POLYMERIZATION OF POLYESTERS IN CARBON DIOXIDE: STUDY OF DEGRADATION

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INTRODUCTION

Carbon dioxide has been recently used for applications in polymer processing. There are several examples in the literature regarding polylactide (PLA) and polyglycolide (PGA), most of them are related to polymer composites, microcellular foaming and particle production [1-3]. The main advantage of polymer processing in CO_2 is the considerable reduction in the viscosity of molten polymer [3]. The temperature of the polymer processing process depends on several parameters, such as crystallinity and thermal properties of the polymer, but it is usually above glass transition temperature (Tg) or melting point (Tm), for amorphous or semi-crystalline polymers, respectively. However, in CO_2 the temperature of the process can be lower than in the conventional processing processes because of the plasticization of the polymers [4,5]. An additional advantage in polymer processing in carbon dioxide could be the *in situ* polymerization due to the elimination of using organic solvents for the polymer production. Nevertheless, up to now, there are only few examples in the literature, and even less about the abovementioned polymers [6,7]. On the other hand, degradation of poly(L,L-lactide), PLLA, was observed at temperatures close to its melting point. According to previous studies the thermal degradation of polyesters follows a complex process which is the result of the contributions of different pathways, such as (1) hydrolysis by trace amounts of water; (2) zipper-like depolymerization; (3) oxidative, random main-chain scission; (4) intermolecular and intramolecular transesterifications [8]. However, the experimental results showed that the main contribution to thermal degradation of PLA goes through the transesterification reactions, especially the intramolecular ones which produce cyclic oligomers [9]; moreover, the presence of residual traces of catalyst accelerates the degradation by the intramolecular transesterification even at temperatures as low as 160ºC [8]. More recently, two kinds of intramolecular transesterification reactions have been pointed out as effective for the degradation process, the first one, called random chain scission is operative at low temperatures, whereas the second one (specific chain end scission) takes place at higher temperatures [10]. Similar results have also been observed for the thermal degradation of PGA [11]. Apart from differences in the composition of the degradation products, and in the activation energy of the processes, the random chain scission and specific chain end scission reactions can be distinguished for their opposite effect on both molecular weight and mass loss. Whereas the random chain scission produces a high reduction in the molecular weight of the sample without practically any mass loss [10,12]; the specific chain end scission does not affect the number average molecular weight (Mn), i.e. the mole number of polymer chains, but it highly increases the mass loss of the sample because of the production of low molecular weight species [10]. Due to the different thermal properties of poly(D,L-lactide) (PDLLA), poly(D,D-lactide) (PDLA), PLLA and PGA, the temperatures of degradation are also different. So, Gogolewski et al. [12] reported a significant reduction in molecular weight after injection molding for PDLLA, PDLA and PLLA at 148, 174 and 188ºC, respectively. Jamshidi et al. [8] observed this reduction in Mn for PLLA above temperatures of 190ºC, but mass loss of purified polymer, i.e. without catalyst, was not observed below 220ºC. On the other hand, for PGA a significant mass loss was observed above 270ºC [11]. In general, the results related to mass loss agree quite well with data given by Sivalingam and Madras [10]

regarding PDLLA and PGA. The aim of this work is to analyze the thermal degradation of PGA at low temperature and to study the effect of CO_2 on this process.

MATERIALS AND METHODS

Materials. The materials used were glycolide (1,4-dioxane-2,5-dione; Purac Biochem bv, The Netherlands) with purity higher than 99.5%. Zinc octoate (ZnOct$_2$, zinc (II) 2-ethylhexanoate; Nusa, Spain) with a metal content of 12%. %. Methanol anhydre (MeOH) (SDS S.A., Spain) with purity higher than 99.85%. And carbon dioxide (Carburos Metálicos, S.A., Spain) with a purity of 99.8%. All products were used as received.

Procedures. Experiments in supercritical media were carried out in the lab-scale unit described in a previous paper [13]. The procedure followed was: the amounts of monomer, catalyst and initiator were directly charged in the reactor at room temperature. The recipe followed was: 5 g of monomer; the molar ratio of monomer to catalyst was 100; the molar ratio of initiator to catalyst was 0.5; and the reaction temperature was fixed at 160ºC. Reactor was sealed and filled with 100 g of CO_2. After, the stirring (1000 rpm) and the heating started. The zero time was considered when temperature reached 80ºC. Then, the reaction was run for each reaction time. To quench the reaction, the reactor was cooled near to room temperature and later it was depressurized and open, and the sample was taken for characterization. Bulk reactions were carried out in a stirred-tank reactor with controlled temperature and a constant high enough nitrogen flow in order to remove air and humidity from the system. The stirring was initially set at 100 rpm but due to the increase in the viscosity of the system, it was necessary to stop it. Firstly, 100 g of monomer was added and heated until 160ºC. After complete thermal equilibration, the same molar ratios of monomer to catalyst and initiator to catalyst as in supercritical conditions were injected into the reactor. Several samples were taking during the reaction.

