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TÍTULO: **Copolymerization of carbon dioxide and propylene oxide using zinc glutarate heterogeneous catalyst under subcritical conditions**

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1. RESUMEN

El dióxido de carbono (CO_2) es el mayor constituyente en emisiones de gases de efecto invernadero. Científicos están investigando utilizar CO_2 como fuente de carbono para mantener una industria viable. Reacciones de copolimerización de apertura de anillo son una de las soluciones para reducir el CO_2 atmosférico.

Un catalizador heterogéneo de glutarato de zinc (ZnGA) fue preparado usando óxido de zinc (ZnO), ácido glutárico (GA) y tolueno. Un estudio completo fue llevado a cabo usando diversas técnicas.

Reacciones de copolimerización de apertura de anillo fueron implementadas usando CO_2 y óxido de propileno (PO) como monómeros, y polipropilen glicol (PPG) como iniciador bajo condiciones subcríticas.

Los resultados muestran que el rendimiento se ve favorecido incrementando la cantidad de catalizador. La cinética de reacción ha mostrado leves mejores resultados a una temperatura mayor. La presión no participa en la ecuación cinética. Un peso molecular esperado de reacción de 725 g/mol logra resultados no deseados. También las reacciones llevadas a cabo con un tiempo de reacción de 20h han obtenido resultados insatisfactorios.

Keywords: zinc glutarate (ZnGA) catalyst, ring opening polymerization reactions, carbon dioxide (CO_2), propylene oxide (PO), polypropylene glycol (PPG).

Copolymerization of carbon dioxide and propylene oxide using zinc glutarate heterogeneous catalyst under subcritical conditions

Master´s Thesis

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1. ABSTRACT

Copolymerization of carbon dioxide and propylene oxide using zinc glutarate heterogeneous catalyst reactions under subcritical conditions.

Sergio Pérez Nogal

Master thesis, Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Faculty of Science and Chemical Engineering, Åbo Akademi University (ÅA), Åbo 2015-2016.

Carbon dioxide (CO_2) is a major constituent of greenhouse gas emissions. Scientists are investigating to utilize CO_2 as a source of chemical carbon to maintain a feasible industry. Ring opening polymerization reactions are one of the solutions to reduce atmospheric CO_2 because CO_2 can be incorporated in the polymer chain and thus the sustainability of the process improves. Another reason CO_2 is inexpensive comparing with propylene oxide price.

A heterogeneous zinc glutarate (ZnGA) catalyst was prepared using zinc oxide (ZnO), glutaric acid (GA) and toluene. The structure of ZnGA catalyst is decisive to characterize and illustrate its activity in copolymerization reactions. A complete study was carried out including techniques as Fourier Transform Infrared (FTIR), Light Scattering (LS), Powder X-Ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Inductively Coupled Plasma (ICP) and Physisorption.

Ring opening copolymerization reactions were implemented using CO_2 and propylene oxide (PO) as the monomers, and polypropylene glycol (PPG) as the starter under subcritical conditions. The effect of operational parameters, such as amount of the catalyst (0.3, 0.6, 1.0, 1.5 g), reaction pressure (5, 10, 20 bar), temperature (60, 80 °C), the expected molecular weight of the final polymer (3000, 725 g/mol) and reaction time (20, 40 h) were also studied and discussed.

The results showed that yield is favored increasing the amount of catalyst (1.5 g). Polymeric reactions made by 1 g of catalyst show the same amount of product than byproduct. Reactions

performed with 0.3 and 0.6 g of catalyst have a production almost negligible. Reaction kinetics had shown mild better results at a temperature of 80 °C than a temperature of 60 °C because polymeric reactions take 40 h, so reaction kinetics is slow. Pressure does not take part in the kinetic equation, since the results obtained by FITR in product and byproduct peaks are similar after changing the pressure. The desired final molecular weight and the reaction time should also be taken into account for copolymerization reactions. An expected molecular weight of 725 g/mol reaction achieved undesirable results. Also reactions carry out at a reaction time 20h (half of the reaction time) have shown unsatisfactory results.

1. RESUMEN

Copolimerización del dióxido de carbono y del óxido de propileno usando un catalizador heterogéneo de glutarato de zinc bajo condiciones subcríticas.

Sergio Pérez Nogal

El dióxido de carbono (CO_2) es el mayor constituyente en emisiones de gases de efecto invernadero. Científicos están investigando utilizar CO_2 como fuente de carbono para mantener una industria viable. Reacciones de copolimerización de apertura de anillo son una de las soluciones para reducir el CO_2 atmosférico, ya que el CO_2 puede ser incorporado en la cadena polimérica y así la sostenibilidad del proceso mejora. Otra de las razones es el bajo precio del CO_2 en comparación con el precio del óxido de proileno.

Un catalizador heterogéneo de glutarato de zinc (ZnGA) fue preparado usando óxido de zinc (ZnO), ácido glutárico (GA) y tolueno. La estructura del catalizador ZnGA es decisiva para caracterizar e ilustrar su actividad en reacciones de copolimerización. Un estudio completo fue llevado a cabo usando técnicas como Espectrometría infrarroja con transformada de Fourier (FTIR), Dispersión de luz (LS), Difracción de rayos X (PXRD), Microscopía electrónica de barrido (SEM), Espectroscopia de fotoelectrones emitidos por rayos X (XPS), Espectrometría con plasma acoplado (ICP) and Fisisorción.

Reacciones de copolimerización de apertura de anillo fueron implementadas usando CO_2 y óxido de propileno (PO) como monómeros, y polipropilen glicol (PPG) como iniciador bajo condiciones subcríticas. El efecto de parámetros operaciones como cantidad de catalizador (0.3, 0.6, 1.0, 1.5 g), presión de reacción (5, 10, 20 bar), temperatura (60, 80 °C), el peso molecular final esperado del polímero (3000, 725 g/mol) y tiempo de reacción (20, 40 h) fueron también estudiadas y comentadas.

Los resultados muestran que el rendimiento se ve favorecido incrementando la cantidad de catalizador (1.5 g). Reacciones de copolimerización hechas con 1 g de catalizador muestran la misma cantidad de producto que de subproducto. Reacciones llevadas a cabo con 0.3 y 0.6 g de catalizador tienen una producción casi insignificante. La cinética de reacción ha mostrado leves mejores resultados a una temperatura de 80 °C que a una temperatura de 60 °C porque las reacciones poliméricas toman 40 h, por lo que la cinética de reacción es lenta. La presión no participa en la ecuación cinética, ya que los resultados obtenidos por FITR en picos de productos y subproductos son similares después de cambiar la presión. El peso molecular final deseado y el tiempo de reacción deben también ser tenidos en cuenta en las reacciones de copolimerización. Un peso molecular esperado de reacción de 725 g/mol logra resultados no deseados. También las reacciones llevadas a cabo con un tiempo de reacción de 20h (la mitad del tiempo de reacción) han obtenido resultados satisfactorios.

2. INTRODUCTION

The growing demand of fossil fuels in recent years has resulted in an increase of greenhouse gas emissions. The International Energy Agency has concluded that no more than one-third of fossil fuels reserves can be wasted before 2050, unless carbons capture and storage (CCS) technology is widely expanded [1-3]. Carbon dioxide (CO_2) is one of the most influential greenhouse gases and one of the main greenhouse gases contributing to global warming. Since 1970, CO_2 emissions have been increased by approximately 90% and its contribution by gas is estimated at around 65% of the global greenhouse gas emissions [1, 4-5].

Different methods have been developed to control CO_2 emissions from industries [4, 5]. The utilization of carbon dioxide as a source of chemical carbon can contribute to maintain a sustainable industry. One of the possible solutions is to produce polymeric materials using carbon dioxide.

CO_2 was used as a monomer along with propylene oxide in the presence of a catalyst to create a polymer. Propylene oxide (PO) was discovered to react with groups PhCOO-Zn and RNHCOO-Zn (Inoué, 1969). All references found, ring opening polymerizations are made using heterogeneous catalysis. (Donald J. Darensbourg et al, 1996) discussed obtaining few samples of successful carbon dioxide utilization, coupled with the high reactivity of epoxides using alkali metal salts. In many researches, carbon dioxide (CO_2) reacted with (PO) using a metal alkoxide as a catalyst [7, 8, 11, 12, 14]. During the following years, researches had tried to develop catalysts to obtain better yields. (Vincent Bergeot et al, 2002) performed ring opening polymerization reactions in supercritical conditions of CO_2 using metal alkoxi catalyst. (Ree et al, 2006) used a heterogeneous zinc glutarate (ZnGA) catalyst in polymerization reactions and also discussed that the structural details of ZnGA catalyst are crucial to elucidate its activity in copolymerization reaction between CO_2 and alkylene oxides. (Loumbra et al, 2013) explained that the yield was strongly dependent on the amount of CO_2 added to the system and that the phase behavior strongly changes along the reaction pathway. The main objective for the current work is to achieve a zinc glutarate (ZnGA) catalyst [6]. Recently other types of heterogeneous catalysts called Double Metal Cyanide (DMC) are investigated to use in copolymerization reactions [13].

Carbon dioxide has been used as a monomer in the presence of a catalyst to create a polymer. [6-13]. Characteristics as number and durability of new carbon dioxide based products, obtained by a catalytic copolymerization reaction with epoxides to form polycarbonates, are used to prepare foams, adhesives, coatings and fibers, thus representing a multi-million ton per annum industry [9].

Lactones and oxiranes have been used in anionic ring opening polymerization reactions [7, 8, 10, 13]. An efficient incorporation of carbon dioxide in the chain is required to obtain products with the desirable properties. Generally, the incorporation efficiency is above 20 wt% [9, 10].

The current work is focused on the synthesis and study of zinc glutarate (ZnGA) as a catalyst in ring opening polymerization reactions. In this study of ZnGA, some variables have been modified such as amount of catalyst, pressure, temperature, final molecular weight and reaction time in polymerization reactions using as reactants carbon dioxide (CO_2) and propylene oxide (PO). The values that have been used in the experiments are amount of the catalyst (0.3, 0.6, 1.0, 1.5 g), pressure (5, 10, 20 bar), temperature of the reactor (60, 80 °C), the molecular weight of the final polymer (3000, 725 g/mol) and reaction time (20, 40 h).
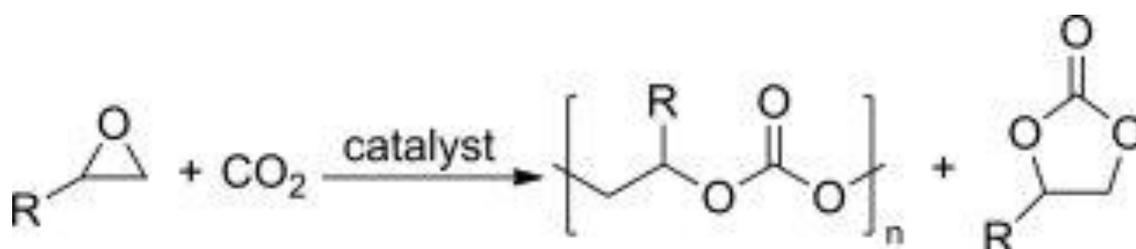

Figure 01. Synthesis of poly(propylene carbonate) from carbon dioxide and propylene oxide.

The main objective of the project is to produce copolymers using carbon dioxide (CO_2) and propylene oxide (PO) as the monomers, polypropylene glycol (PPG) as the starter in order to increase the hydroxide bonds due to the limited number of epoxides to improve the selectivity [11], and the effect of different parameters concerning to obtain an optimum polymeric

product under subcritical conditions. The catalyst, made of glutaric acid (GA) and zinc oxide (ZnO), is synthesized in the laboratory for handling it in copolymerization reaction.

This aim will be developed following the next specific objectives:

- The design and built up of a laboratory plant for the copolymerization reaction.
- The study of parameters that could change the properties of the polymeric product is another objective in the current work. These parameters could be temperature, pressure, amount of catalyst, changing the molecular weight and time.

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Synthesis of Zinc Glutarate (ZnGA)

The catalyst was prepared using zinc oxide (ZnO puriss. p.a., ACS reagent, $\geq 99.0\%$ (KT)) and glutaric acid (GA: 99%) as the reactants. Both are supplied by Sigma-Aldrich and have to be ground in fine powder using a mortar.

