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Thermal degradation studies on homopolymers and copolymers based on trimethylene carbonate and glycolide units

Elena Díaz-Celorio, Lourdes Franco, Yolanda Márquez, Alfonso Rodríguez-Galán, Jordi Puiggalí*

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Av. Diagonal 647, E-08028 Barcelona, Spain

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ABSTRACT

The non-isothermal degradation kinetics of poly(trimethylene carbonate) (PTMC) and polyglycolide (PGL) was investigated by thermogravimetric (TG and DTG) analysis in the temperature range between 50 and 550 °C at different heating rates (0.5–40 °C/min). Both homopolymers showed a complex multi-step degradation process. Kinetic analysis was successfully performed for the main degradation steps using the isoconversional Kissinger–Akahira–Sunose and Friedman methods. Activation energies of these steps were practically independent of the degree of conversion. The true kinetic triplets ($E, A, f(\alpha)$) were determined by the Coats–Redfern method. The results clearly indicated that the two homopolymers mainly degraded by quite different mechanisms, i.e. A_3 and F_1, which may be associated with different depolymerization processes (e.g. decarboxylation or unzipping).

Degradation of copolymers of trimethylene carbonate and glycolide with different chemical microstructures (i.e. random, blocky and segmented) and of blends with different percentages of both homopolymers was also studied. Interestingly, a deceleration and an acceleration for the decomposition of trimethylene carbonate and glycolide segments were observed, respectively. Specifically, the two-step degradation process of the blend with 50 wt% of each homopolymer was analyzed by the above methodologies. Kinetic data indicated that the main degradation process involved a different mechanism from that previously determined for PTMC and PGL, and that the activation energy was intermediate (i.e. $E_{\mathrm{PTMC}} < E_{\mathrm{Blend}} < E_{\mathrm{PGL}}$).

1. Introduction

Biodegradable polymers are currently the preferred candidates for temporary biomedical applications. Rapid development in this field has led to major advances in materials science driven by the complex requirements of clinical applications [1–3].

Polyglycolide (PGL) is probably one of the most employed biodegradable polymers for such specialized uses. Commercialization of PGL started in 1962 with the development of the first synthetic absorbable suture [4], and then extended to implantable medical devices (e.g. anastomosis rings, pins, rods, plates and screws) [5], tissue engineering scaffolds [6] and controlled drug delivery systems [7]. Polyglycolide is a highly crystalline material, and therefore has a high tensile modulus and very low solubility in organic solvents [8]. This polymer is also characterized by rapid hydrolytic degradation, which leads to glycolic acid [9].

Poly(trimethylene carbonate) (PTMC), another well known biodegradable synthetic polymer, is amorphous or crystalline in the relaxed or stretched state, respectively [10]. It has high flexibility and a slow hydrolytic degradation rate at 37 °C, which distinguishes it from PGL [11]. Several studies have shown the potential of PTMC as a biomaterial, in particular in soft tissue engineering [12–14]. However, its low mechanical performance limits its application for other uses significantly. For this reason, several copolymers with different lactones have been developed. These materials have mainly been applied as monofilament surgical sutures due to their high flexibility and adequate tensile strength (e.g. the copolymer constituted by glycolide and trimethylene carbonate (Maxon$^{\mathrm{TM}}$) [15] or the terpolymers constituted by glycolide, ε-caprolactone and trimethylene carbonate (Monosyn$^{\mathrm{TM}}$) [16] or by glycolide, *p*-dioxanone and trimethylene carbonate (Biosyn$^{\mathrm{TM}}$) [17]).

The high melting point of polyglycolide and indeed of most commercial copolymers constituted by glycolide (GL) and trimethylene carbonate (TMC) makes their thermal degradation an interesting object of study since these materials are usually processed from the melt state. Little information is currently available on the thermal degradation kinetics of this kind of copolymers, and especially on the influence of composition and microstructure (random, blocky or segmented). It should be pointed out that most commercial copolymers used as surgical sutures are specifically designed with a middle soft segment based on a random distribution of the two monomers and two hard segments constituted by glycolide only.

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* Corresponding author. Tel.: +34 34016684; fax: +34 34017150.
E-mail address: Jordi.Puiggali@upc.es (J. Puiggalí).

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Previous degradation studies conducted with the two homopolymers indicate that they have different thermal stability as the maximum rate of decomposition of PTMC was observed at a temperature significantly lower than for PGL (i.e. 288 and 362 °C in tests performed in N_2 at a heating rate of 10 °C/min) [18,19]. It was also reported that different processes were involved in the decomposition: a non-radical ester interchange reaction, which leads to the corresponding cyclic monomers, and decarboxylation reactions since small amounts of carbon dioxide were also detected in the degradation products [18,19].

Degradation by different mechanisms is currently well established for related polylactones [20–22]. Thus, recent studies conducted with polycaprolactone have revealed again the existence of two well-differentiated steps through analyses of evolved products: chain cleavages randomly distributed along the chain with formation of H_2O, CO_2 and 5-hexenoic acid for the low temperature decomposition process and depolymerization via an unzipping polymerization process for the high temperature step [22].

