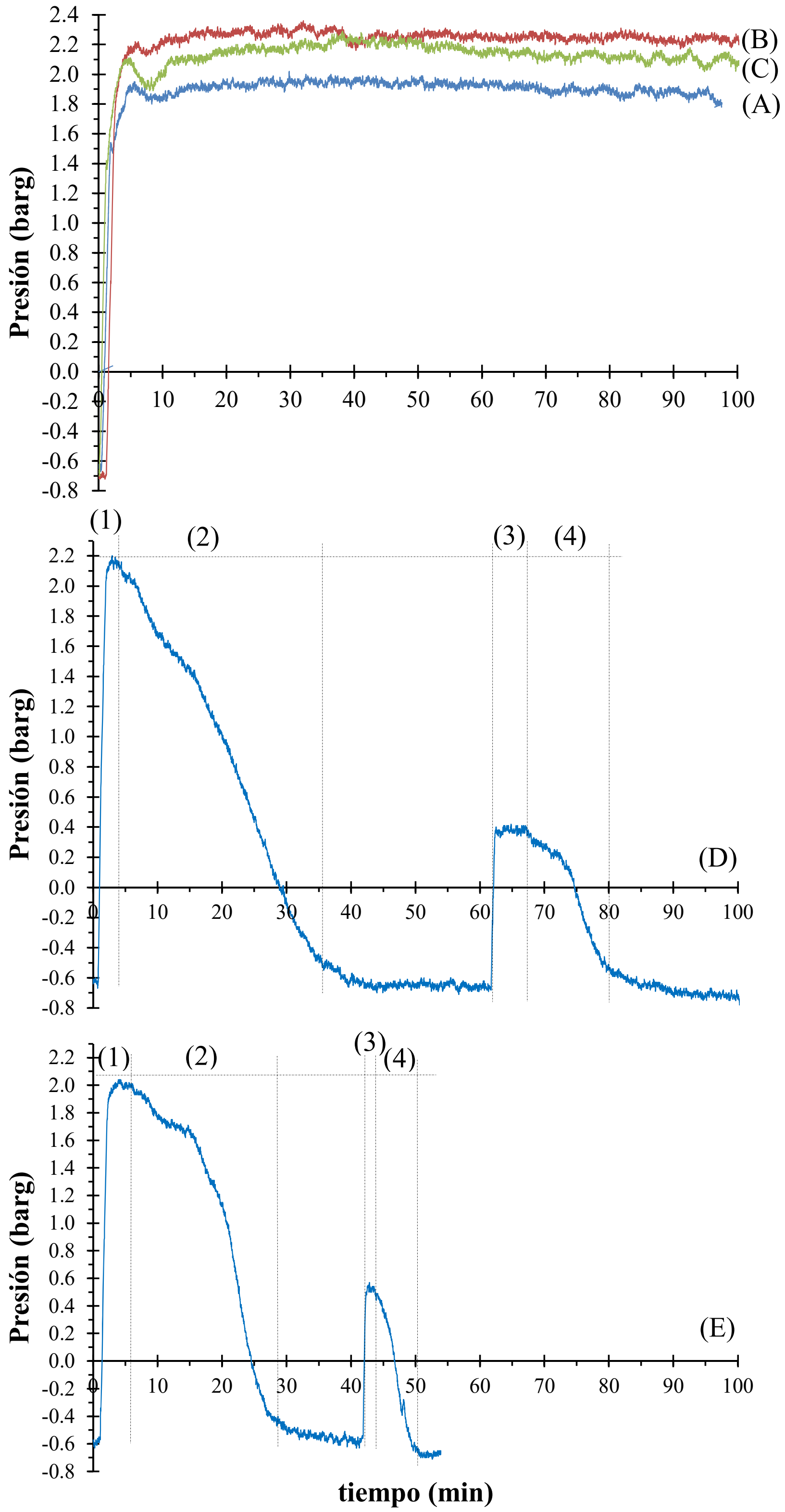

Figura 5. Etapa de activación de los catalizadores. A, B y C no son activos, D y E sí son catalizadores activados. (1) Primera activación, (2) periodo de consume de PO, (3) segunda activación, (4) segundo periodo de consumo de PO.

Por otra parte, los copolímeros obtenidos en las diversas reacciones fueron analizados mediante Fourier transform infrared spectroscopy (FTIR) y Gel Permeation Chromatography (GPC). Los resultados obtenidos se muestran en la Tabla 2.

Tabla 2. Datos de copolimerización de CO_2 y PO para los catalizadores activos$^{(a)}$

Cataliz.	**PPG/DMC (g/mg)**	**t (h)**	**Rendim$^{(b)}$**	**TON$^{(c)}$**	**TOF$^{(c)}$**	**$W_{PC}$$^{(d)}$ (%wt)**	**CTR$^{(d)}$ (%wt)**	**PPC producto**		**PDI**
								Mw	**Mn**	
D	30/42	6.5	1.4	34	7	0.4	5.6	25267	1930	13.09
E	30/41	6.0	2.5	99	14	0.3	6.7	15930	2660	5.97

(a) Todas las polimerizaciones se llevaron cabo a 105ºC, 10 barg con 30 gr de PPG (725 g/mol) y 90 gr de PO.

(b) Calculado por kg polymer/g catalyst

(c) TON calculado como mol PPC/mol catalizador, TOF calculado como TON/h

(d) Unidad con contenido en carbonato (CTR) y ratio de subproducto (carbonato cíclico, PC) en el producto (W_{PC}) determinado por NMR

Con estos resultados, se observa con el catalizador DMC E una elevada actividad catalítica (2.5 kg polímero / g catalizador), mayor incorporación de CO_2 (6.7 %) y menor producción de PC (0.3%).

CAPÍTULO 3. Estudio de activación de los catalizadores DMC en reacciones de copolimerización.

El objetivo principal de este capítulo consiste en hacer un estudio de la productividad variando la cantidad de catalizador DMC.

El catalizador, denominado DMC A, se sintetizó a partir de hexacianocobaltato de potasio y cloruro de zinc, como en el capítulo anterior.

En el estudio, las cantidades de PO y DMC se han variado para determinar cuáles son las mejores condiciones para obtener la máxima eficiencia en el proceso de copolimerización.

Las condiciones de estudio han sido 30 g de PPG y 130 ºC como temperatura de activación (Tabla 3).