Toluene was supplied by J.T. Baker (Baker analyzed; 92.14 g/mol).

3.1.2 Copolymerization Reactions

Zinc glutarate (ZnO/GA) was prepared as described below. Carbon dioxide (CO_2 AGA Voukrapullo 99.99%) and propylene oxide (PO ReagentPlus®, $\geq 99\%$) were going to be the main reactants of the polymer. Propylene Glycol (PPG average Mn425) was used as the starter in the reaction. All of them were purchased by Sigma-Aldrich.

A bottle of nitrogen (N_2 AGA 5.0) must be demanded to inertize and for leaks.

Etylenglycol ($C_6H_6O_2$) was used as a refrigerant to condensate all the PO that is not introduced on the polymer chain.

3.2 Experimental set-up and methods

3.2.1 Synthesis of Zinc Glutarate (ZnGA)

The synthesis of ZnGA was carried out in a rotary Laborota 4000-efficient (Heidolph Intruments GmbH & Co. KG, Germany).

A vacuubrand PC 3001 Vario was equipped to work at the desire vacuum pressure.

Fourier Transform Infrared (FTIR) is one of the techniques most important and useful in quantitative analyses spectroscopy. FTIR analyses were carried out in ATI Mattson Infinity series FTIR with a frequency range of 7500-370 cm^{-1} and a beamsplitter of multilayer coating of KBr.

FTIR technique can determine unknown materials; stablish the quality or consistency of a sample and the amount of components in a mixture.

A background spectrum must also be reproduced to have a relative scale to compare with the sample. The background spectrum can be handling for many samples measurements.

In the current work, FTIR is used to analyze the catalyst and the polymerization product [8, 11, 12, 14, 21].

Figure 02. Fourier Transform Infrared (FTIR) equipment. Åbo Akademi University (ÅA). Laboratory of Industrial Chemistry and Reaction Engineering.

Size-Exclusion Chromatography (SEC) is a chromatographic technique uses to analyze macromolecular complexes or industrial polymers as in this case. The aim of the technique is to separate the molecules in solution by their size [8].

The sample needs to be dissolved in an aqueous solution or in an organic solvent. SEC analyses were performed in a column Jordi X-stream 50x10 mm + 300x10mm. The eluent used for experiments was made with AcOH-MeOH-H2O 50:40:10, 1 ml/min and the detector is ELSD. A Shumadzu LC-10ATVP HPLC pump was used to pumped the solvent delivery and a Shumadzu CTO-10 Avp Column oven provided precise temperature control for stable analytical results.

Many eluents were employed to dilute samples 9 to 15. Eluents such us methanol (MeOH), acetone, ethanol (EtOH), ethyl methyl ketone, acetonitrile (ACN), tetrahydrofuran (THF), methyl iso-butyl ketone, chloroform, 1-methilpyrrolidone, dimethyl sulfoxide (DMSO) and acetic acid (AcOH) were used to dilute the samples.

Only acetic acid (AcOH) and dimethyl sulfoxide (DMSO) produced clear solutions, although only after several days in room temperature. A solvent mixture containing about 50% acetic acid-methanol solubilized in a few minutes at room temperature. A small addition of water (about 10%) to the above binary solution improves solubility.

Advantages of using this method are perfect separation between large and small molecules. Also it could be associated with others techniques as it is saying before and the separations times in the column are quite differentiated and the bonds are well defined, so SEC is a really sensitive technique

Figure 03. Size-Exclusion Chromatography (SEC) equipment. Åbo Akademi University (ÅA). Laboratoy of Wood and Paper Chemistry.

Light scattering (LS) allows knowing useful information about the size distribution and the morphology and components of the sample [12].

LS equipment used in the analyses is a Mastersizer 2000 (Malvern Instruments Ltd) available for suspensions, emulsions and dry powders particles sizes. The particles sizes detected has to be between 0.01 and 3500 μm and with and accuracy better than 0.6%

Figure 04. Light Scattering (LS) equipment. Åbo Akademi University (ÅA). Department of Process Design and System Engineering.

Powder X-ray Diffraction (PXRD) is an indispensable and powerful method in materials characterization. PXRD technique is used to clarify the crystalline shape of materials because the distance between atoms and X-ray wavelength are similar [16].

The Philips X'Pert Pro MPD X-ray powder diffractometer was employed in the XRD measurements using a monochromatized Cu-Kα radiation (λ = 1.541874 Å). 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° - 65.0°, with a step size of 0.026° and measurement time of 100 s per step. The sample was measured on a Cu sample holder.

Figure 05. Powder X-ray Diffraction (PXRD) equipment. University of Turku, Department of Physics and Astronomy.

In the present assignment PXRD is used to analyze the catalyst [6, 16, 20, 21].

Scanning electron microscopy (SEM) method is an alternative method to obtain fast and detailed information of polymers. SEM is an important tool for the examination of polymer analyses. The aim of SEM technique is to study the particle size. In the current work, SEM technique gives much information about characteristics of the catalyst [6, 10, 12, 17, 18, 20]. Specific and preferential solvents are selected due to the wide field of polymers study.

A SEM LEO GEMINI 1530 by Helmholtz Zentrum Berlin company, equipped with SE detectors and EDX system by Thermo Fisher was used to obtain accurate images of ZnGA catalyst.
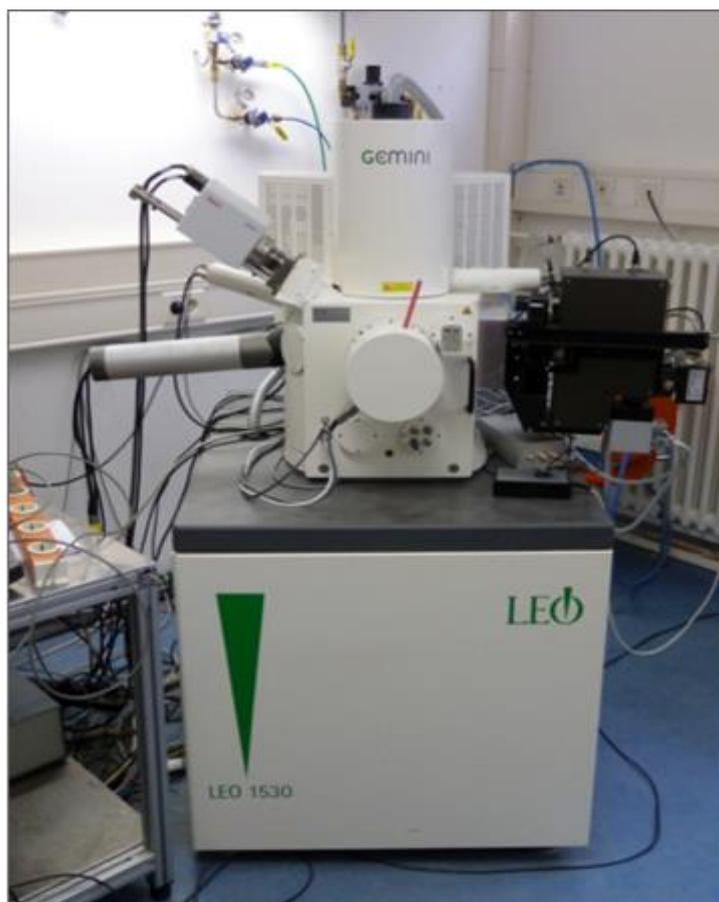
Figure 06. Scanning Electron Microscopy (SEM) equipment. Åbo Akademi University (ÅA). Laboratory of Industrial Chemistry and Reaction Engineering.

X-ray photoelectron spectroscopy (XPS) is a quantitative technique that measures the elemental composition, chemical state and electronic state of the elements in materials.

In the field of polymers analyses, XPS technique can be used to analyze the surface chemistry [19].

A Perkin-Elmer PHI 5400 spectrometer with a Mg $K\alpha$ X-ray source operated at 14 kV and 200 W was used in the XPS-analysis of the samples. The pass energy of the analyzer was 17.9 eV and the energy step 0.025 eV.

Peak fitting was performed with the program XPS Peak 4.1. The background was corrected with the Shirley function. The sensitivity factors used in the quantitative analysis for C 1s, N 1s, and O 1s were 0.296, 0.477 and 0.711, respectively.

Figure 07. X-ray Photoelectron Spectroscopy (XPS) equipment. University of Turku. Department of Physics and Astronomy.

Inductively coupled plasma technique (ICP) is an analytical technique adopted to perceive trace metals. ICP technique is a flame technique using quite high temperatures. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was performed for catalyst sample. Approximately a few grams of catalyst was introduced into a Teflon bomband digested in a microwave oven with H_2SO_4 (96%) and HNO_3 (65%). The sample was diluted to 500 mL prior to the ICP-OES analysis.

In the current assignment, ICP technique was used to appreciate the amount of zinc that is in the catalyst [21].

Physisorption is an analytical technique as Inductively Coupled Plasma (ICP). The total surface area was calculated using Sorptomatic 1900 by Carlo Erba Instruments Company.

Figure 08. Physisorption equipment. Åbo Akademi University (ÅA). Laboratory of Industrial Chemistry and Reaction Engineering.

3.2.2 Copolymerization Reactions

The reaction was carried out in a 382 mL reactor (Parr Instruments Company Moline, IL, USA) equipped with a mechanic stirrer drives for Parr reactor, a heating jacket to preserve the temperature and a cooling system to reduce so quickly the reaction temperature due to the presence of hotspots during the polymerization. A temperature indicator controller and a pressure indicator were also equipped in the reactor (R-101).

The process flow diagram of the copolymerization reaction and an image of the build plant are shown below.
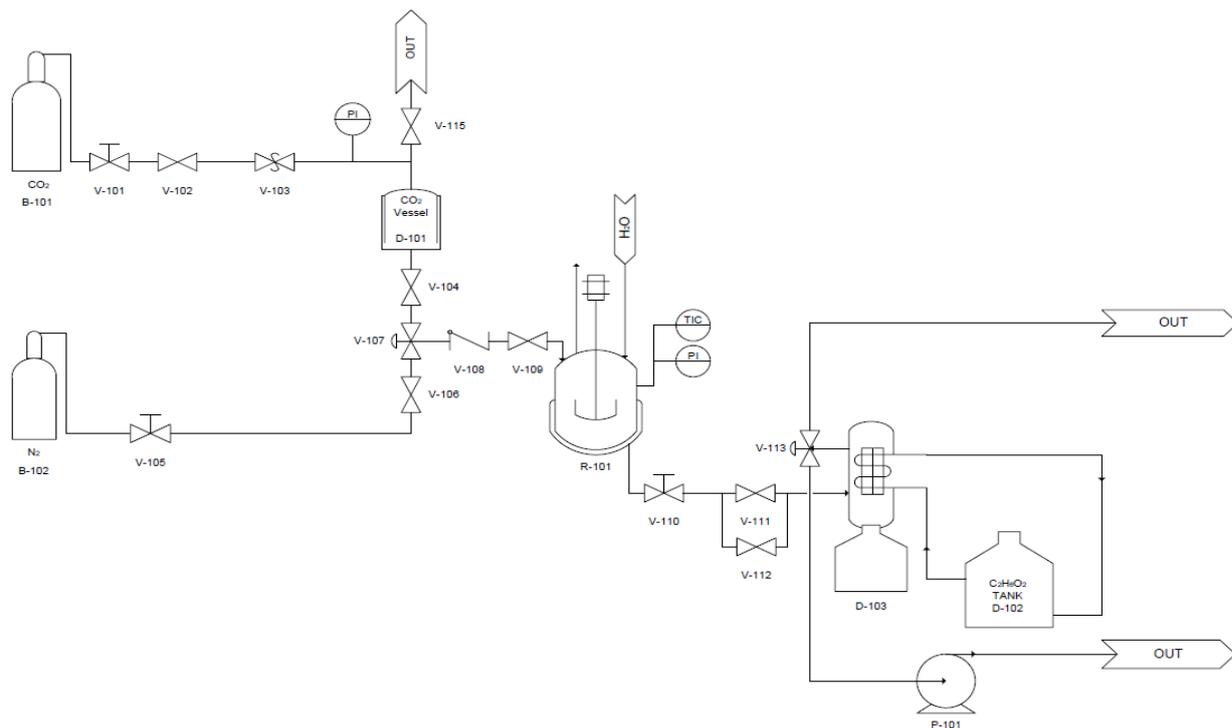
Figure 09. Process flow diagram (PFD).