2. Experimental

2.1. Materials

Monomers (glycolide and trimethylene carbonate), initiator (diethylene glycol, DEG), and catalyst ($Sn(Oct)_2$) were purchased from Boehringer Ingelheim, Panreac and Sigma–Aldrich, respectively. Polymerizations were performed under a nitrogen atmosphere in a stainless steel jacketed batch reactor with a capacity of 250 mL at 0.2 MPa and temperatures that ranged between 180 and 220 °C. Synthesis of segmented copolymers followed a two-step strategy where firstly a soft segment with a theoretically random distribution was prepared by reaction of the two monomers, and then two hard segments were incorporated at each end of the middle soft segment by a subsequent polymerization of glycolide. Block copolymers were obtained from a soft segment constituted only by trimethylene carbonate whereas random copolymers corresponded to those attained after the first polymerization step. PGL and PTMC samples were obtained by one-step synthesis under similar reaction conditions. Synthesis, characterization and evaluation of basic properties of these samples had previously been performed [23]. Relevant data concerning the samples used in this work are summarized in Table 1. All copolymers are named as GL-*b*-[TMC-*co*-GL]-*b*-GL *x*-*z*, where *x* and *z* stand for TMC weight percentage in the soft segment and in the final sample, respectively. Random and triblock copolymers are particular cases where $x = z$ and $x = 100$, respectively.

Blends of both homopolymers were prepared by melting and mixing the appropriate amount of each polymer in the furnace sample pan. Mixtures are named as PGL/PTMC *x*/*y* where *x* and *y* indicate in this case the weight percentage of PGL and PTMC, respectively.

2.2. Measurements

^1H NMR spectra were obtained with a Bruker AMX-300 spectrometer operating at 300.1 MHz. Chemical shifts were calibrated using tetramethylsilane as an internal standard. Dried dimethyl sulfoxide-d_6 (DMSO) was used as solvent at a temperature of 90–95 °C to enhance solubility and resolution.

Thermal degradation was determined at heating rates of 0.5, 1, 2, 5, 10, 20 and 40 °C/min with around 5 mg samples in a Q50 thermogravimetric analyzer of TA Instruments and under a flow of dry (40 mL/min) and in the temperature range from 50 to 550 °C. Deconvolution of the derivative thermogravimetric analysis (DTG) curve was performed with the PeakFit v4 program by Jandel Scientific Software using an asymmetric function known as “asymmetric double sigmoidal”.

2.3. Evaluation of the activation energy for the thermal degradation

According to non-isothermal kinetic theory, thermal degradation of a sample can be expressed by the following function:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

where β is the heating rate, T is the absolute temperature, R is the gas constant, $f(\alpha)$ is the differential conversion function, and A and E are the preexponential factor and the activation energy for the studied decomposition reaction step, respectively.

Activation energies can be determined by advanced isoconversional methods such as Kissinger–Akahira–Sunose (KAS) [24,25] and Friedman [26,27], which do not require the knowledge of the exact thermodegradation mechanism. Integral (KAS) and differential (Friedman) isoconversional methods make use of the isoconversional principle, which states that at a constant extent of conversion the reaction rate is a function of the temperature only.

In order to calculate the activation energy during the whole degradation process, the KAS method [24,25] can be applied. It is based on the integration of Eq. (1), which after a reordering, becomes:

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT} \tag{2}$$

where $g(\alpha)$ is the integral conversion function (i.e. $g(\alpha) = \int_0^{\alpha} (d\alpha/f(\alpha))$).

For each degree of conversion the activation energy is obtained from the slope of the linear representation of $\ln(\beta/T^2)$ versus $1/T$.

Table 1
Characterization data of GL-*b*-[TMC-*co*-GL]-*b*-GL *x*-*z* samples.[a]

Sample		Hard segment (wt%)	4.83 ppm[b]	4.64 ppm[b]	M_n [c] (g/mol)	T_g [d] (°C)	T_m [d] (°C)
x	*z*						
0	0	100	100	–	80,900	37.2	222.2
100	100	0	–	–	46,600	−15.0	–
32.5	32.5	0	75	1.5	82,000	21.2	–
100	32.5	67.5	93	0	51,000	−13.2/33.7	215.8
85	32.5	61.8	86	7	65,000	19.7	208.1
75	32.5	56.7	80	9	58,000	18.4	201.3
65	32.5	50.0	80	8	75,000	19.4	187.2
60	23	61.7	80	5	60,000	24.8	203.2

[a] Polyglycolide and polytrimethylene samples are represented by $x = z = 0$ and $x = z = 100$, respectively.

[b] Percentage of the indicated ^1H NMR signal referred to the total area of glycolyl signals.

[c] From GPC data.

[d] DSC data from melt quenched samples.