Tabla 3. Cantidades de catalizador y de PO utilizados en cada experimento de activación.

Catalizador (g)	PO (g)		
	1ª activación	2ª activación	Total
	3.00	1.00	4.00
	6.20	2.00	8.20
	11.90	6.30	18.20
	3.00	1.00	4.00
	6.10	2.10	8.20
	12.00	6.00	18.00
0.040	3.00	1.20	4.20
	6.10	2.00	8.10
	12.00	6.10	18.10
0.080	3.20	1.00	4.20
	6.10	2.10	8.20
	12.00	6.00	18.00

La muestra fue caracterizada mediante diversas técnicas de análisis como Fourier transform infrared spectroscopy (FTIR), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), Environmental Scanning Electron Microscope (ESEM), N_2-physisorption y X-ray powder diffraction (XRD).

El catalizador sintetiza se ha preparado a partir de $K_3[Co(CN)_6]_2$ y $ZnCl_2$, donde $KZn[Co(CN)_6]$ y los iones K^+ también pueden formarse. Como ya se ha comentado en el capítulo anterior, elevadas cantidades de K^+ conllevan a una menor actividad catalítica del DMC. Este catalizador sólo contiene 0.0002 mol/ g cat de K^+ mientras que de Zinc contiene 0.0036 mol/ g cat.

La morfología de este catalizador corresponde a una estructura en láminas con aglomerados esféricos. (Figura 7)

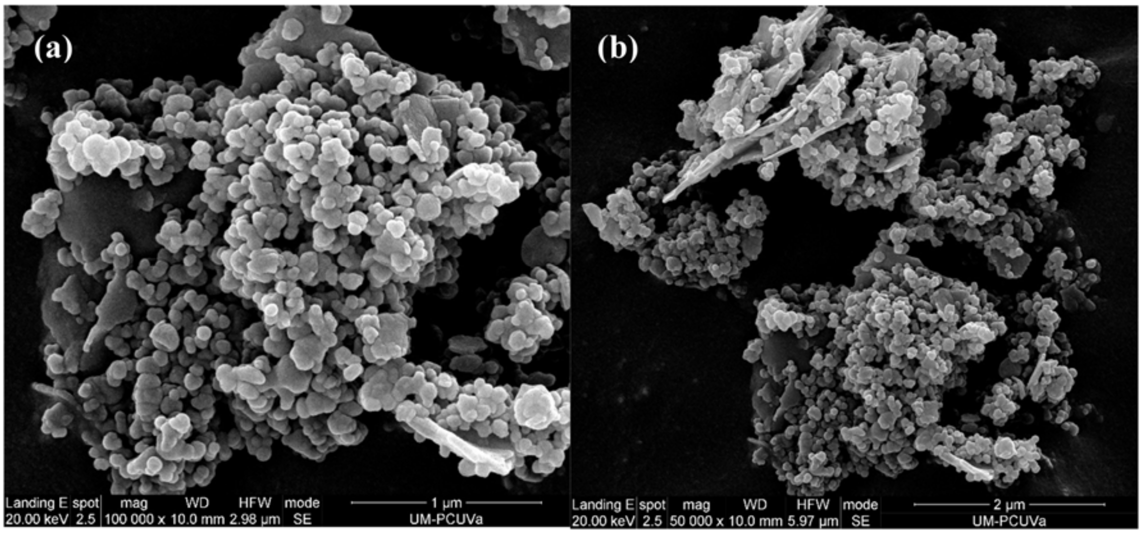

Figura 7. Imagen ESEM del catalizador de estudio

Este DMC tiene un área superficial de microporos de 714.12 m^2/g con un volumen de microporo de 0.254 cm^3/g. Por otra parte, el área correspondiente a macroporos es de 393.69 m^2/g con un volumen asociado de poro de 0.364 cm^3/g. Este catalizador dispone de muchos centros activos para las reacciones de copolimerización.

En cuanto a los copolímeros obtenidos, estos se han analizado mediante Fourier transform infrared spectroscopy (FTIR), Nuclear magnetic resonance (H-NMR) y Size exclusión chromatography (SEC).

Los experimentos llevados a cabo para este estudio de actividades de catalizadores DMC han sido 12, con 10, 20, 40 y 80 mg de catalizador y 4, 8 y 18 g de óxido de propileno (PO) en total.

En la Figura 8 se muestran los gráficos correspondientes a cada activación en los diferentes experimentos, mientras que en la Tabla 4 se muestran los resultados de las copolimerizaciones.