Figure 10. Experimental set up used in copolymerization reactions. Åbo Akademi University (ÅA). Laboratory of Industrial Chemistry and Reaction Engineering.

The carbon dioxide (CO_2) gas inlet (B-101) was conducted to a Swakelog tank 304 L stainless steel to control the pressure using valves (V-101, V-102, V-115). A relief pressure valve was used as a security measure (V-103). The pressure of CO_2 in the tank was shown by a pressure indicator.

Nitrogen (N_2) was also equipped as a gas inlet (B-102) and was controlled by its corresponding valve (V-105).

A three-way valve and a check valve (V-107 and V-108) were used to select the gas inlet to the reactor and to prevent the change of direction in the flow respectively.

Once the reaction has taken place a Go-back pressure valve (V-113) was used to establish the pressure in the reactor assuring that no leaks are through the system. In the case that the reaction pressure can be high, it is possible to decrease the pressure slowly and a refrigeration system consisting of a cooler coil and a vessel with glycol (D-102) was used to remove all unreacted monomers (D-103).

Both pressure and temperature were shown on a computer with PicoLog TC datalogger and PicoLog software.

The polymeric product was analyzed by the following techniques: Fourier transform infrared spectroscopy (FTIR) and Sized-Exclusion Chromatography (SEC) described previously.

3.3 Experimental procedure

3.3.1 Synthesis of Zinc Glutarate ZnGA

The catalyst ZnGA was prepared following the guidelines of Ree et al [6]. A Rotary system with a vacuum pump was used for this purpose. In a bottom flask were added 150 ml of toluene, zinc oxide (ZnO) and glutaric acid (GA) in a molar rate 1:1. (12.95 g GA and 8.14 g ZnO). Both ZnGA and GA were needed in fine powder.

The bottom flash was submerged in a bath of silicone oil at 55 °C for 4 h with an intensive agitation. After 4 h, the reaction mixture was cooling to room temperature and was filtrated in a vacuum flask using acetone.

After the filtration was completed, the product was dried in the rotary system at vacuum conditions (18 mbar) at 100 °C for 2 days. Once dried, the catalyst was grounded using a mortar and the fine powder obtained was dried again at 100 °C, 25 mbar for 3 days.

The block diagram of the synthesis of zinc glutarate (ZnGA) and the copolymerization reaction is shown in the following figure.
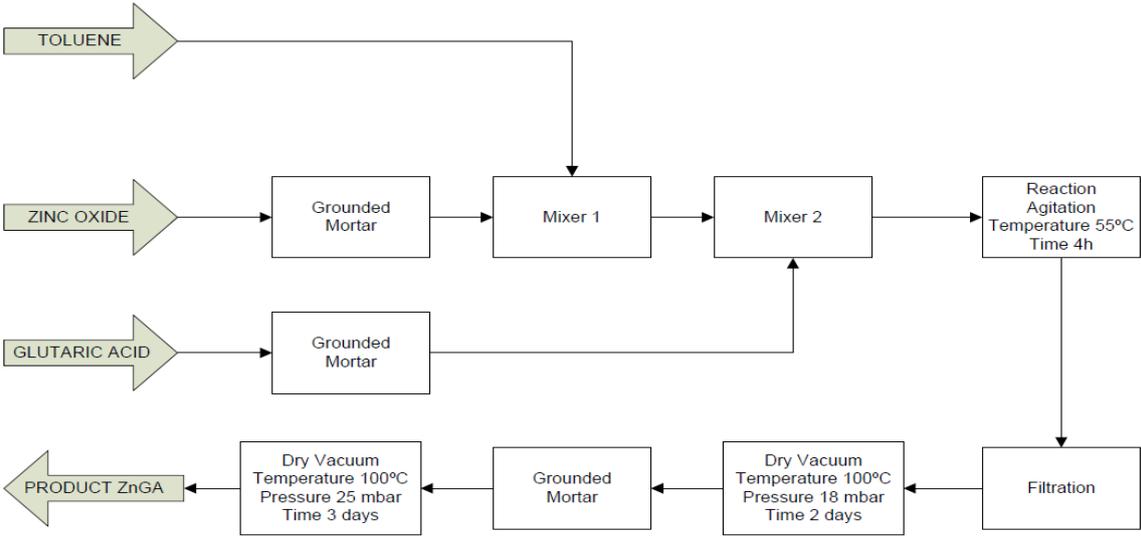

**Figure 11. Block diagram of the synthesis of zinc glutarate (ZnGA).**
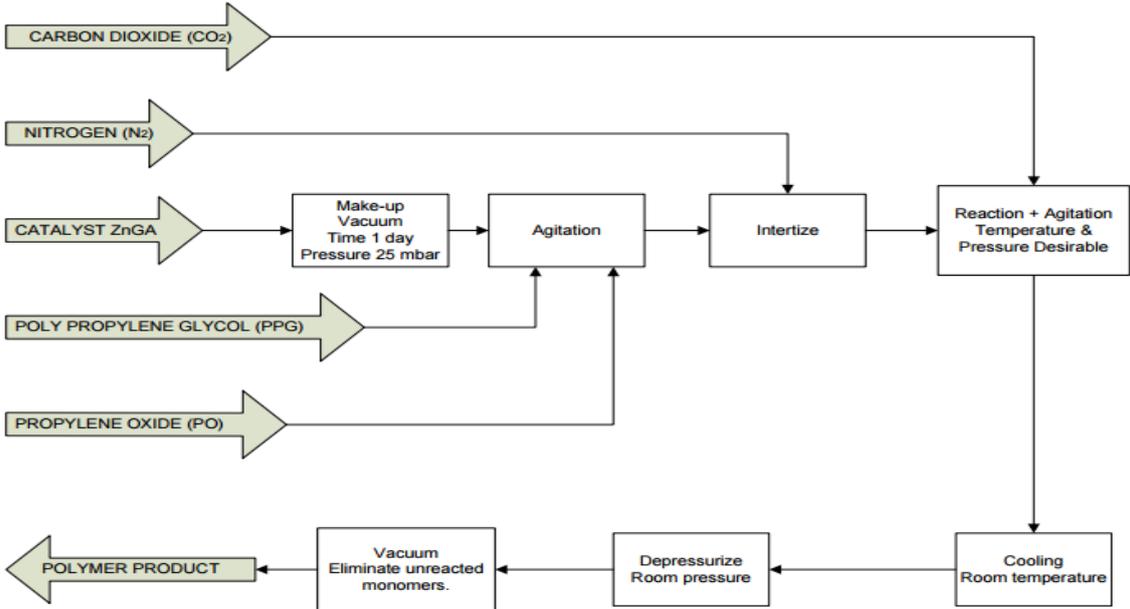
Figure 12. Block diagram of the copolymerization reaction.

3.3.2 Copolymerization Reactions

In the reactor described previously in figure 10, the catalyst was added in the desired amount and dried with vacuum system at 1 day at 25 mbar for removing any moisture.

Depending on the study to carry out, the amount of polypropylene glycol (PPG) and propylene oxide (PO) to insert in the reactor were modified. Both, PPG and PO were added slowly and with agitation to the catalyst in the reactor. Several experiments were performed modifying different operational parameters, such as amount of the catalyst, reaction pressure, temperature, the expected molecular weight of the final polymer and reaction time as it is shown in the following table.

Table 01. Copolymerization reaction experiments.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S1	0,3	5	60	3000	40
S2	0,3	5	60	3000	40
S3	0,6	5	60	3000	40
S4	0,6	5	60	3000	40
S5	1	5	60	3000	40
S6	1	5	60	3000	40
S7	1,5	5	60	3000	40
S8	1,5	5	60	3000	40
S9	1,5	25	60	3000	40
S10	1,5	25	80	3000	40
S11	1,5	25	80	3000	40
S12	1,5	25	80	725	40
S13	1,5	25	80	3000	20
S14	1,5	5	60	3000	20

The system was connected with nitrogen and CO_2. Nitrogen was used to assure the absence of leakage and to inertize. CO_2 was inserted in the reactor in a continuous flow. The desire pressure was set by the CO_2 flow. At the same time, the system temperature was heated up by a heating jacket. Both, temperature and pressure was kept during the reaction. Once the reaction was finished, the unreacted propylene oxide monomers were extracted, measured and saved from the polymeric product using a vacuum trap. The reacted polymeric samples were introduced in labeled vials and stored in the refrigerator for a later analysis.

4. RESULTS AND DISCUSSION

4.1 Characterization and catalyst study

Techniques described in chapter 3, are used to describe and to carry out a complete study of zinc glutarate (ZnGA) catalyst.

Fourier Transform Infrared (FTIR) was used to analyze the formatted bonds that are in the catalyst.

The FTIR of ZnGA catalyst is shown below in figure 13.
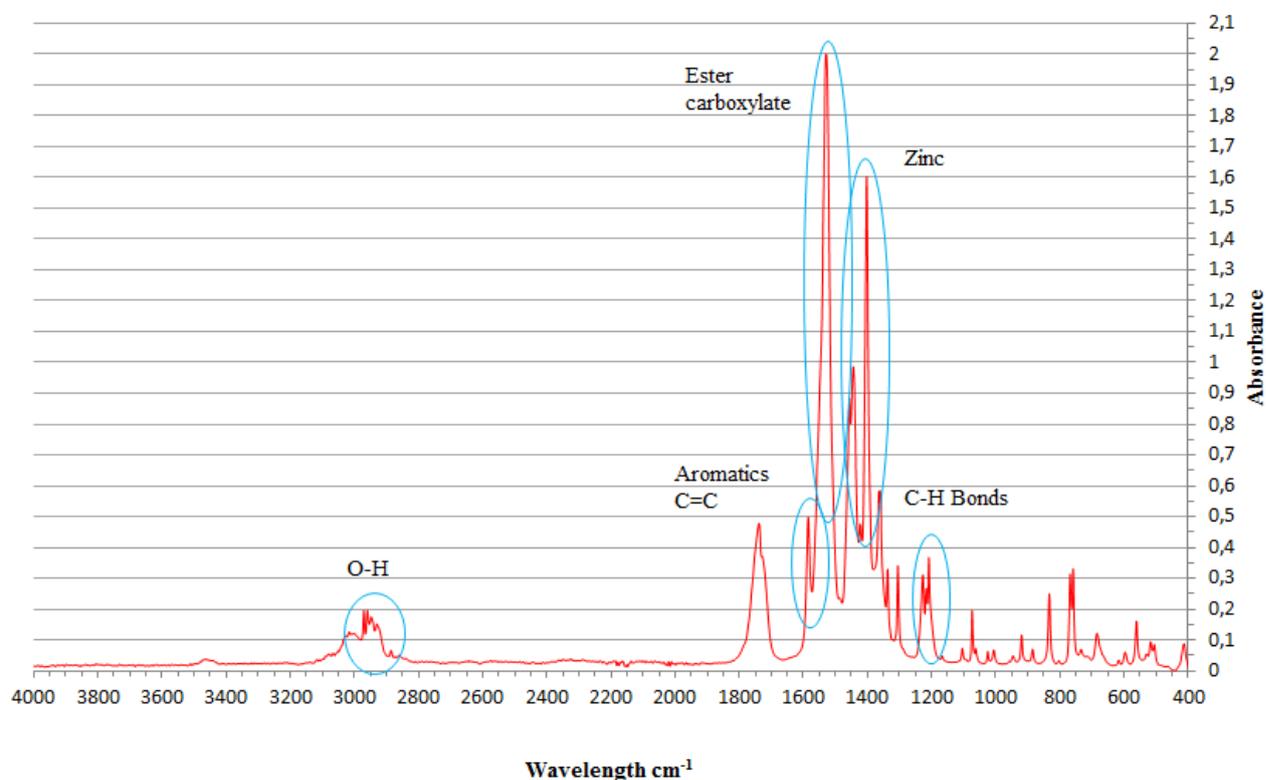
Figure 13. FTIR of ZnGA catalyst Åbo Akademi University (ÅA) & University of Valladolid (UVa).

