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QUANTITATIVE ANALYSIS OF BIODEGRADABLE AMPHIPHILIC POLY(*L*-LACTIDE)-BLOCK-POLY(ETHYLENEGLYCOL)-BLOCK-POLY(*L*-LACTIDE) BY USING TG, FTIR AND NMR

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The thermogravimetric analysis (TG) of two series of tri-block copolymers based on poly(*L*,*L*-lactide) (PLLA) and poly(ethyleneglycol) (PEG) segments, having molar mass of 4000 or 600 g mol^{-1}, respectively, is reported. The prepared block copolymers presented wide range of molecular masses (800 to 47500 g mol^{-1}) and compositions (16 to 80 mass% PEG). The thermal stability increased with the PLLA and/or PEG segment size and the tri-block copolymers prepared from PEG 4000 started to decompose at higher temperatures compared to those copolymers from PEG 600. The copolymers compositions were determined by thermogravimetric analysis and the results were compared to other traditional quantitative spectroscopic methods, hydrogen nuclear magnetic resonance spectrometry (^{1}HNMR) and Fourier transform infrared spectrometry (FTIR). The PEG 4000 copolymer compositions calculated by TG and by ^{1}HNMR, presented differences of 1%, demonstrating feasibility of using thermogravimetric analysis for quantitative purposes.

Keywords: *biodegradable, block copolymers, poly(lactic acid), thermogravimetry*

Introduction

The chemical and bioactive substance encapsulation expertise is already a requisite in several applications, such as pesticide encapsulation in the agricultural sector, allowing limited toxicity in manipulation and during spraying. Stabilizer, flavor, minerals and aroma encapsulation in the food industry, pigments and dyes encapsulation in the ink and coating industry and drugs and medicines encapsulation in the pharmaceutical industry are other applications. The encapsulation materials are usually biodegradable natural polysaccharides and polypeptides in food and drugs applications, while (polymeric) surfactants and emulsifiers are applied in general uses. Copolymers of *L*-lactide with a hydrophilic monomer such as ethylene glycol have been suggested for many medical and pharmaceutical applications due to its amphiphilic nature and biodegradability. Additionally, copolymers of poly(ethylene glycol) are very promising as biomaterials, specially as encapsulating materials in the novel smart drug industry, because it does not stimulate inflammation reaction, nor phagocytic uptake by the immune system. At the same time it presents ability to protect drug carriers and allows their long-term blood circulation.

The composition, morphology and crystallinity of block copolymers strongly influence their mechanical properties and rate of biodegradation. By carefully adjusting the block copolymer segment sizes through the polymerization parameters, it is possible to modulate the material characteristics in order to suit a particular application.

Thermal behavior and thermal degradative behavior are important aspects of the characterization of the physical properties of different poly(lactide) and poly(ethylene glycol) homopolymers and copolymers [1–7]. The thermogravimetric analysis (TG) measures the susceptibility to thermal degradation of different polymers and has been used to investigate various types of block copolymers containing multi-block segments of poly(lactide-co-glycolide) and diol-terminated poly(*L*-caprolactone) or poly(ethylene glycol) (PEG) segments [8], and triblock copolymers of poly(*p*-dioxanone) or poly(*L*,*L*-lactide) PLLA or poly(dioxanone-co-*L*,*L*-lactide) and diol-terminated PEG segment [9] with the aim of relating the molecular structure with their thermodegradative behavior. On the other hand, differential scanning calorimetry and gel permeation chromatography have been used to examine the thermooxidative degradation processes of thermally aged samples of a PEG/PLLA blend [10].