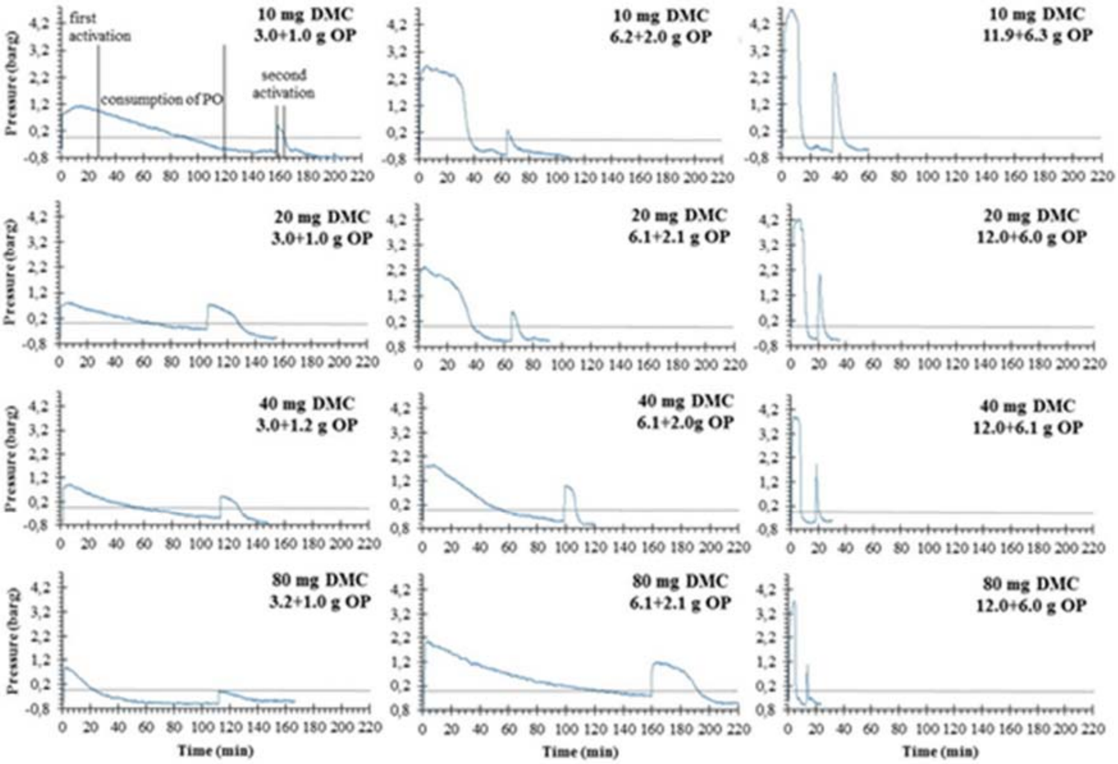

Figura 8. Activaciones del catalizador con distintas cantidades de PO y DMC

Tabla 4. Datos de las reacciones de copolimerización con el catalizador DMC A, a diferentes condiciones[(a)]

Catalyst	**PPG/DMC (g/mg)**	**t (h)**	**TON[(b)]**	**TOF[(b)]**	**W_{PC}[(c)] (%wt)**	**CTR[(c)] (%wt)**	**PPC product**		**PDI**
							Mw	**Mn**	
A	30/10	6.0	135	22	0.7	5.9	10002	1283	7.79
A	30/20	4.7	146	31	1.1	7.6	7745	1435	5.40
A	30/40	3.7	49	13	2.1	9.4	11048	1779	6.21
A	30/80	2.9	24	8	2.7	8.5	12713	1583	8.03

(a) Todas las copolimerizaciones se llevaron a cabo a 105ºC, 20 barg con 30 g de PPG (725 g/mol) y 50 g de PO en total.

(b) TON calculado en mol PPC/mol catalizador, TOF calculado como TON/h

(c) Contenido en carbonato (CTR) y ratio de PC en el product (W_{PC}) determinado por NMR.

Este tipo de catalizadores no son selectivos así que ambos productos son obtenidos. Cuando se aumenta la cantidad de DMC, la cantidad de subproducto aumenta, manteniendo constante la incorporación de CO_2 en el polímero.

Utilizando sólo 20 mg de catalizador, la reacción produce mayor cantidad de PPC y menor de PC, los valores de TON y TOF son los mayores que se han obtenido y la PDI muestra el menor valor de todos. Estos resultados también se confirman con el espectro de FTIR obtenido para 20 mg de catalizador.

ANEXO 1. Estudio de la solubilidad de CO_2 en policarbonatos obtenidos en reacciones de copolimerización utilizando catalizadores heterogéneos Double Metal Cyanide (DMC).

4. CONCLUSIONS

Esta investigación sobre la obtención de polialcoholes, policarbonatos y, por ende, poliuretanos en reacciones de copolimerización es una contribución más al empleo de tecnología verde (Green technology) en cualquier proceso desde escala laboratorio a escala industrial.

En esta investigación, dos catalizadores heterogéneos, con un comportamiento diferente, se han utilizado para llevar a cabo reacciones de copolimerización entre óxido de propileno y CO_2.

Diversas técnicas se han utilizado para la caracterización tanto de los catalizadores sintetizados como de los copolímeros obtenidos en cada reacción.

Esta tesis doctoral consta de tres papers en proceso de publicación, que se muestran en este documento escrito como Capítulo 1, Capítulo 2 y Capítulo 3 y, además, de dos anexos con trabajo que se ha desarrollado también durante estos años de investigación.

El Capítulo 1 se centra en el estudio del catalizador Glutarato de zinc (ZnGA) mientras que tanto el Capítulo 2 como el Capítulo 3 se dedican al estudio de los catalizadores Double Metal Cyanide (DMC).

Prácticamente se han utilizado las mismas técnicas analíticas para la caracterización de ambos catalizadores, mostrando diferencias entre ellos en el área superficial, volumen de poro, configuración estructural, forma y tamaño de las partículas y actividad catalítica en las reacciones de copolimerización.

En cuanto al estudio del catalizador ZnGA, se ha demostrado que éste no tiene poros ni sitios ácidos en él, con lo cual, toda la superficie activa del catalizador corresponde a la superficie externa siendo, los Zn^{2+} los centros activos del catalizador.

La morfología de las partículas está definida en forma de placa rectangular con un tamaño medio de 321.6 nm y la cantidad de zinc en el catalizador es de 353 mg Zn / g catalizador.

Sobre el comportamiento del catalizador en las reacciones de copolimerización, se ha llevado a cabo un estudio modificando diversas variables de proceso.

Así, se ha determinado que las mejores condiciones de reacción para obtener un copolímero de 3000 g/mol son 1.5 g de catalizador, 25 barg, 80 ºC and 40 h de reacción. Aunque este catalizador es capaz de abrir el epóxido y formar copolímeros, su comportamiento es extremadamente lento con valores de TON y TOF realmente bajos.

Un comportamiento diferente se ha observado al utilizar catalizadores tipo DMC.

Cinco catalizadores Double Metal Cyanide (DMC) se han sintetizado variando la relación de metal en ellos, determinando así su efecto en la actividad catalítica.

El objetivo principal fue encontrar un catalizador que produjese muy poca cantidad de subproducto (PC, carbonato cíclico) y una cantidad elevada del producto deseado (PPC, carbonato de polipropileno).

La caracterización de estos catalizadores muestra un catalizador poroso con un importante contenido en agua en los poros y un área superficial alrededor de 850 m^2/g. Su morfología es laminar con aglomerados de partículas esféricos. Los grupos Zn-OH de estos catalizadores se han determinado como los centros activos para las reacciones de polimerización.

De los cinco catalizadores diferentes que se sintetizaron y se utilizaron para las reacciones de polimerización entre el óxido de propileno y el CO_2, sólo dos de ellos llegaron a activarse.

El sistema de agitación resultó ser una variable muy importante en estos tipos de reacción. Valores previos de PDI estaban comprendidos entre 5.97 y 13.09 debido a la alta viscosidad del medio de reacción. Implementando un sistema de agitación mecánico en lugar del magnético, los valores de PDI disminuyeron drásticamente hasta el valor 1. Una menor PDI implica cadenas más cortas de polímero y más distribuidas en el medio de reacción.