Groups O-H are formed in a wavelength of 3450 cm^{-1}, the highest peak represents the ester carboxylate group necessary to increase the chain appeared at a wavelength of 1540 cm^{-1}, zinc and C-H bonds appears at a wavelength of 1400 cm^{-1} and 1220 cm^{-1}. Aromatics C=C bonds appears at a wavelength of 1740 cm^{-1}.

Images of Scanning Electron Microscopy (SEM) technique show how the microstructure of the ZnGA catalyst is.

At a scale bar of 20 µm, it appears some particles with a partial circular shape surrounded by other smaller particles.

Some of the images are shown below.
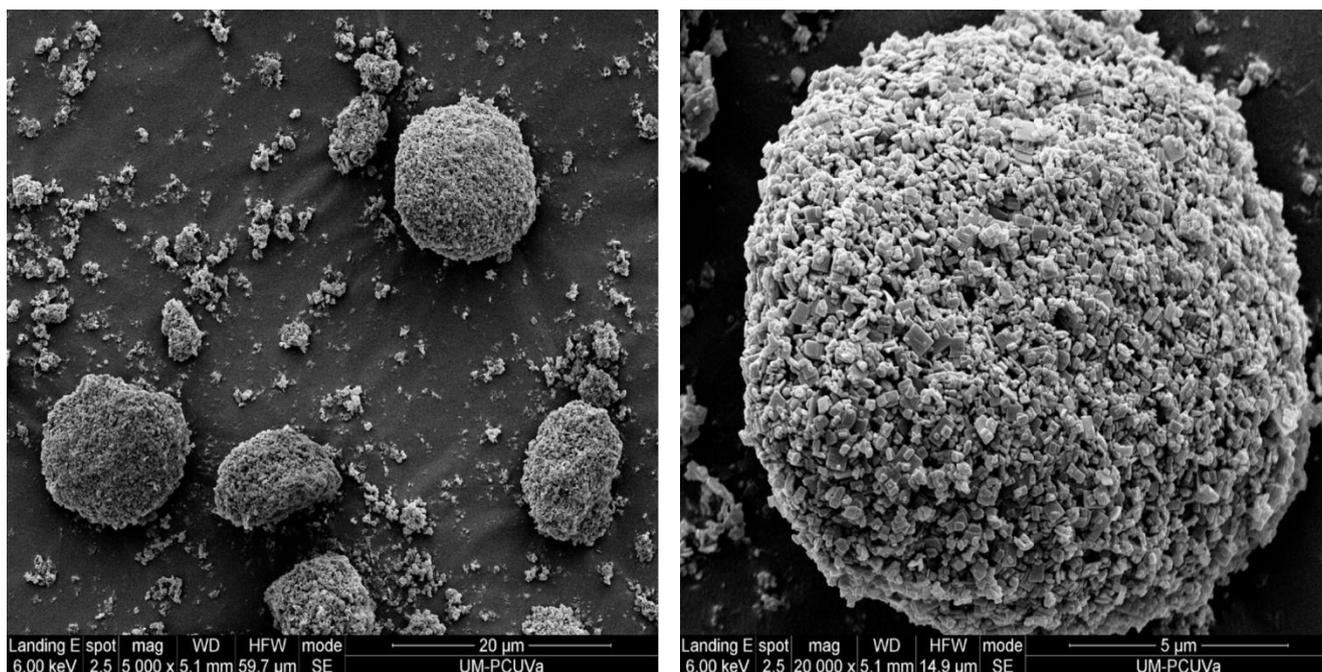
Figure 14 and 15. Structure of ZnGA catalyst using SEM technique Scale bar 20 µm and 5 µm respectively. University of Valladolid (UVa).

Increasing the scale bar to 1 µm, the heterogeneous zinc glutarate particles present the following shape showing in figures 14 and 15.
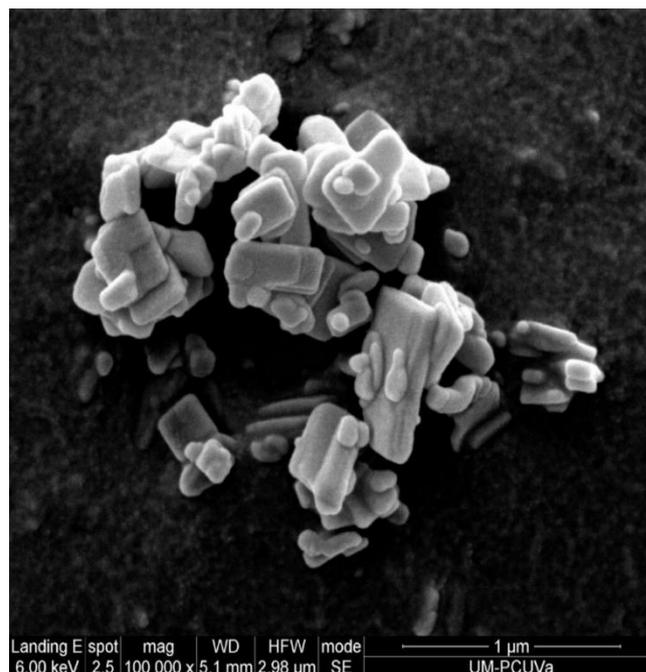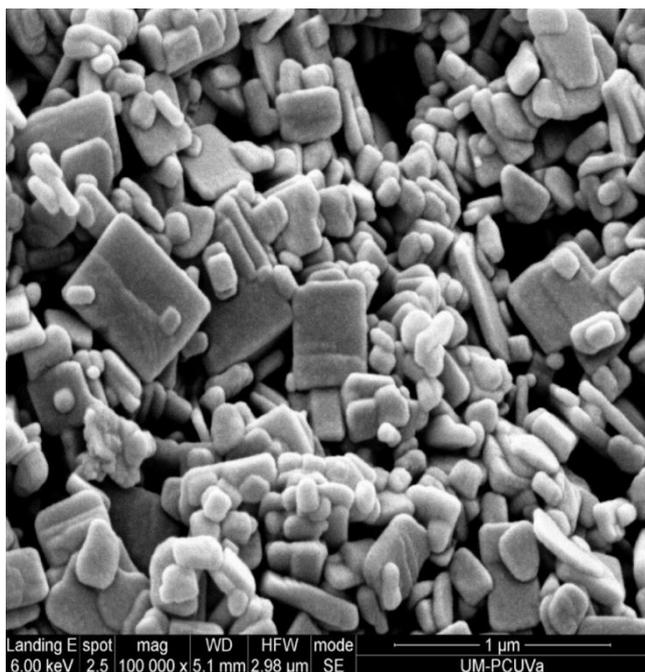
Figure 16 and 17. Structure of ZnGA catalyst using SEM technique Scale bar 1 μm. University of Valladolid (UVa).

Increasing the scale bar until 200 nm, the ZnGA catalyst presents a shape a bit more complex showing in figures 16 and 17.
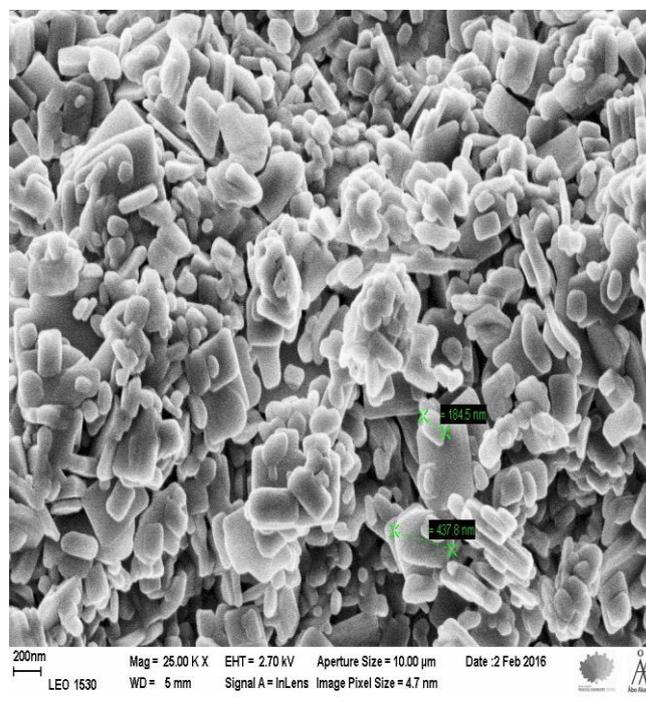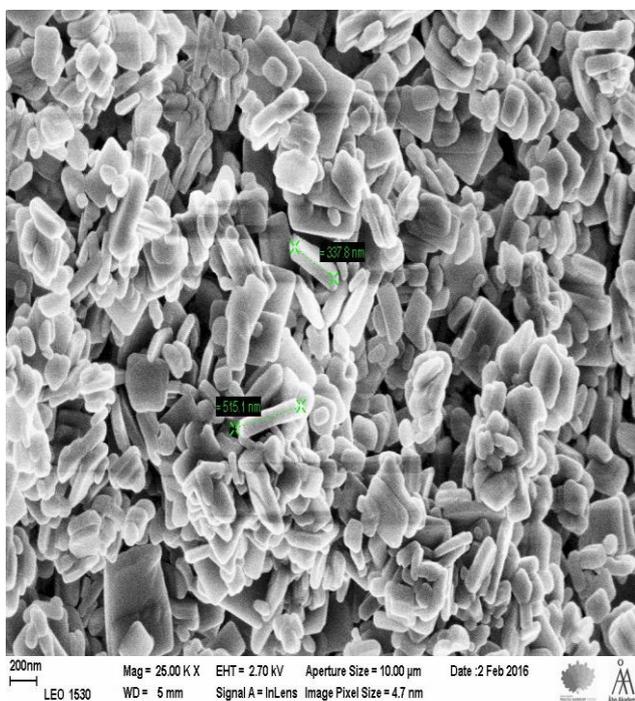
Figure 18 and 19. Structure of ZnGA catalyst using SEM technique Scale bar 200 nm. Åbo Akademi University (ÅA).

Inductively Coupled Plasma (ICP) was described in section emperimental set-up and methods. The amount of metal compound (Zn) in the catalyst is measured using ICP technique.

ZnGA catalyst contains between 362 and 368 mg of zinc per g of catalyst.

Powder X-Ray Difraction (PXRD) is used to described the crystalline shape of materials.

The measured and background corrected zinc glutarate diffractograms is presented in figure 18.
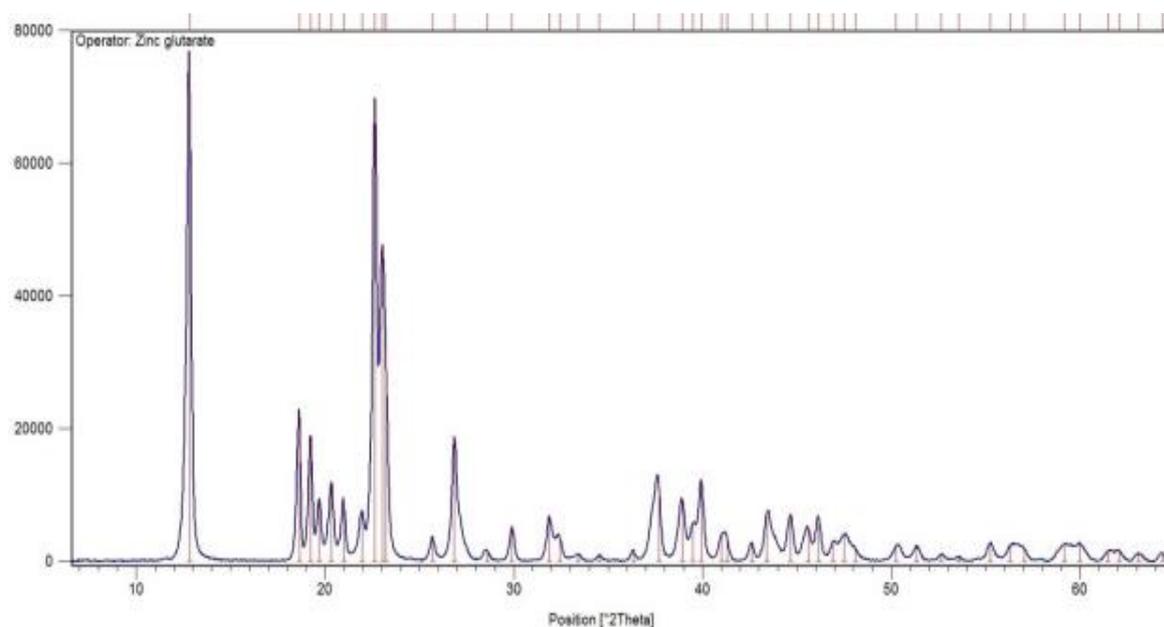
Figure 20. Powder X-Ray Diffraction (PXRD) patterns in ZnGA catalyst. University of Turku. Department of Physics and Astronomy.