Although thermal degradation studies of polymeric systems comprised of PEG and PLLA have been already reported and TG curves were reported to present two steps due to the segment differences, no quantitative correlation has been demonstrated between mass loss and copolymer composition. This study describes the preparation of biodegradable poly(*L*-lactide)-b--poly(ethyleneglycol)-b-poly(*L*-lactide) (PLLA-PEG-PLLA) (Fig. 1) from two different PEG

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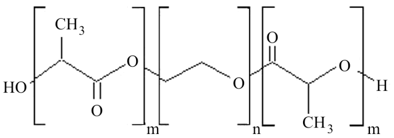

Fig. 1 Chemical structure of poly(*L*-lactide)-block-poly(ethylene glycol)-block-poly(*L*-lactide) (PLLA-PEG-PLLA)

prepolymers (M_n=4000 or 600 g mol^{-1}) and various PLLA segment sizes; the PLLA degree of polymerization (DP_{PLLA}) varied from 1.2 up to 302.0. The copolymers compositions were determined by thermogravimetric analysis and the results were compared to other traditional quantitative spectroscopic methods, hydrogen nuclear magnetic resonance spectrometry (^{1}HNMR) and Fourier transform infrared spectrometry (FTIR).

Experimental

Two series of triblock copolymers PLLA-PEG-PLLA were prepared by cyclopolymerization of *L*-lactide using stannous 2-ethylhexanoate as initiator and PEG (M_n=600 or 4000 g mol^{-1}) as co-initiator. The bulk polymerization reaction was performed at 120°C for 22 h.

The copolymers thus prepared were characterized by ^{1}HNMR and FTIR spectroscopies. ^{1}HNMR spectra were measured at 200 MHz in $CDCl_3$ solution using a Bruker AC-200 spectrometer and tetramethylsilane (TMS) as an internal reference. The infrared spectra were recorded in $CHCl_3$ solution, using a Nicolet Magna-IR 560 FTIR spectrometer (Nicolet Instruments Inc.). Compositions of copolymers were determined by FTIR spectra using a calibration curve. Solutions containing different concentrations of PLA were analyzed using a liquid cell, and the absorbance area under the carbonyl absorption, from 1820 to 1706 cm^{-1}, was integrated to estimate the LA:EO ratio in the copolymers.

DSC runs were performed using a Mettler Toledo 822 instrument under nitrogen flux and samples were sealed in aluminum pans. Each sample of about 10–15 mg was pre-heated to 180°C and kept at this temperature for 5 min, cooled down at a rate of 20°C min^{-1} to –65°C and, after remaining at this temperature for 5 min, was heated up to 250°C at a rate of 10°C min^{-1}.

TG-DTA runs were performed in a TG-DTA simultaneous equipment, model SDT 2960, TA Instruments, under nitrogen flux at 20 mL min^{-1}. Samples of about 10–12 mg were heated up to 600°C at a rate of 10°C min^{-1}.

Results and discussion

Two series of tri-block copolymers with different lengths of PLLA segments (polymerization degree, *DP*=1.2 to 302.0) were obtained by variation of the relative mass of *L*-lactide in the feed, added to a pre-weighed amount of PEG (M_n=4000 or 600 g mol^{-1}). For composition characterization, ^{1}HNMR spectra were recorded at 200 MHz to estimate the LA:EO molar ratio in the copolymer. PLLA segments presented the following absorptions: δ 5.23–5.15 multiplet, inner methine units; δ 4.2–4.4 multiplet, end chain methine units; δ 1.4–1.6 inner methyl units. PEG segments presented the following absorptions: δ 3.65 singlet, inner methylene units; δ 4.2–4.4 multiplet, methylene protons of the acylated PEG end unit.

The prepared block copolymers presented wide range of molecular masses (800 to 47500 g mol^{-1}) and compositions (16 to 80 mass% PEG) (Table 1).