De todos los catalizadores sintetizados, el catalizador denominado DMC E mostró la mayor actividad catalítica (2.5 kg polímero/g catalizador), más incorporación de CO_2 (6.7%) y la menor producción de carbonato cíclico (0.3%).

Una vez esclarecido cuál de todos los DMC sintetizados fue el mejor de cara a reacción, para aumentar la productividad del proceso, la siguiente investigación que se realizó fue un estudio de la etapa de activación previa a la de reacción.

Este catalizador (DMC A) es exactamente el mismo que el catalizador DMC E, previamente discutido pero, en este documento concretamente en el Capítulo 3, aparece con la nomenclatura de la publicación correspondiente.

Una vez conocido sobre qué catalizador se iba a hacer el estudio, se variaron las cantidades de óxido de propileno (PO) y de catalizador DMC. Doce experimentos fueron los que se llevaron a cabo utilizando 10, 20, 40 y 80 mg de catalizador y 4, 8 y 18 g de óxido de propileno (PO) en total.

Los resultados mostraron que el empleo de sólo 20 mg de catalizador, producía mayor cantidad de PPC y menor de PC. Además, los valores de TON y TOF fueron los mayores que se obtuvieron y la PDI mostró el menor valor de todos.

Estos resultados también se confirman con el espectro de FTIR obtenido para 20 mg de catalizador.

Hasta aquí se ha discutido todo lo relacionado con los capítulos y posteriores publicaciones de la tesis.

El primer anexo (Anexo I), muestra la solubilidad del CO_2 en diversos PPC obtenidos y en distintas condiciones. La solubilidad del CO_2 en los PPC producidos fue de 0,022 g_CO_2 / g_PPC a 4,8 bar absoluto y 18ºC y de 0,637 g_CO_2 / g_PPC al 76,2 bara y 120ºC. La solubilidad aumentó junto con la presión y la temperatura.

FUTURE WORK

At the beginning of this PhD thesis, the author tried to produce PPC using, first of all, a well-known zinc glutarate catalyst.

However, the difficulties arising from the use of this catalyst were evident. Nevertheless a considerable amount of CO_2 is incorporated in the polymer chain, and the viscosity of the resulting polymer is very high. This behaviour causes problems with the mass transfer in the reaction and stops it easily.

Furthermore, the amount of catalyst needed is high (in the order of grams per 100 grams of product), which forces to recover the catalyst afterwards.

We have not done this recovery because it involves a lot of time as it requires a complicated number of dilution and extraction steps.

This will be on the future works: to achieve the precipitation of the polymer, recover the catalyst and analyse this ***spent catalyst***.

After knowing the behaviour of ZnGA in copolymerization reactions, DMC catalysts have been studied. Chapter 2 and Chapter 3 were focus on the use of DMC catalyst. Unfortunately, in both chapters were not possible to recover and analyse the spent catalyst, as well. This could give important information about the activity and changes on the morphology of the catalyst.

More analysis and experiments are needed to show differences among catalysts activated and catalysts that are not. So more catalysts have to be synthesized.

One aspect that makes author and supervisors to be interested on is to study all these reactions at ***supercritical conditions of CO_2***.

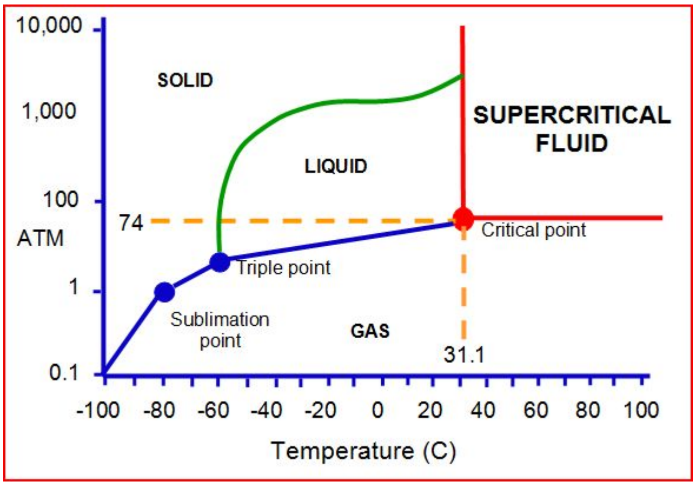

Figure 1. CO_2 Phase Diagram (www.novasterilis.com)

Although the reactivity is too low with zinc glutarate, the use of CO_2 under supercritical conditions may improve the mass transfer of the bulk polymer phase and probably it will improve the reactionability, for both types of catalysts.

Our research group in Valladolid, High Pressure Processes Group (HPP), is really strong on this technology with a long-time experience on diverse process at supercritical conditions of carbon dioxide.

The author and the supervisors of this PhD thesis are keen on starting researches with carbon dioxide and propylene oxide in ***terpolymerization reactions***. This means, using one more monomer (3^{rd}) is involved for the final polymer to make these polymerization reactions.

This topic is a really new one and it is practically unexplored.

The 3rd monomer thought and suggested has been the ε-caprolactone, cyclic esther, colourless and it is the precursor of caprolactams. Poly ε-caprolactone is a biodegradable polymer and can be used in polyurethanes.

APPENDIX I

SOLUBILITY OF CO_2 IN SEVERAL POLYPROPYLENE CARBONATES AT DIFFERENT CONDITIONS

1. INTRODUCTION

The solubility of carbon dioxide (CO_2) in mixtures with water has been modelled in subcritical conditions [1] and also, mixtures of CO_2/epoxide have been studied at supercritical conditions [2].

Several authors proposed different procedures for measuring its solubility like the cloud point or the gravimetric extraction [3, 4]. Techniques such as Fourier Transform Infrared Spectroscopy (FTIR) help to determine the amount of the components in each phase, using as epoxide styrene oxide and cyclohexene oxide and observing the variation on concentration as a function of temperature and pressure [2].

Mantor et al., studied the system CO_2-PC in a huge range of temperatures from 27 to 104 ºC and system pressures from 20-70 barg [5].

Murrieta-Guevara et al. [6] and Williams et al. [7], considered the same system studying the equilibrium phases of the system CO_2-PC at the same range of temperatures (25-100 ºC) but higher pressures than Mantor et al., raising more than 200 barg. Hongling et al maintain the study at the same temperatures but presssures raised 130 barg [8].