The Cu sample holder may partially contribute to the peaks detected at $2\theta = 43.4°$ and $50.3°$, as the peak positions coincide with the Cu (111) and Cu (200) peak positions.

X-ray diffraction pattern obtained in figure 18 is more defined and presents quite similarities with the X-ray diffraction pattern shown in figure 3 of Ree et al.

Ree et al. described that all Zn ion centers of the crystal thus coordinate to four carboxyl oxygen atoms on different glutarate ligands via four syn–anti bridges, forming a distorted tetrahedral geometry.

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Light Scattering (LS) technique was used to determine the particle size distribution. LS analyses were reported in two different mediums, air and water.

The results of the analysis report are presented below.

In air medium the particle size distribution is described in the next figure.
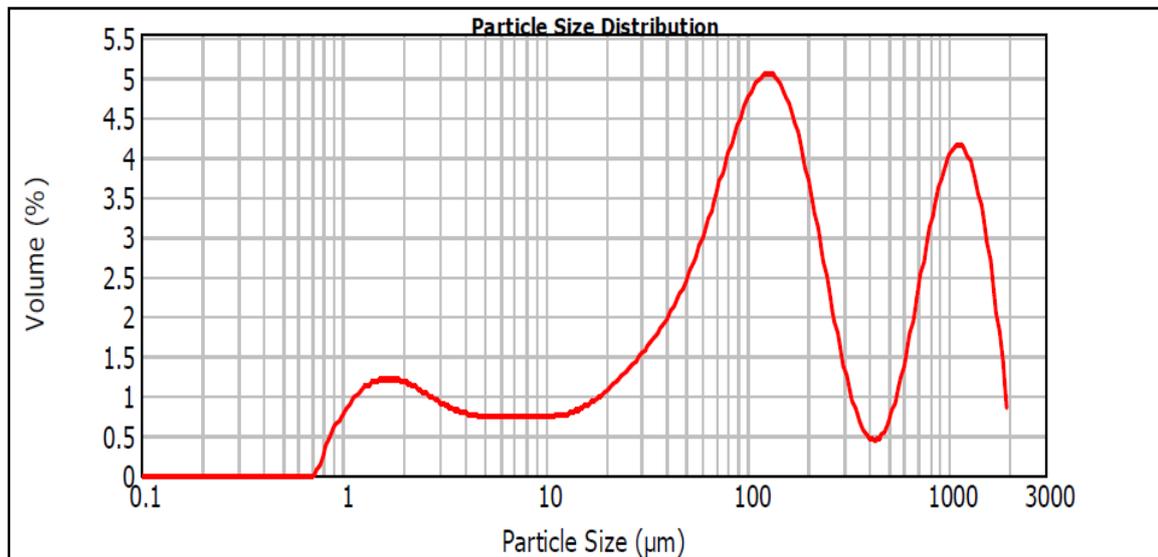
Figure 21. Light Scattering (LS) pattern in ZnGA catalyst. Universidad de Valladolid (UVa), Laboratory of Chemical Engineering.

The minimum particles sizes detected is about 0.7 µm and the particle volume (%) has a maximum at 135 µm and at 1200 µm of particle size, as long as the particle volume (%) has a minimum at 420 µm.

The Particle Refractive Index, showed in the equipment use is 1.520.

The surface of a particle of ZnGA catalyst called Specific Surface Area is 0.475 m^2/g.

Table 02. Light Scattering (LS) distribution size.

p	d_P (µm)
0.1	3.766
0.5	118.208
0.9	1167.161

The term d_{50}, which means the particle size that is behind or equal of the total amount size is 118.208 µm.

In the first analysis made in distilled water, it is obtained the graphic below.
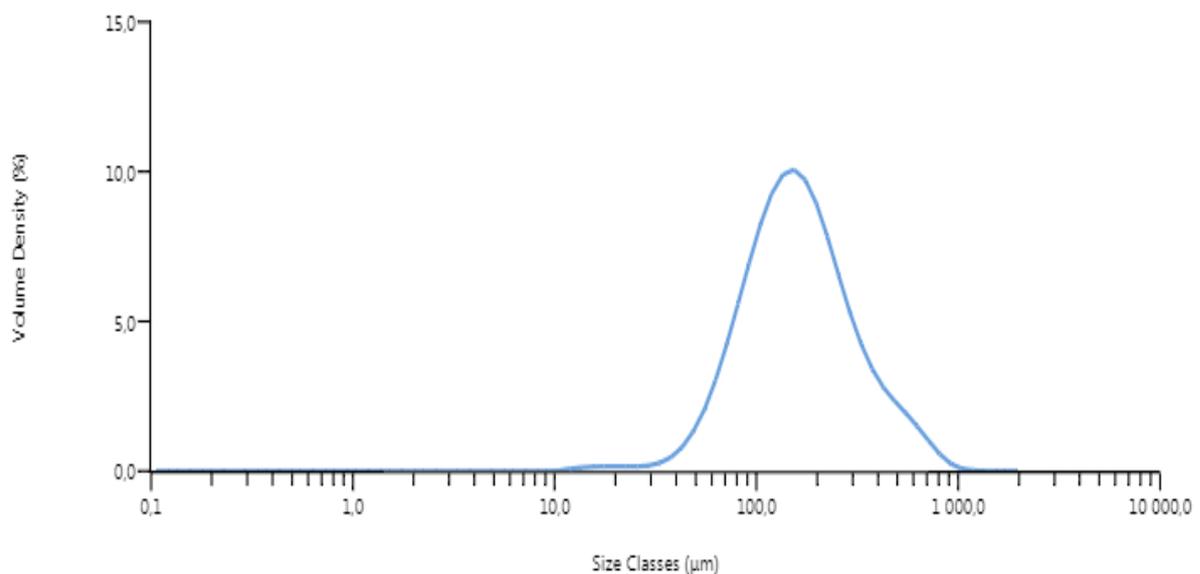
Figure 22. Light Scattering (LS) pattern in ZnGA catalyst. Åbo Akademi University (ÅA), Department of Process Design and System Engineering.

It is shown that the volume (%) in water system (conditions) has a maximum at a size of 175 µm.

The Particle Refractive Index use is 2.008; that is the Particle Refractive Index of Zn finding in the data base of the LS equipment.

The Specific Surface Area is 46.74 m²/kg, ten times smaller than the calculated before using air. Finally the term d_{50} is 157 µm.

More analyses were performed due to the huge difference in values between LS analysis in Specific Surface Area and d_{50} term.

In second and third LS analysis in water, the Particle Refractive Index has changed in order to achieve an available comparison with the LS made in air conditions. The Particle Refractive Index of ZnGA is now 1.520.

Second and third analysis made in water conditions are presented below.
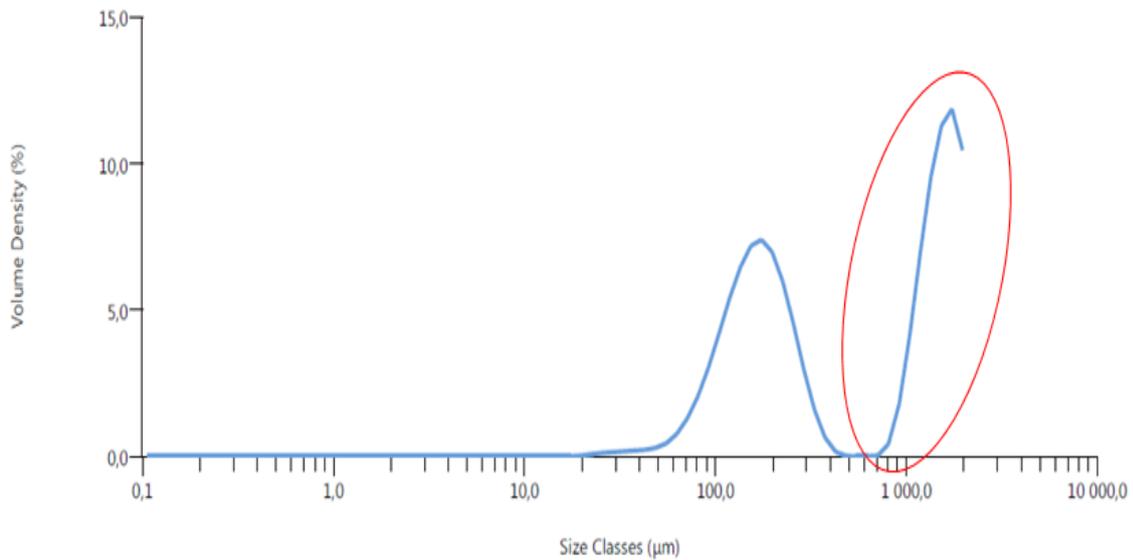

Figure 23. Light Scattering (LS) pattern in ZnGA catalyst. Åbo Akademi University (ÅA), Department of Process Design and System Engineering.
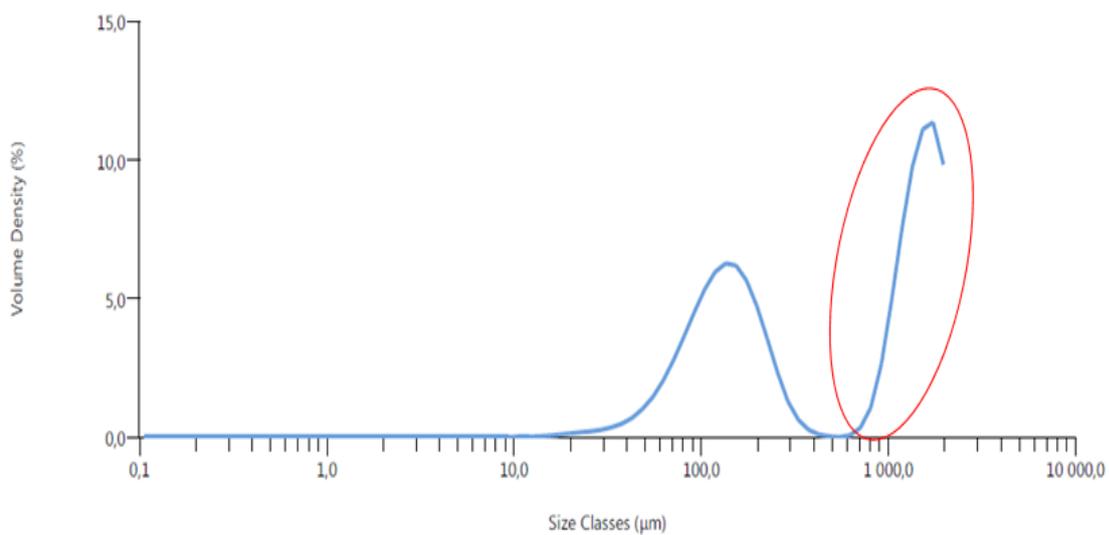
Figure 24. Light Scattering (LS) pattern in ZnGA catalyst. Åbo Akademi University (ÅA), Department of Process Design and System Engineering.

The Specific Surface Area is 24.60 m^2/kg and 30.74 m^2/kg respectively. The d_{50} term is 307 µm and 350 µm respectively.

The changing in the Particle Refractive Index shows the same maximum at 135 µm and at 1200 µm of particle size, so LS techniques in water and air shows the same results.

The ten times specific surface area of difference in LS analysis using air instead of using water can be reside in comparing both LS patterns. In figure 19 the minimum particles sizes detected is about 0.7 µm whereas in figure 21 and 22 the minimum particles sizes detected is about 15 µm. These increments in volume density (%) detected in LS in air can contribute in the increasing of surface area.