TGA (Thermal Gravimetric Analysis). In order to determine the conversion, the thermogravimetric analysis was used. A TGA (TA Instruments, Q600) with a refrigerated cooling system and purged with nitrogen gas. **DSC (Differential Scanning Calorimetry).** A DSC (TA Instruments Q1000) equipped with a refrigerated cooling system and autosampler was used for the measurement of the fusion enthalpy, glass transition temperature and percent of crystallinity. The sample (4-10 mg) was heated until 250ºC followed by a cooling until -50ºC and, finally, it was heated until 250ºC again. Heating and cooling were carried out with a heating rate of 10ºC min^{-1}. **MALDI-TOF mass spectrometry (Matrix-assisted laser desorption/ionization – time of flight mass spectrometry).** MALDI-TOF mass spectra were measured by an Autoflex II TOF/TOF Bruker spectrometer (Bremen, Germany) using IAA as matrix material. Samples cocrystallized with matrix on the probe were ionized by a nitrogen laser pulse (337 nm) and accelerated under 20 kV with time-delayed extraction before entering the time-of-flight mass spectrometer. Matrix (10 mg mL^{-1}) and sample (1 mg mL^{-1}) were carefully mixed as powder. Typically, 5 μL mixture of matrix and sample was applied to a MALDI-TOF MS probe and air- dried. All spectra were preformed in positive reflection mode. External calibration was performed by using Peptide Calibration Standard II (covered mass range: ~700 Da-3200 Da), Protein Calibration Standard I (covered mass range: ~5000 Da-17500 Da) and Protein Calibration Standard II (covered mass range: ~20000 Da- 70000 Da) from Care (Bruker).

RESULTS

In order to study the influence of carbon dioxide on the degradation of PGA, two sets of experiments were carried out at 160°C in bulk and in CO_2. Due to the impossibility of taking samples during the reaction in CO_2, the same reaction was carried out at different reaction times. To check the reproducibility of the experiments in carbon dioxide, the profile of pressure versus time is plotted in Figure 1. A good agreement among all the data is observed what means that the reproducibility of the experiments is fine.
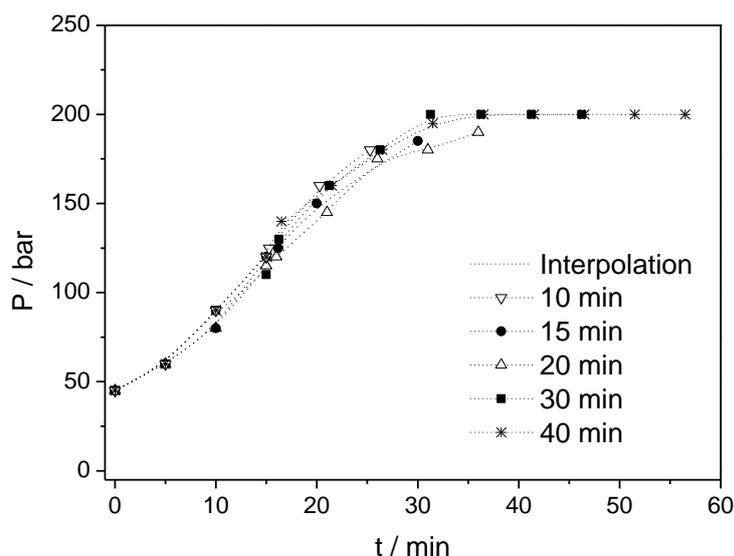
Figure 1. Reproducibility study of homopolymerization glycolide in CO_2. Catalyst: $ZnOct_2$. Initiator: methanol. T: 160°C. N: 1000 rpm. $m_{monomer}$: 5 g. Molar ratio monomer to catalyst: 100. Molar ratio initiator to catalyst: 0.5. m_{CO2}: 100 g.

On the other hand, the samples were analysed by MALDI-TOF to determine if the kinetic mechanism of the reaction is the same in both systems. Figure 2 shows the MALDI-TOF spectra of two samples, one from the bulk polymerization and the other from the polymerization in carbon dioxide. The same two main families are observed in both cases, which correspond to the species produced by initiation of water and methanol, a and b, respectively, following the kinetic scheme previously described in the literature [14,15]. Nevertheless, the proportion between them is a little bit different, being less important the contribution of species produced by methanol in the bulk polymerization. This could indicate a loss of methanol during the bulk polymerization since the system is open. Moreover, practically any cycle oligomer is observed even for longer reaction times.
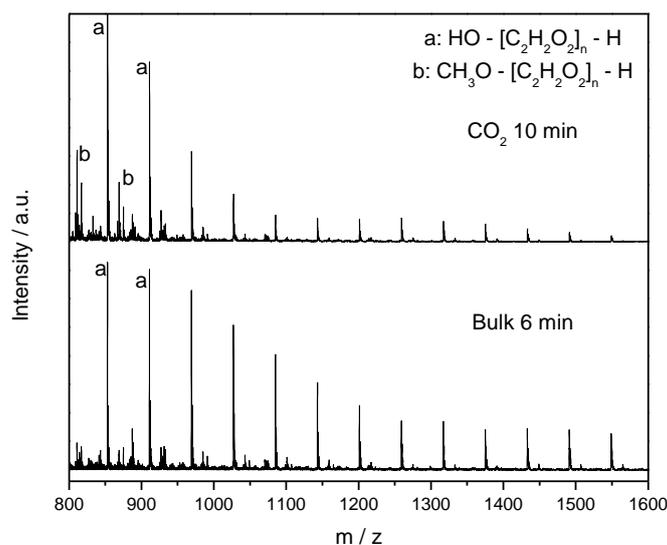
Figure 2. MALDI-TOF spectra of two samples of PGA. Up from the polymerization in carbon dioxide and down from the bulk polymerization process.