Table 1 Copolymer characteristics

Copolymer	Physical aspect	DP_{PLLA}[a]	M_n/g mol^{-1}	Composition		T_g/°C	T_m/°C	Comopsition[c]
				PEG[a]/mass%	PEG[b]/mass%			PEG/mass%
co4000-1	solid	6.8	5000	80.3	81.4	–48	53	81.3
co4000-2	solid	15.9	6300	63.6	59.3	–46	18; 42	58.9
co4000-3	solid	35.9	9200	43.6	52.2	–44	17; 47	42.7
co4000-4	solid	57.8	12300	32.5	38.2	–46	14; 93	32.0
co4000-5	solid	145.6	25000	16.0	16.2	–45	100	15.5
co4000-6	solid	130.0	22700	17.6	16.4	–45	166	16.7
co4000-7	solid	136.0	23600	16.9	16.0	–44	163	17.3
co4000-8	solid	302.0	47500	8.4	8.0	–46	167	9.1
co600-1	liquid	1.2	800	78.2	81.4	–44	4	32.3
co600-2	liquid	3.3	1100	55.5	53.1	–44	–	50.6
co600-3	liquid	4.6	1300	47.7	38.4	–46	–	38.8
co600-4	wax	6.8	1600	37.9	30.4	–40	94	33.1
co600-5	wax	8.9	1900	32.0	35.1	–39	100	23.5

Polymerization degree (*DP*), molar mass (M_n) and composition calculated from: [a] ^{1}H-NMR spectra, [b]FTIR spectra and [c]TG.

The FTIR spectra of PLLA in chloroform solution at different concentrations were used to prepare a calibration curve using a liquid cell, which allowed the quantitative analyses of the block copolymers composition. The absorbance area under the carbonyl absorption, from 1820 to 1706 cm^{-1}, was integrated to estimate the lactate to ethylene oxide ratio, LA:EO, in the copolymers (Table 1).

Differential scanning calorimetric data for tri-block copolymers are reported on Table 1. It has previously been shown [11] that PLLA-PEG-PLLA copolymer phase behavior depends on the relative segment sizes. Short PEG and/or PLLA blocks lead to amorphous materials. Increased segment sizes leads to the formation of semicrystalline materials. Some copolymer containing longer PLLA segments and PEG 4000, displayed two melting peaks (T_m) as observed by DSC (samples co4000-2, co4000-3 and co4000-4), reflecting crystalline phases for both segments. The presence of the crystalline phases depends on the solubility in the miscible amorphous phase. The amorphous phase displays nearly constant composition as attested by the glass transition temperature (T_g) observed for all copolymers, around –43±5°C.

Block copolymers with different composition ratios and with different lengths of segments were subjected to thermogravimetry to investigate the influence of structure on the degradative behavior of these materials. The mass loss and differential mass loss curves for the copolymers along with differential thermal analysis results were carefully analyzed. Quantitative assessment of the endothermic degradation steps was possible.

TG under nitrogen revealed two degradation processes that can be ascribed to the PLLA and PEG segments, respectively. The overall thermal degradation was due to endothermic chain scissions, as shown by DTA curves.

These results are in accordance to those previously reported [8–10]. In the first stage, copolymer degradation proceeds by a PLLA segment chain end ‘unzipping’ mechanism. This process is favored by six-membered cyclic di-lactide formation. The thermal behavior of amorphous homo- and copolylactide prepared from *D*,*L*-lactide has been previously reported and the degradation mechanism has been shown to occur by a cyclodepolymerization process [12, 13]. And, in a second stage, at higher temperature, thermal scission of the PEG main chain occurs [2, 3].

The TG analyses have shown that the copolymers are comprised of two segment types with very distinct thermal stabilities. The PEG segment is more thermally resistant and the degradation onset temperature observed by DTA is around 400°C. In contrast, the PLLA segment starts to decompose at temperatures as low as 300°C, for copolymers