The agglomeration of the catalyst particles in water is maybe one of the possible reasons of this phenomenon.

The agglomeration of ZnGA particles in water reduces the particle pores, meaning a decrease of Specific Surface Area and an increase of d_{50} term due to the particles size are higher and it could be same particles so huge retained in the capillary.

4.2 Characterization and polymer study

Once the catalyst has been synthesize, several experiments were carried out to produce a desire polymeric product using as the reactants carbon dioxide (CO_2) and propylene oxide (PO). In these experiments several variables such as amount of catalyst, pressure, temperature, final molecular weight and reaction time were modified to achieve the best yield.

Fourier Transform Infrared (FTIR) and Size-Exclusion Chromatography (SEC) were the techniques used to discuss the results obtained.

4.2.1 Fourier Transform Infrared (FTIR) on polymer study

4.2.1.1 Variation in the amount of catalyst

The amount of catalyst was one of the most important variables to discuss. It is completely necessary to know the exact amount of catalyst to be added. The lack of catalyst in the polymerization reaction would not produce the complete and correct reaction getting an undesired polymeric product. Excess of the catalyst would be an unnecessary waste.

FTIR analyses of the samples modifying the amount of catalyst are shown below.

Table 03. Experiments changing the amount of catalyst.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S1	0.3	5	60	3000	40
S2	0.3	5	60	3000	40
S3	0.6	5	60	3000	40
S4	0.6	5	60	3000	40
S5	1.0	5	60	3000	40
S6	1.0	5	60	3000	40
S7	1.5	5	60	3000	40
S8	1.5	5	60	3000	40

Samples 1 to 8 are obtained changing the amount of catalyst while pressure, temperature, final molecular weight and reaction time are constant.
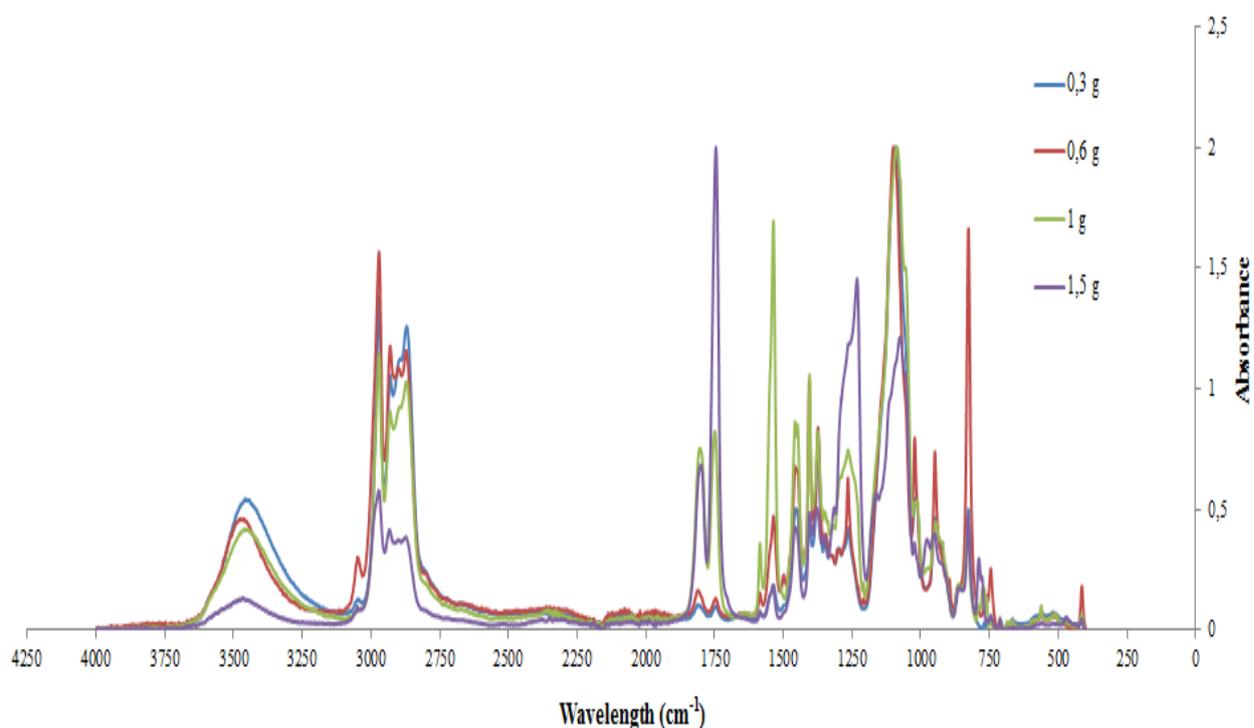
Figure 25. FTIR of polymeric product catalyst. Åbo Akademi University (ÅA) & University of Valladolid (UVa).

The desired polymeric product appears at a wavelength of 1745 cm^{-1}, byproduct at 1802 cm^{-1} and O-H bonds appear at a wavelength of 3459 cm^{-1}.

At a wavelength of 1740 cm^{-1}, samples 7 and 8 made by 1.5 g has an absorbance of 2, higher than any other polymeric reactions made by less catalyst. Polymeric reactions made by 1 g of

catalyst have 0.8 of absorbance. Reactions using 0.3 and 0.6 g of catalyst have an absorbance almost negligible.

Byproduct is shown at a wavelength of 1802 cm^{-1} but with the remarkable difference between polymeric product and byproduct are in the catalyst weighted of 1.5 g of catalyst.

O-H bonds represent the free bonds to improve the copolymerization reaction. A low peak at a wavelength of 3459 cm^{-1} means that some amount of these O-H bonds is used in the reaction. 1.5 g samples have the minimum peaks at a wavelength of 3459 cm^{-1}. In contrast samples of 0.3 and 0.6 g of catalyst have the highest peaks due to O-H bonds are not used to increase polymerization chain.

The best yield was obtained using the highest amount of ZnGA catalyst (1.5 g of catalyst) in copolymerization reactions. Results achieved with 1 g of catalyst show the same production of product-byproduct. Copolymerization reactions results using fewer amounts of catalyst (0.3 and 0.6 g of catalyst) were not satisfactory.

4.2.1.2 Variation of the pressure

Pressure should not be a fundamental factor because it does not take part in the kinetic equation in polymeric reactions.

In sample 9, the amount of catalyst and the rest of variables are maintained but the pressure is increased.

Table 04. Experiments changing the reaction pressure.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S7	1.5	5	60	3000	40
S9	1.5	25	60	3000	40

The FTIR changing the reaction pressure is shown below.
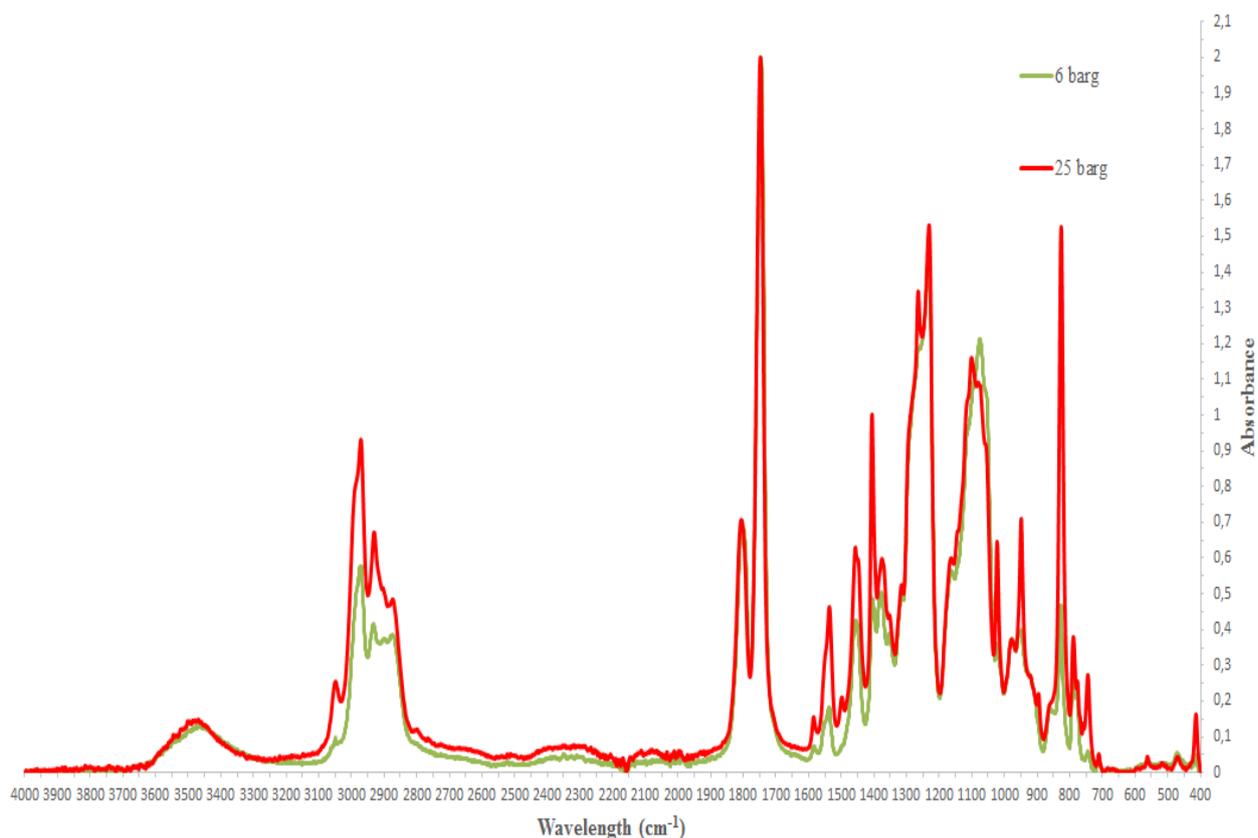
Figure 26. FTIR of polymeric product catalyst. Åbo Akademi University (ÅA) & University of Valladolid (UVa).

Samples performed at 5 and 25 barg are overlap at product, byproduct and OH bonds absorbance, so pressure is not an influential variable. Changing the pressure does not present any differences as it is shown in figure 24 due to it's not a kinetic variable.

Other copolymerization reaction was carried out at 10 barg with undesired results, so that it was removed in the graphic

4.2.1.3 Variation of the temperature

Temperature is an important variable in kinetics and in the final polymers properties.

Ring opening polymerization reactions using propylene oxide (PO) are exothermic reactions. Temperature should be high for increase the reactions velocity but as exothermic reaction, it should not be so high to avoid hotspots.

In samples 11 and 12 temperature was increased softly whereas the rest of the variables are constant.