Other studies like the one made by Wang et al., studied the equilibrium of CO_2 in an epoxide (PO, propylene oxide) at a range of temperatures between 30-80 ºC and pressures under 100 barg [9].

The study of Fonseca et al., considered several systems to calculate the phases equilibrium [10]. They studied system with 2 and 3 components at different conditions. Same systems were studied by B. M. de Almeida [11] but at lower equilibrium pressures than Fonseca et al.

Finally, Langanke et al., showed solubility data of CO_2 and also important information for modelling the copolymerization reaction [12].

Table 1 shows in detail all these experimental works about the equilibrium data of CO_2 in propylene oxide (PO), cyclic carbonate (PC) or polyether polycarbonate polyols (PPP) made by several authors.

Table 1. Review of equilibrium phases data among CO_2-OP-PC-PPP mixtures.

Reference	System	T (^{0}C)	P (barg)
[2]	CO_2-PO	40-100	20-140
[5]	CO_2-PC	27-104	20-70
[6]	CO_2-PC	25-100	5-220
[7]	CO_2-PC	25-100	40-210
[8]	CO_2-PC	40-100	20-130
[9]	CO_2-PO	30-80	6-90
[10]	CO_2-PPP	90-140	15-100
	CO_2-PPP-PC	110	15-100
	PO-PPP	90-140	0.6-3
	PO-PPP-PC	110	10-15
[11]	CO_2-PPP	100-120	10-70
	CO_2-PPP-PC	100	10-70
	PO-PPP	100-120	0-1
	PO-PPP-PC	100	0-1

In this appendix I, authors focused on the solubility study of CO_2 in a PO/CO_2 copolymer obtained using a synthesized DMC catalyst (DMC A in Chapter 3).

2. OBJECTIVES

The main goal is to determine the temperature effect on the solubility of CO_2 in a PO/CO_2 copolymer.

Find a possible system where the experiments can carry out the measurements was a specific objective to achieve.

3. MATERIALS

A stainless steel reactor with a volume of 15 ml, PO/CO_2 copolymer obtained after a copolymerization reaction and a chromatograph oven to maintain the different temperatures during all the experiments.

4. RESULTS

Several experiments were carried on at different temperatures to observe the effect of temperature on the solubility of CO_2 in different polymers.

The experiments were done at 18 ºC, 75 ºC, 90 ºC, 105 ºC and 120 ºC.

Taking into account the initial and the final number of CO_2 moles, it is possible to determine the value of the solubility at any temperature.

Table 2. Solubility data for the experiment at 18 ºC

Pressure (bara)	Solubility (g CO_2 / g Polymer)
4.80	0.0218
6.57	0.0262
14.78	0.0386
19.21	0.0813
27.21	0.1419
36.59	0.2296
50.03	0.1145
51.85	0.1317

The reactor is fill with the amount of polymer desired (1 g) and then is pressurize with CO_2 until, in this case, 52 bara.

The behaviour of the solubility can be observed in Table 2 or in the Figure 1. Both show an increase on solubility at around 36 bara with a subsequent decrease on it.

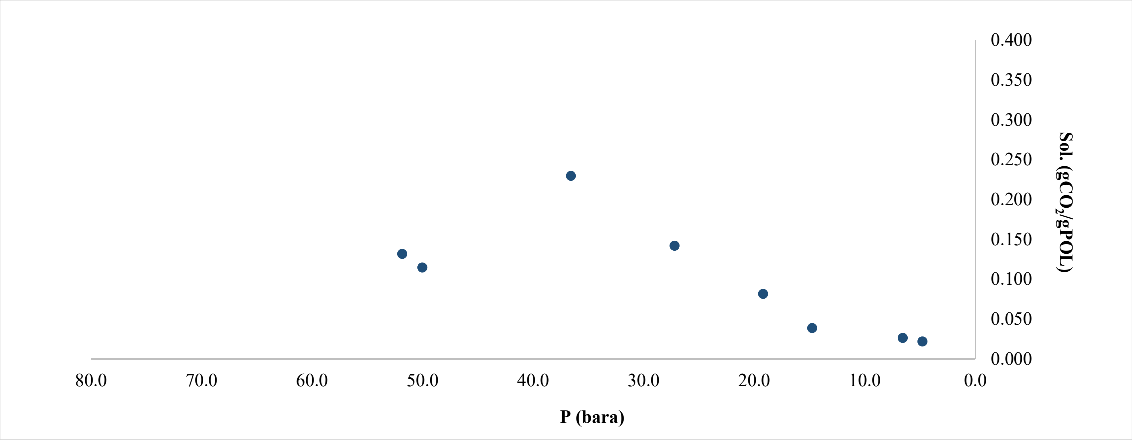

Figure 1. CO_2 solubility profile for a temperature of 18 ºC

When an increase on temperature from 18 ºC to 75 ºC was done, the results were the following:

Table 3. Solubility data for the experiment at 75 ºC

Pressure (bara)	Solubility ($g\ CO_2$ / g Polymer)
6.36	0.0110
8.30	0.0188
18.41	0.0345
25.17	0.0571
36.06	0.1078
50.07	0.2052
65.56	0.4232
69.88	0.3939

Here it is shown that at 65 bara the solubility of CO_2 raised the maximum value for the experiment.

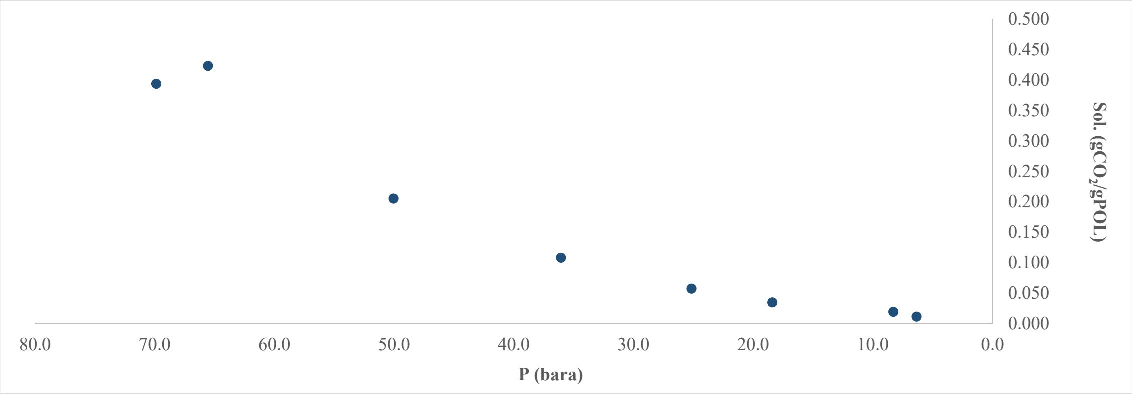

Figure 2. CO_2 solubility profile for a temperature of 75 ºC

Here the tendency seems a little more linear than in the first experiment but it is not clear yet. Fonseca et al., establish that the variation on solubility with pressure follows a linear correlation.