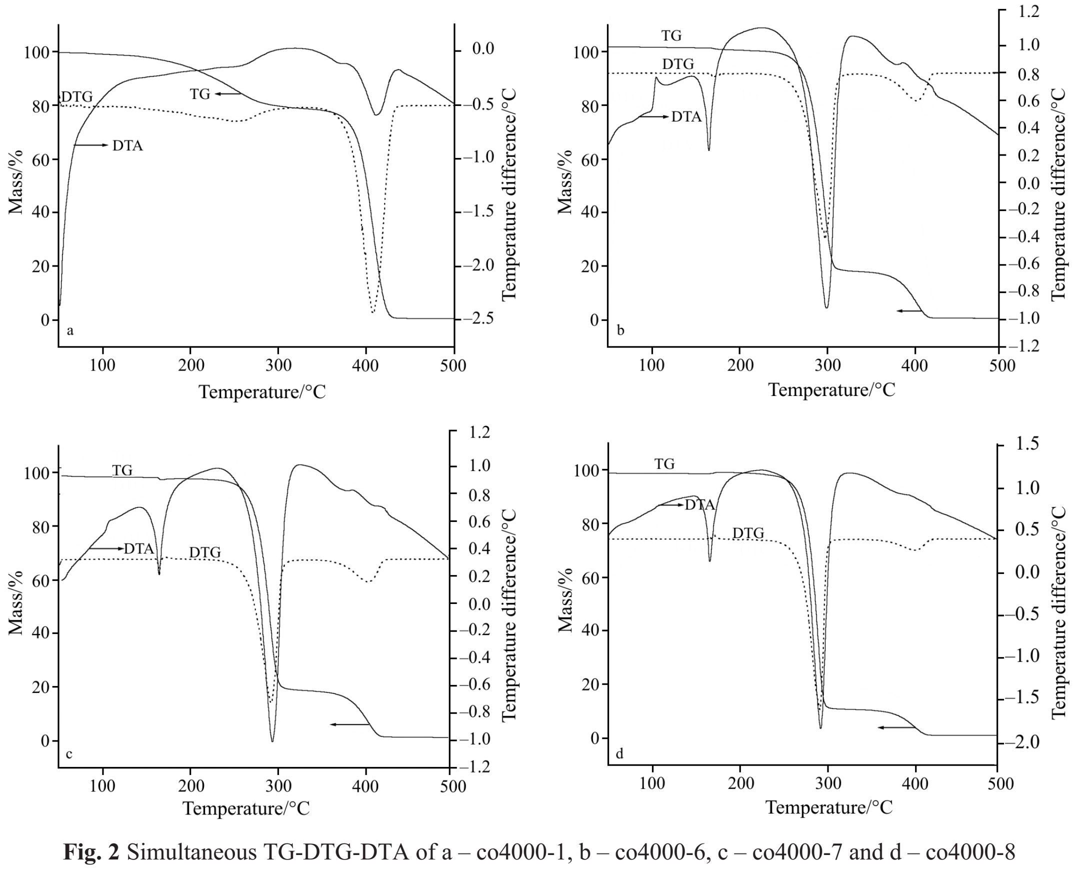

Fig. 2 Simultaneous TG-DTG-DTA of a – co4000-1, b – co4000-6, c – co4000-7 and d – co4000-8