Table 05. Experiments changing the temperature.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S9	1.5	25	60	3000	40
S10	1.5	25	80	3000	40
S11	1.5	25	80	3000	40

The FTIR obtained is.
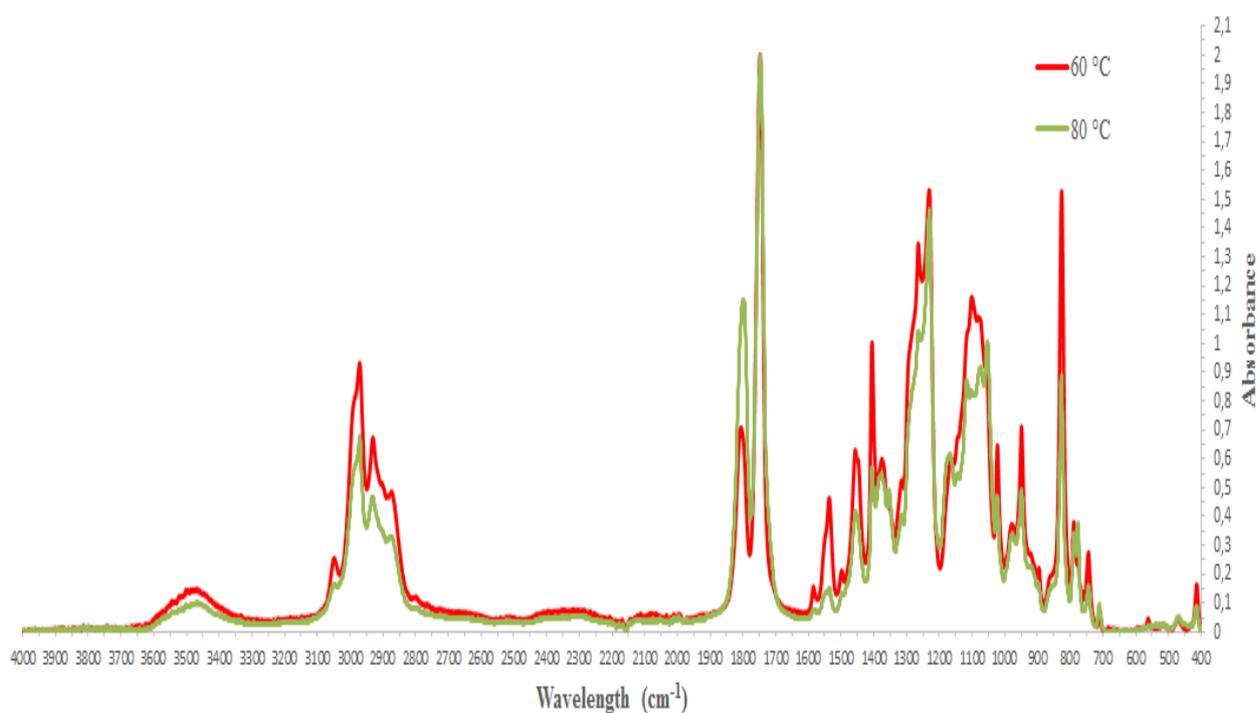
Figure 27. FTIR of polymeric product catalyst. Åbo Akademi University (ÅA) & University of Valladolid (UVa).

The absorbance of carbonate bonds (wavelength of 1745 cm^{-1}) and byproduct (wavelength at 1802 cm^{-1}) at 80 °C is higher than a 60 °C. Also hydroxide bonds absorbance at 80 °C is less than at 60 °C.

Discussing about polymeric product absorbance at 60 and 80 °C, the difference in absorbance is almost insignificant. Polymeric reactions take 40 h, so reaction kinetics is slow. Propylene oxide in ring opening copolymerization reaction is so exothermic, higher temperatures improve the kinetics reaction but increase also the possibility of hotspots.

4.2.1.4 Variation of the final molecular weight

The final molecular weight is reduced to 3000 g/mol to 725 g/mol. Amount of propylene oxide (PO) and polypropylene glycol (PPG) are modified to reach the target.

Table 06. Experiments changing the expected final molecular weight.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S11	1.5	25	80	3000	40
S12	1.5	25	80	725	40

The plot acquired comparing samples 12 and 13 is.
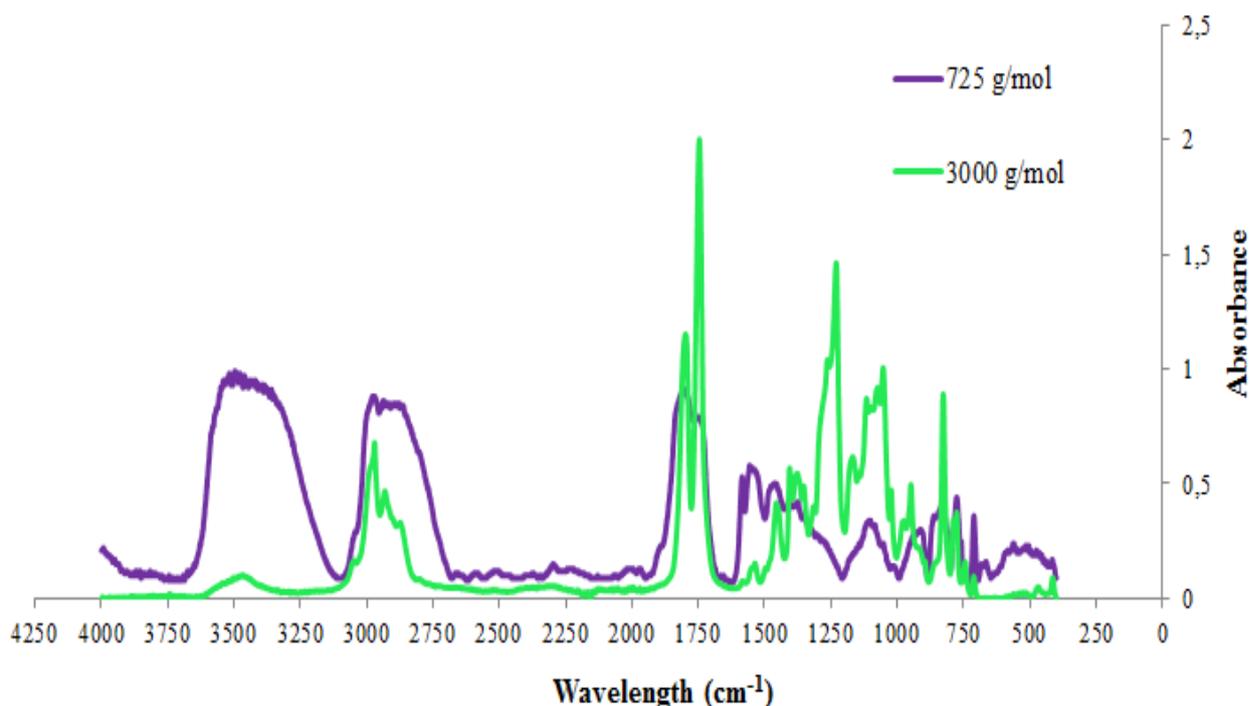
Figure 28. FTIR of polymeric product catalyst. Åbo Akademi University (ÅA) & University of Valladolid (UVa).

In sample 13, cyclic byproduct is in more amount than product. Polymeric product peak, in the sample of 725 g/mol of molecular weight, is not comparable with the peak of polymeric product at a molecular weight of 3000 g/mol. The difference in OH bonds available in sample 13 comparing with sample 12 is also huge.

4.2.1.5 Variation of the reaction time

Time is an important variable in reaction kinetics. Reaction time described in Ree et al [6] is 40 h. Experiments are performed to reduce reaction time in 20 h.

Once the reaction has finished, the unreacted propylene oxide monomers were extracted from the polymeric product using a vacuum trap.

As the reaction time was insufficient, almost all the propylene oxide added in these experiments was collected in the vacuum trap.

Experiments performed changing the reaction time are.

Table 07. Experiments changing the reaction time.

Samples	Amount of catalyst (g)	Pressure (bar)	Temperature (°C)	MW (g/mol)	Reaction time (h)
S14	1.5	25	80	3000	20
S15	1.5	5	60	3000	20

FTIR graphics obtained at a reaction time of 20 h are.
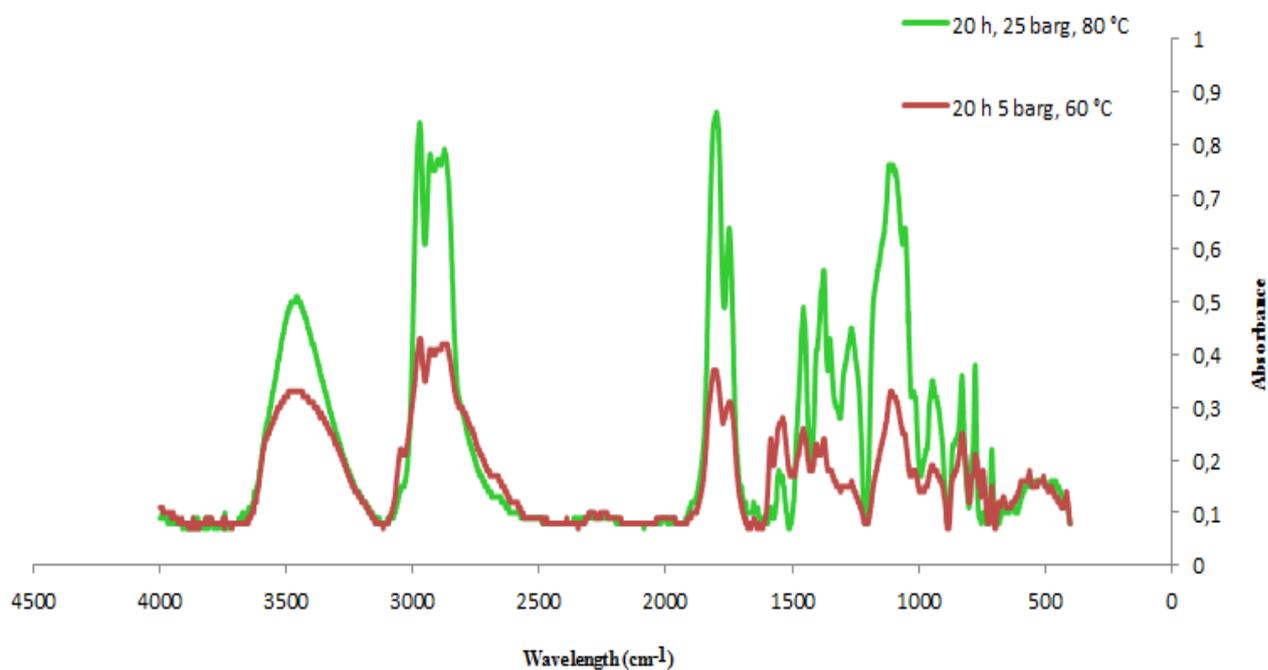
Figure 29. FTIR of polymeric product catalyst. Åbo Akademi University (ÅA) & University of Valladolid (UVa).

Polymeric reactions produced at 80 °C and 25 barg shown better results than at 60 °C and 5 barg, even though in sample 14 byproduct peak is higher than polymeric peak.

4.2.2 Size-Exclusion Chromatography (SEC) on polymer study

SEC technique was also used to discuss the polymerization reaction using ZnGA as the catalyst.

Samples must be soluble in the eluent for a perfect characterization.

Only acetic acid (AcOH) and dimethyl sulfoxide (DMSO) produced clear solutions, although only after several days in room temperature. A solvent mixture containing about 50% acetic acid-methanol solubilized in a few minutes at room temperature. A small addition of water (about 10%) to the above binary solution improves solubility.

SEC analyses were performed in a column Jordi X-stream 50x10 mm + 300x10mm. The eluent used for experiments was made with AcOH-MeOH-H2O 50:40:10, 1 ml/min and the detector is ELSD.