When another increase on temperature was done, the result was the next one:

Table 4. Solubility data for the experiment at 90 ºC

Pressure (bara)	Solubility ($g\ CO_2$ / g Polymer)
6.61	0.0117
8.61	0.0202
19.22	0.0366
26.39	0.0591
37.94	0.1117
52.90	0.2145
68.55	0.4740
72.93	0.4655

At 68 bara the solubility of CO_2 is higher than at other pressures at 90 ºC. Both values, pressure and solubility are closed enough to the last experience.

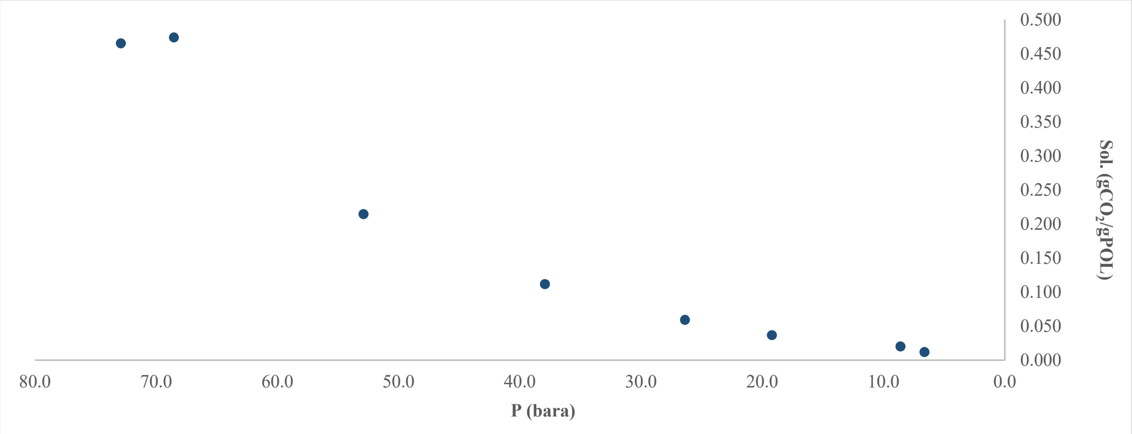

Figure 3. CO_2 solubility profile for a temperature of 90 ºC

If the temperature increased to 105 ºC, the solubility profile was the following:

Table 4. Solubility data for the experiment at 105 ºC

Pressure (bara)	**Solubility ($g\ CO_2$ / g Polymer)**
6.85	0.0126
9.00	0.0199
20.05	0.0381
27.51	0.0629
39.89	0.1130
55.53	0.2265
70.87	0.5307
75.30	0.5398

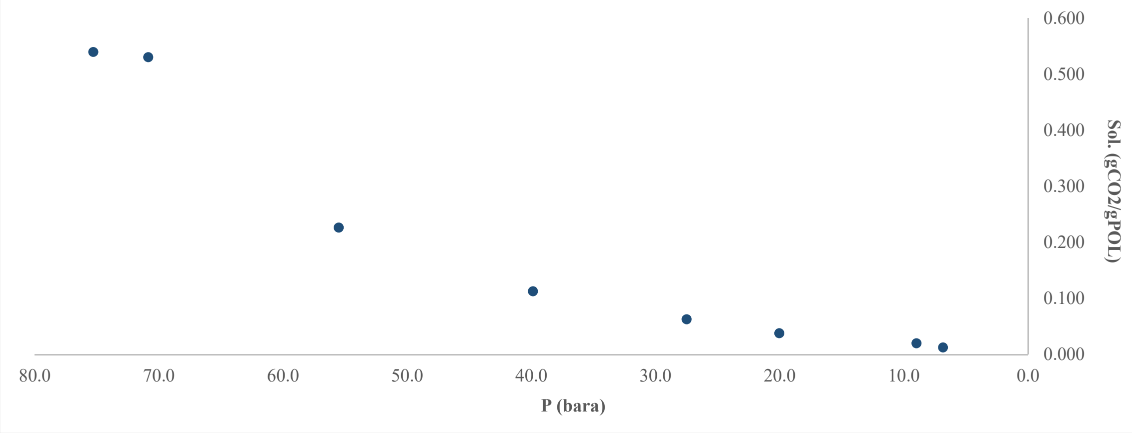

Figure 4. CO_2 solubility profile for a temperature of 105 ºC

Changing the temperature to 120 ºC, the solubility profile obtained was the following:

Table 4. Solubility data for the experiment at 120 ºC

Pressure (bara)	Solubility ($g\ CO_2$ / g Polymer)
7.16	0.0121
9.39	0.0197
20.90	0.0389
28.52	0.0685
41.96	0.1111
58.04	0.2391
73.30	0.5741
76.23	0.6368

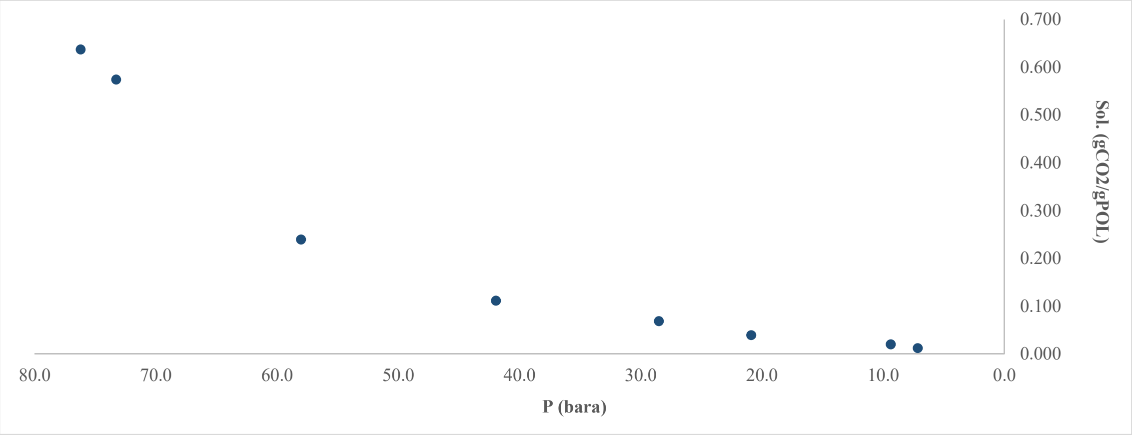

Figure 5. CO_2 solubility profile for a temperature of 120 ºC

To sum up the effect of all the temperatures:

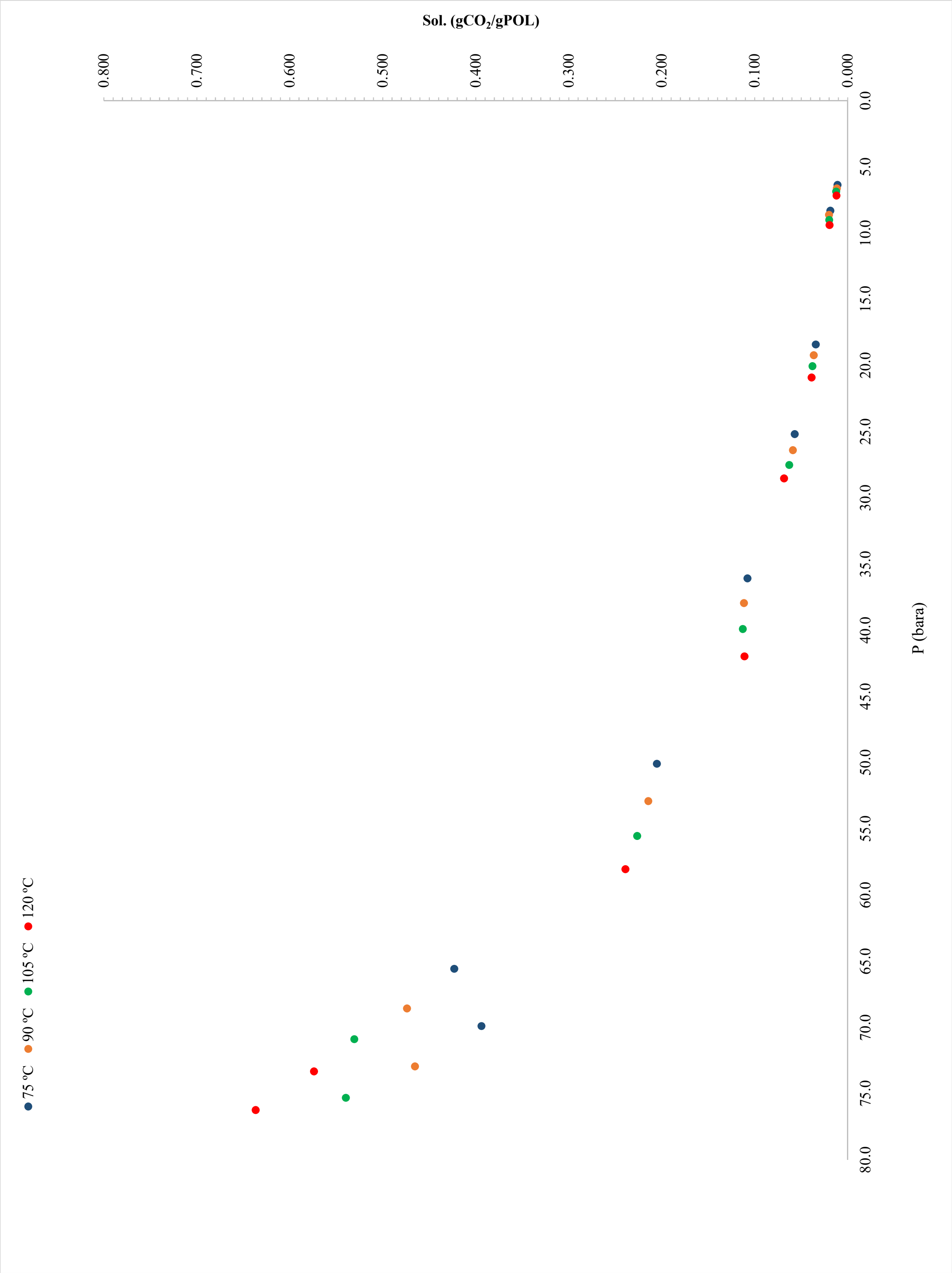

Figure 6. CO_2 solubility versus Temperature and Pressure

Bien Tan et al.'s results suggest that it is difficult to give an exact description of the solubility profiles for these polymers using cloud points alone, particularly in cases where there is a broad distribution of molecular weights.

5. CONCLUSIONS

It was no easy to give a clear tendency on solubility with temperature. For some authors the tendency is linear but our results did not follow the same tendency.

The solubility of CO_2 in several different PPC produced at different conditions was measured to be from 0.022 g_CO_2/g_PPC at 4.8 bara and 18ºC to 0.637 g_CO_2/g_PPC at 76.2 bara and 120ºC.

The solubility increased along with pressure and temperature.

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ABOUT THE AUTHOR

María Pinilla de Dios was born the 2nd August 1985 in Segovia, Spain. After concluding High School Educational studies in Valladolid, she started her *Chemical Engineering Degree* at the University of Valladolid (Valladolid, Spain), researching about "Sewage sludge pre-treatment by ultrasounds in mesophilic anaerobic reactors" (2008-2009). Her Bachelor thesis was focus on "Lavandin essential oil formulations production by PGSS-drying process" (2010-2011). After that, she coursed Master's degree in *Investigation in Processes and Systems Engineering* where she researched about "Higher Heating Values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass" (2011-2012). This work was a collaboration among the Chemical Engineering and Environmental Technology from the University of Valladolid and the Department of Thermodynamics and Applied Physics from the Sciences Faculty of the University of Valladolid. She continued researching about a biorefinery topic "Hydrothermal hydrolysis of spent coffee in subcritical water" (2012-2013) and, immediately, she started her academically formation with her Double PhD Degree at the High Pressure Processes Group from the Chemical Engineering and Environmental Technology from the University of Valladolid and at the Industrial Chemistry and Reaction Engineering Department from Johan Gadolin Process Chemistry Centre of Åbo Akademi University (doctoral stay at Åbo / Turku, Finland, during 15 months).