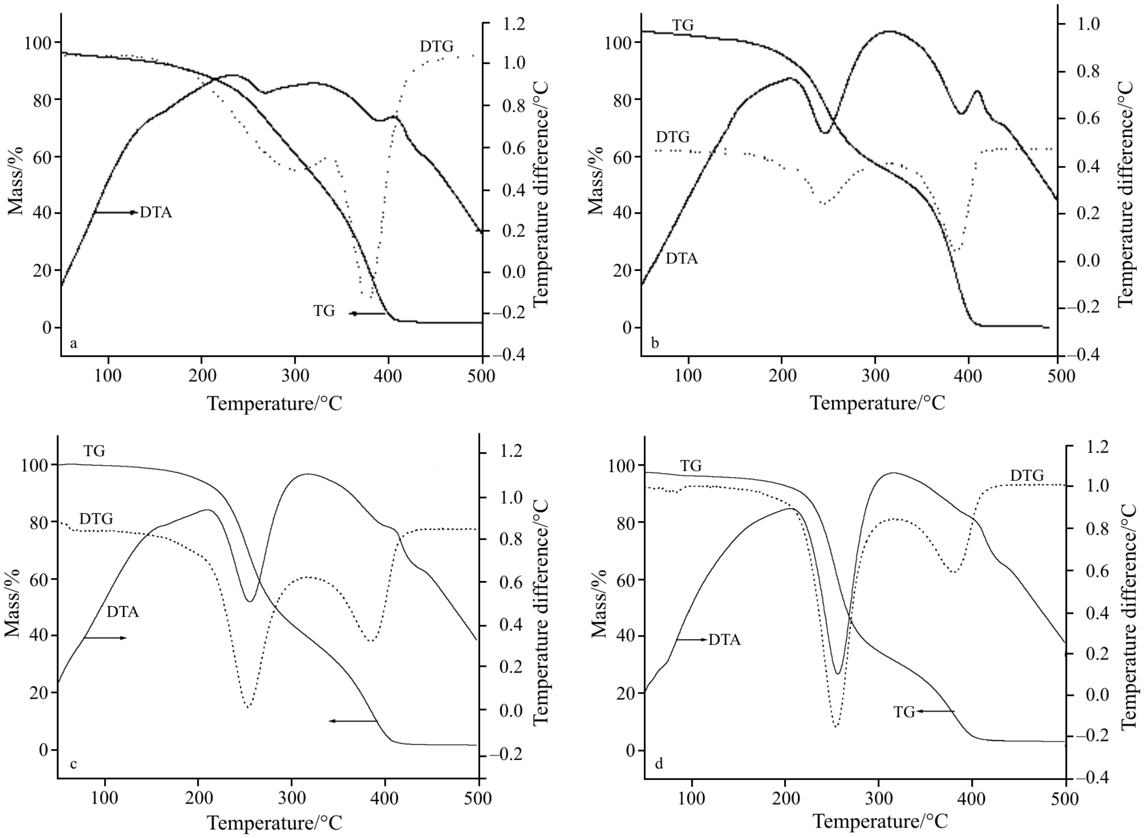

Fig. 3 Simultaneous TG-DTG-DTA of a – co600-1, b – co600-2, c – co600-3 and d – co600-4

prepared from PEG 4000. For copolymers prepared from PEG 600, the degradation onset temperatures observed by DTA were around 250 and 370°C for the PLLA and PEG segments, respectively (Figs 2 and 3).

Each TG derivative curve was submitted to multiple peak deconvulation using Origin 6.0 software. Integration of the areas of the deconvulated peaks provided the copolymer mass composition in terms of the PLLA and PEG segments, shown in Table 1.

For the PEG 4000 series, the mass losses reflect the mass% of the two segments in the copolymer. The compositions suggested by TG are in accordance to those determined by ^{1}HNMR and FTIR (Fig. 2 and Table 1).

The PLLA/PEG copolymer compositions from TG compares favorably with that determined by ^{1}HNMR. Differences smaller than one percent were observed. The feasibility of thermogravimetric analysis for quantitative assessment of segment size for copolymers of this type is, therefore, demonstrated.

On the other hand, for the PEG 600 series, the mass losses observed by TG did not correspond to the copolymer composition as determined by NMR and FTIR spectroscopies (Fig. 3 and Table 1). The second step mass loss, which should correspond to the PEG content in copolymer was smaller than expected. This results from a superposition of both degradation and evaporation processes.

Conclusions

Copolymers of lactide and ethylene glycol with wide range of molar masses and relative composition have been prepared. The products were obtained as liquid, wax or solid polymeric materials.

The copolymers were quantitatively characterized by FTIR spectroscopy and NMR spectrometry and their thermal behavior was studied by DSC and simultaneous TG/DTA.

TG plots of copolymers were carefully analyzed and it was possible to do a direct correlation between the copolymer composition and the degradation steps. For the PEG 4000 series, the mass losses correspond to the mass percentages of both segments. The compositions observed by TG are in accordance to those determined by ^{1}HNMR and FTIR. This is in contrast to the behavior of copolymers prepared from PEG 600 series. Because of the shorter PEG segment in these copolymers, the degradation temperature of the PEG is quite similar to that of the poly(lactide) segments and the corresponding TG peaks overlap.

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