A calibration curve was performed using polyethylene glycol with a R2 coefficient of 0.9851.
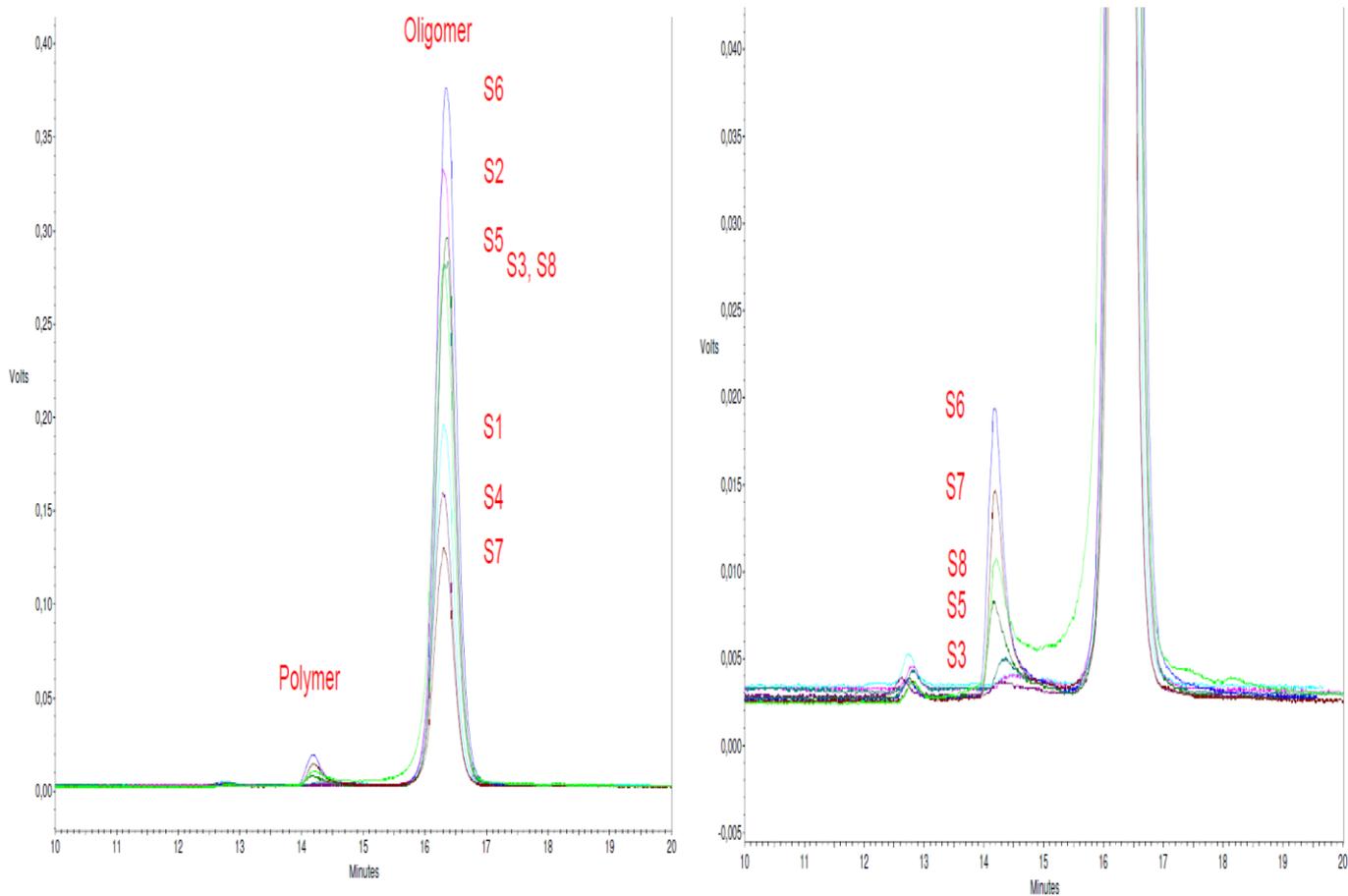
Figure 30 and 31. SEC of polymeric product catalyst. Åbo Akademi University (ÅA). Department of Wood and Paper Chemistry.

Samples 1 to 8 are perfectly soluble in the eluent, so results are reliable. The width or narrowness of the peak will show the molecular weight distribution mass in the time that the sample compound appears.

In SEC analysis are represented two peaks, the first one at a time of 14.3 minutes which represents the wished polymer and a second one at a time 16.4 minutes that represents the undesired oligomer.

Results show that the molecular weight of the polymeric product is around 3000 g/mol. The expected incorporation of CO_2 into the polymeric chain it's around the 10%.

A balance between a high peak in the polymer and a low peak in the oligomer will be the determined objective.

Sample five and specially sample six (1 g of catalyst) have a really remarkable peak in polymers although oligomer's peak are also very high.

Samples seven and sample eight (1.5 g of catalyst) have an important peak on polymer´s peak against the lowest oligomer´s peak of sample seven.

Samples 1 and 2 (0.3 g of catalyst) and three and four (0.6 g of catalyst) have a no representative polymer´s peak.
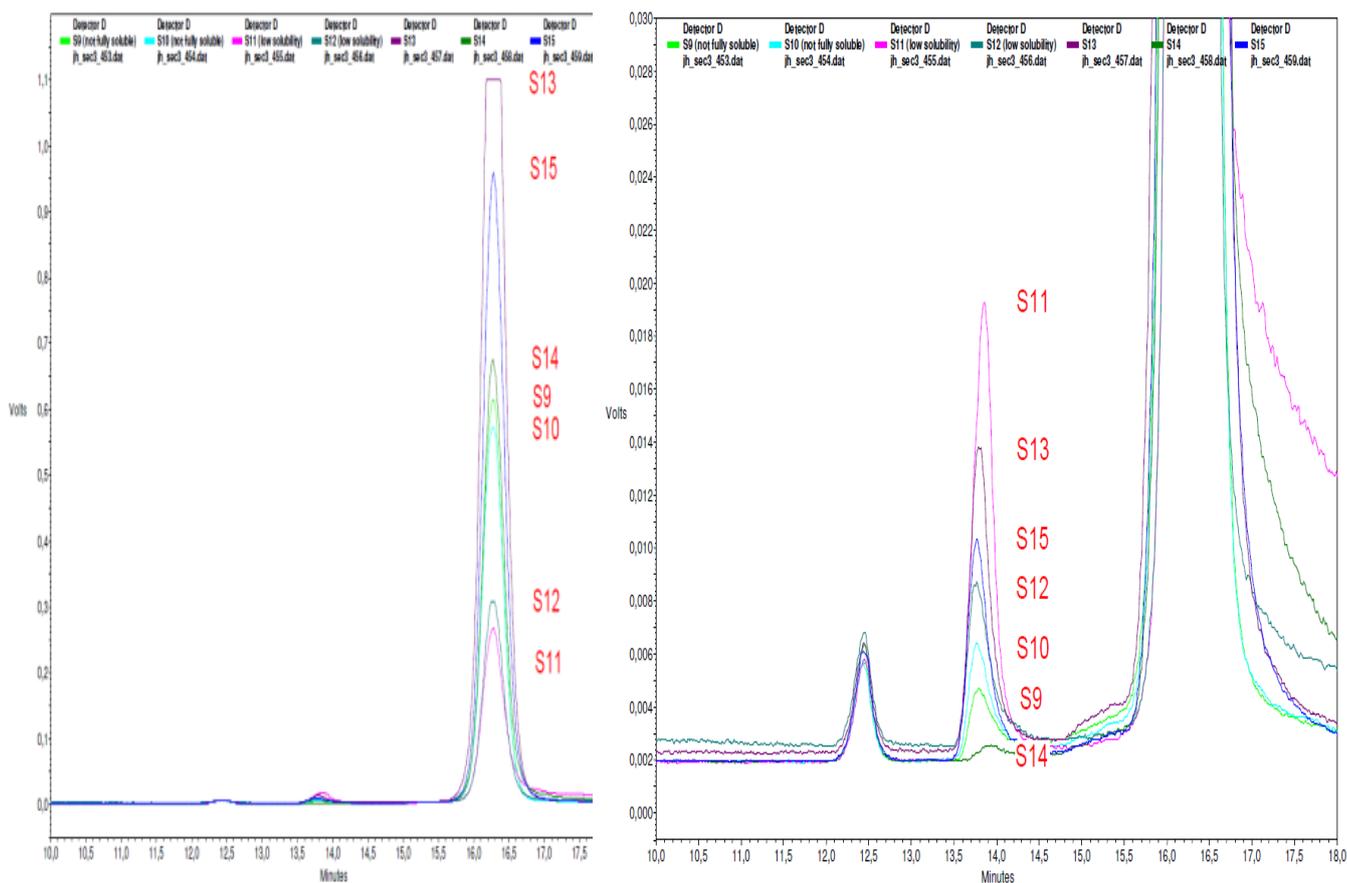
Figure 32 and 33. SEC of polymeric product catalyst. Åbo Akademi University (ÅA). Department of Wood and Paper Chemistry

Many eluents were employed to dilute samples 9 to 15. Eluents such us methanol (MeOH), acetone, ethanol (EtOH), ethyl methyl ketone, acetonitrile (ACN), tetrahydrofuran (THF), methyl iso-butyl ketone, chloroform, 1-methilpyrrolidone, dimethyl sulfoxide (DMSO) and acetic acid (AcOH) were used to dilute the samples.

Samples 9 to 15 are not completely soluble in the eluent, so results are not assurance of certainty.

5. CONCLUSIONS

The synthesis and study of catalyst produced by zinc oxide (ZnO), glutaric acid (GA) and toluene are the main goal of the research. Ring opening polymerization reactions using propylene oxide (PO) and carbon dioxide (CO_2) as the monomers, the previous catalyst synthesized and polypropylene glycol (PPG) as the starter were performed in a batch reactors under subcritical conditions. Different variables, such as the amount of the catalyst (0.3, 0.6, 1.0, 1.5 g), reaction pressure (5, 10, 20 bar), temperature (60, 80 °C), the final molecular weight of the polymer (3000, 725 g/mol) and reaction time (20, 40 h) were modified to obtain the best yield.

Analytical techniques like Fourier Transform Infrared (FTIR), Light Scattering (LS), Powder X-Ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Inductivity Coupled Plasma (ICP) and Physisorption were handled to analyze the zinc glutarate (ZnGA) catalyst and the polymeric product collected.

FTIR was used to analyze the formatted bonds that are in the catalyst as it is shown in figure 13. Hydroxide, aromatics alquene, esther carboxylate, zinc and alkane bonds are also represented in figure 13. SEM and Physisorption techniques supply information about the micromolecular shape of the catalyst as it is appreciated in figures 12-17. Physisorption allows quantifying the surface area and the internal shape. The synthesized catalyst does not have any pores so there is no internal diffusion. All catalytic reaction appears on the catalytic surface.

PXRD is used to discribe the crystalline shape of materials. The peaks and shape of the catalyst structural represented by PXRD are better defined comparing with XRD related on Ree et al article.

ICP is used to determine the corresponding amount of zinc per grammes of ZnGA catalyst. The amount of zinc contained in ZnGA catalyst is between 362 and 368 mg of zinc per g of catalyst.

LS analyses were performed in water and in air as it is presented in figures 19-22 obtaining the same particles sizes distribution patterns to characterize completely the ZnGA catalyst.

As it is described in Ree et al, the structural determination of the ZnGA catalyst is crutial to understand the nature of its activity in the CO_2/PO copolymerization reaction. The activity of the ZnGA catalyst in the copolymerization of CO_2 and PO was found to depend on the zinc source used in the catalyst synthesis. This zinc source dependency was attributed to the morphology differences (e.g., crystallinity and surface area) in the resulting ZnGA catalysts.

Polymerization reactions were performed in a batch reactor under subcritical conditions and results are achieved using FTIR and SEC. In the experiments carried out, using the highest amount of ZnGA catalyst (1.5 g of catalyst) was obtained the best yield. Results achieved with 1 g of catalyst show the same production of product-byproduct; and using less amount of catalyst results are not satisfactory. Results changing the amount of catalyst have been checked using FTIR technique and also SEC technique due to samples were dissolved in the eluent (figures 23, 28-29). The calculated molecular weight of the samples using SEC technique is around 3000 g/mol.

FTIR analysis modifying pressures (5, 25 barg) figure 24, are overlap in polymeric product, aromatic byproduct peaks. Pressure does not pressent any differences in the behavior due to it's not a kinetic variable.

FTIR analysis changing temperatures (60, 80 °C), figure 25, are also almost overlapping. Propylene oxide employed in ring opening polymerization reaction produced exothermic reactions. Increasing the temperature improves the kinetics reaction but it also increases the possibility of undesired hotspots.

Polymeric reactions reducing molecular weight to 725 g/mol, shown worse results than polymeric reactions with a molecular weight of 3000 g/mol, as it is advertised in figure 26.

Reaction time is also an important variable as it is shown in figure 27. In polymeric reactions carried out at 20 h, the amount of unreacted propylene oxide (PO) is quite important. FTIR analyses demonstrated that reactions at higher temperature and pressure are better although reaction time was insufficient. At 20 h of reaction time, cyclic byproduct amount is higher than carbonate product.

Polymerization reactions take 40 h of time, so kinetic reaction is too slow. Time in chemical industrial processes is an indispensable and fundamental variable, and a process that takes 40 h will not report a high profit.

The high amount of ZnGA catalyst used in copolymerization reaction is also a variable to take into account. A proper production of ZnGA catalyst takes 6 days and 1.5 g of catalyst were employed in each analysis.

Future work will be focused in the study of reduction the amount of catalysts to use in copolymerization reaction for obtain the same or higher yields. Also a reduction in the reaction time will be a considerable advantage in future experiments.

Recently other types of heterogeneous catalysts called Double Metal Cyanide (DMC) are being investigated to use in copolymerization reactions obtaining good results.

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7. FIGURES AND TABLES

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8. REFERENCES

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