Her PhD thesis is called "Heterogeneous catalytic copolymerization reactions of carbon dioxide and propylene oxide over polyalcohols under subcritical conditions" (2013-2016).

LIST OF PUBLICATIONS AND COMMUNICATIONS

PUBLICATIONS IN PROGRESS

- **M. Pinilla de Dios**, A. Cabeza Sánchez, J. García Serna, I. Mozo Ruiz, K. Gavob, P. Fardim. Higher heating values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass.

- **María Pinilla de Dios**, Cristina Andrés-Iglesias, Adrián Fernández, Tapio Salmi, José Román Galdámez and Juan García-Serna. Effect of Zn/Co initial preparation ratio in the activity of a Double Metal Cyanide catalyst for propylene oxide and CO_2 copolymerization.

- **María Pinilla de Dios**, Cristina Andrés-Iglesias, Adrián Fernández, Tapio Salmi, José Román Galdámez and Juan García-Serna. Double metal cyanide catalyst and propylene oxide influence on the activation stage study and copolymerization reaction

- **María Pinilla de Dios**, Tapio Salmi, José Román Galdámez and Juan García-Serna. Heterogeneous Zinc glutarate catalyst study in copolymerization reactions, among propylene oxide and carbon dioxide in batch and subcritical conditions

ORAL COMMUNICATIONS

- 12th International Conference on Renewable Resources and Biorefineries in Ghent, Belgium (May 30th - June 1st, 2016). "Downstream processing of model polyalcohols by catalytic copolymerization reaction of CO_2 and propylene oxide under subcritical conditions" Oral presentation.

- Finnish Young Scientist Forum for Catalysis. Labour Museum Werstas, Tampere, Finland (2016)

POSTER COMMUNICATIONS

- **M. Pinilla de Dios**, J. García Serna, F. Sobrón Grañón, I. Mozo Ruiz, K. Gavob, P. Fardim. Higher heating values of hydrotropic, hydrolytic and alkaline lignin from grape seeds and other types of biomass. 9th International Conference on Renewable Resources and Biorefineries; Antwerp June 2013. Poster presentation.

- **M. Pinilla de Dios**, J. García-Serna, F. Sobrón Grañón and M.J. Cocero. 4th International Congress on Green Processes Engineering (GPE). 7-10 April 2014, Sevilla (Spain). Attendance and Poster representation.

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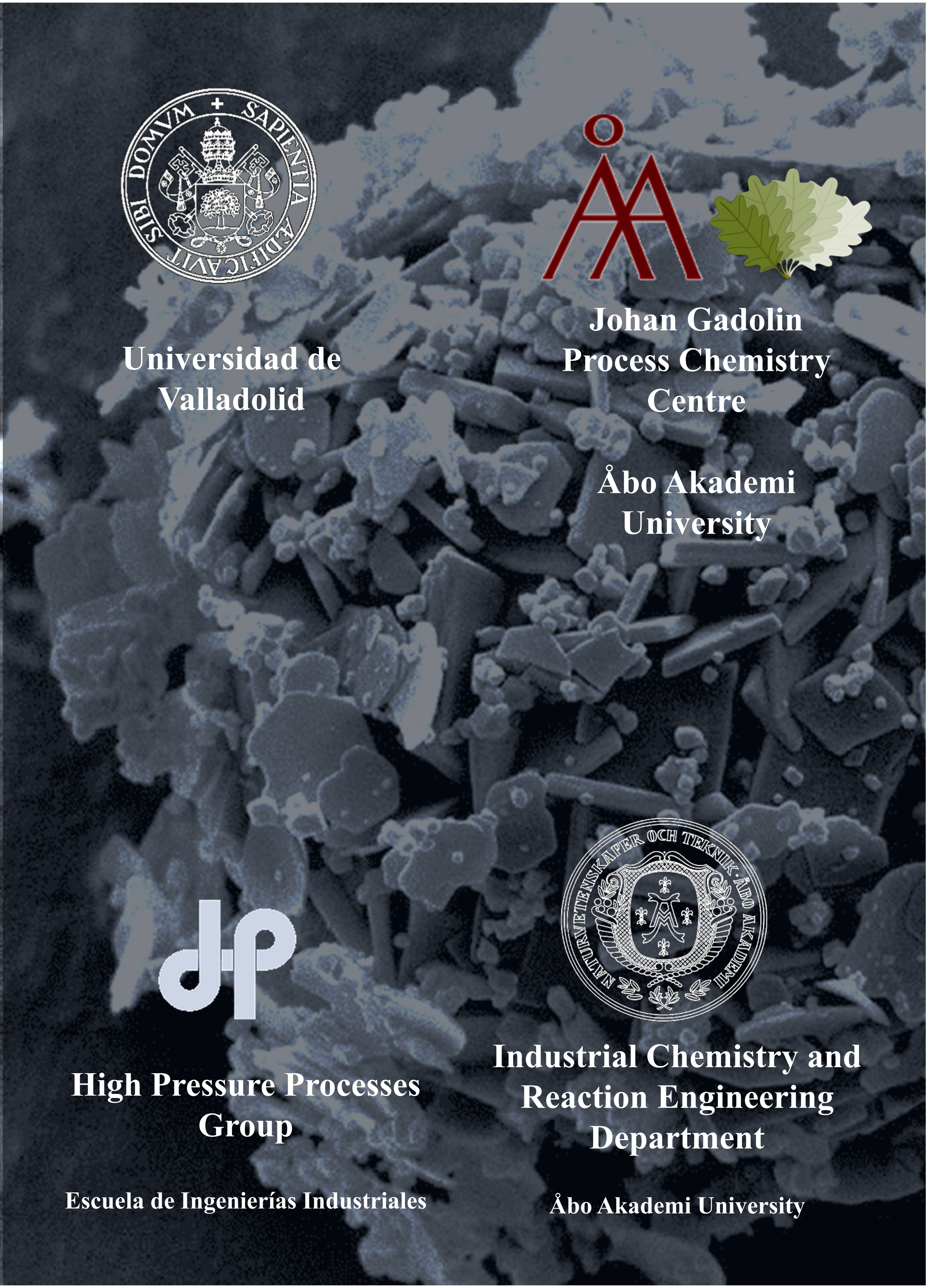

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