In a second step, the evolution of the reaction is analysed by characterization of the products with DSC. The conversion was estimated from TGA analyses. The results for both sets of experiments are shown in Tables 1 and 2. The molecular weight of each sample has been calculated from the Flory-Fox expression (eq. (1)) whose parameters for PGA have recently published by Gautier et al. [16]:

$$T_g = T_g^\infty - \frac{K}{M_n}$$

(1)

Where T_g^∞ is the glass transition temperature for a polymer with an infinitive molecular weight, and K is a constant, the values for PGA are 44.8°C and $1.10 \cdot 10^5$, respectively.

Table 1. Homopolymerization glycolide in CO_2. Catalyst: $ZnOct_2$. Initiator: methanol. T: 160°C. N: 1000 rpm. $m_{monomer}$: 5 g. Molar ratio monomer to catalyst: 100. Molar ratio initiator to catalyst: 0.5. m_{CO2}: 100 g.

t (min)	X (-)	T_g (°C)	M_n (Da)	ΔH_f (J g^{-1})	Xc (-)
10	0.84	40.47	24390	57.20	0.27
15	0.86	36.58	13382	50.91	0.24
20	0.87	10.05	3165	41.41	0.20
30	0.86	1.50	2540	57.16	0.27
40	0.85	-17.90	1754	44.99	0.21

On the other hand, the cristallinity percentage can be calculated using the fusion enthalpy as following:

$$Xc = \frac{\Delta Hf}{\Delta Hc_{PGA}}$$

(2)

Where ΔHc_{PGA} is the melting enthalpy of a pure crystal of polyglycolide, 206,6 J/g [17].

Table 2. Homopolymerization glycolide in bulk. Catalyst: $ZnOct_2$. Initiator: methanol. T: 160ºC. $m_{monomer}$: 100 g. Molar ratio monomer to catalyst: 100. Molar ratio initiator to catalyst: 0.5.

t (min)	X (-)	T_g (ºC)	M_n (Da)	ΔH_f (J g^{-1})	Xc (-)
4.5	0.91	21.73	4768	118.3	0.57
6	0.97	39.36	20221	108.9	0.53
16	0.96	40.8	27574	101.3	0.49
26	0.97	11.8	3333	120.1	0.58
36	0.95	19.4	4324	99.83	0.48
66	0.96	-12.7	1914	125.7	0.61

In both cases it is observed that after reaching the maximum conversion, the molecular weight decreases along with the time increase, what indicates that the degradation process takes place even at such low temperature compared to the melting point of PGA (around 220°C) and it is mainly through a random chain scission process, what it supports by the fact that the mass loss observed after the experiment completion can be considered neglected in both cases [10,12]. However, the Mn decrease is faster in carbon dioxide than in bulk. As a result, to achieve a reduction of 90% in the molecular weight, only 40 minutes are required in CO_2; while to get the same percentage of reduction in the bulk polymerization more than one hour is required. Consequently, it seems that carbon dioxide enhances the degradation process, most probably because the plasticizing effect of CO_2 on the polymer which can enhance the mobility of the chains and accelerates the transesterification process. On the other hand, the intramolecular transesterification seems not to be very important since practically any cycle was observed in MALDI-TOF spectra for longer reaction times. It is also observed that while the values of crystalinity of the samples from the bulk reaction are quite similar to the typical value reported in literature [17], around 50%, they are considerably lower in the case of supercritical reactions. What means that the cooling in supercritical reaction is faster than in the bulk process, which is probably due to the Joule-Thomson effect during the depressurization process. In this way, the cooling time is shorter than the crystallitaion one and the grade of crystallinity achieved is lower than the one expected. Finally, pointing out that the conversion in bulk polymerization could be overestimated because of the glycolide loss during the reaction since the sublimation of glycolide is a fact.

CONCLUSION

The thermal degradation of polyglycolide at low temperature has been studied; it has been demonstrated that random chain scission process has the larger influence on the process. Moreover, the presence of the residual catalyst can contribute to accelerate the process in polymerization in bulk and in carbon dioxide; however, the process in CO_2 is even faster because of the plasticising effect of it on the polymer, which probably enhances the mass transfer and the mobility of the chains.

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