Thermal stability of polylactide with different end-groups depending on the catalyst used for the polymerization

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A B S T R A C T

Thermal stability of polylactides (Mn ~ 4000) containing a different number of hydroxyl and carboxyl end groups synthesized by cationic ring-opening polymerization was studied under non-isothermal conditions. Polylactides (PLAs) were prepared in the presence of hydroxy acids or functional alcohols as initiators and protic acid as a catalyst and in some cases were subjected to the esterification with an acid anhydride in order to increase the number of carboxyl groups. Polymers purified by simple precipitation were characterized by ^{1}H NMR and size exclusion chromatography (SEC) and subsequently analyzed by thermogravimetric analysis (TGA) which indicated that the degradation proceeded in a similar temperature range independently on the end-groups type. An unexpected observation was that the temperatures of the maximum rate of their decomposition were by 40 ÷ 78 °C higher than those determined for analogous PLA prepared (for comparison) in the presence of tin octoate. To exclude the possibility that this effect was due to the different structure of polymers prepared by different mechanisms the traces of tin octoate were added to PLA obtained by cationic polymerization and it was observed that this led to the decrease in temperature of maximum decomposition to the level observed for PLA prepared by coordination polymerization. Thus, we conclude that traces of protic acid used as a cationic catalyst (if present after applying a typical purification procedure) do not have an effect on thermal degradation in contrast to traces of metalorganic catalyst which, as shown earlier, promote thermal degradation.

1. Introduction

There are numerous methods of polymers modification aiming at changes in their properties. Some changes may arise from the presence of different end-groups which can be introduced to polymer chain together with the initiator, with comonomer or by post-polymerization functionalization.

One of the most intensively studied recently polymers, subjected to many modifications is bio-based, biodegradable polylactide. A lot of works concern the modification of thermal stability of polylactide which is considered as rather poor (melting temperature, T_m of high molecular weight PLA is 170–180 °C and the temperature of maximum rate of decomposition, $T_{d\ max}$ is in the range 220–390 °C [1–3]).

The modification of thermal stability of PLA can be achieved by copolymerization, blending with other polymers, application of different additives/fillers or transformation/introduction of specific end groups [4]. It is known, that thermal degradation, especially for those polymers that can depolymerize (i.e. their polymerization is reversible), usually starts from end-groups [3]. A most evident example is polyformaldehyde, which, if synthesized by anionic polymerization of

formaldehyde is terminated with hemiacetal groups. Such crude polymer undergoes degradation at elevated temperatures and its practical application is possible only after esterification of hemiacetal terminal groups (alternative method is cationic copolymerization of formaldehyde trimer – 1,3,5-trioxane with e.g. 1,3-dioxolane) [5].

Polymerization of lactide is a reversible process thus it can be expected that the nature of end-groups may affect its thermal stability. Indeed when PLAs with −OH, −COOH, −NH₂ and −Cl end-groups prepared with tin octoate as a catalyst were compared in respect with their thermal properties [6] it has been found that for four-arm star PLA's with M_n around 30000, the least thermally resistant was PLA with terminal −OH groups ($T_{d\ max}$ around 240 °C), more stable was PLA with −COOH groups ($T_{d\ max}$ around 320 °C and the highest stability had PLA with −NH₂ and −Cl end-groups ($T_{d\ max}$ around 360 and 370 °C respectively). Poor thermal stability of PLA with terminal hydroxyl groups was claimed by many authors [1,4,6–10]. Reported results are, however, sometimes scattered (even after exclusion of errors arising from varied conditions of applied analyses) [11]) and it raises a question whether differences in the temperature of maximum degradation rate from differential curves (DTG) of thermogravimetric analysis

reported in the literature are indeed due to different end-group structure or perhaps other factors are involved.

A few years ago Endo and coworkers published a report on the thermal stability of PLA prepared with tin octoate as a catalyst [12]. Obtained polymers were purified by repeating the liquid-liquid extraction process using a 1 M HCl aqueous solution and after each step, the content of residual tin was determined by atomic absorption flame emission spectrophotometry. It should be pointed out that M_n values remained in the range 76000–104500, thus they did not change significantly what indicates that purification procedures did not lead to the advanced fractionation of the polymer. It has been found that after first purification step the content of tin was equal to 607 ppm and decreased after each subsequent step. However, after six consecutive extractions steps, there was still 20 ppm of residual tin in the sample.

Thermal degradation of each sample was studied under non-isothermal conditions and it was observed that maxima on DTG curves shifted systematically to higher temperatures with the decreasing tin content. Thus, reducing tin content from 600 ppm to 20 ppm led to the shifting of maximum on DTG curve from $\sim 290\,°C$ to $\sim 359\,°C$. It shows that the polymer with exactly the same structure of end-groups degrades at different temperatures depending on the content of residual tin and that even very careful purification does not remove traces of tin catalyst completely. It should be pointed out that typically single dissolution-precipitation step is used in most laboratories and this may be a source of scattered results concerning thermal stability of PLA prepared with tin octoate, reported by different authors. The observation that the catalyst residue is the main impurity which decides about the thermal stability of PLA was additionally supported by Endo who tried to protect terminal PLA hydroxyl groups by acetylation [13]. It appeared that if polymer was carefully purified before acetylation, decomposition temperatures of both - terminated with −OH and acetylated PLA were almost the same. The conclusion from that study was that the contribution of the end-groups acetylation to the stability of PLA was negligible, except for the stabilization effect due to the elimination of residual tin during the acetylation process [13]. Several other authors also noticed the influence of tin catalyst residue on the thermal stability of polylactide [1,3,14–18]. Different mechanisms of thermal degradation proceeding in the absence of water and oxygen were suggested including depolymerization, inter- and intramolecular transesterification followed by lactide elimination, all under tin support. Most probable considered decomposition pathways are depicted in Scheme 1 [12].

PLA is most commonly prepared by coordination polymerization using organometallic catalysts such as tin octoate or aluminum alkoxides [19–21]. It may be expected that with each organometallic catalyst situation may be similar as with tin octoate i.e. complete removal of traces of metal-containing catalyst is practically impossible by the conventional typically used method.

Lactide can also be polymerized by cationic mechanism – cationic polymerization was studied by several research groups including ours [22–29]. Most frequently trifluoromethane sulfonic acid (triflic acid, TFA) is used as a catalyst. PLA prepared with a protic acid as the catalyst does not contain any metal impurities. As it will be shown further in this contribution, purification of such polymer does not affect its thermal stability which means that either catalyst is completely removed or traces of acid catalyst, even if not completely removed by

Scheme 1. Most probable pathways of the tin supported degradation of PLA by backbiting reactions proceeded from polymer chain end (depolymerization) or in the middle of the chain.

conventional dissolution-precipitation procedure, should have no detectable effect on thermal stability.

Therefore, we decided to compare thermal stabilities of PLAs containing hydroxyl and carboxyl end-groups prepared by cationic polymerization and further to compare the results with the thermal stability of polymer prepared with tin octoate as a catalyst to learn what is a major factor determining the thermal stability of PLA; is that a nature of end-groups (hydroxyl versus carboxyl groups) or a nature of catalyst used for ring-opening polymerization of lactide.

2. Experimental

2.1. Materials

L,L-lactide (LA) (Boehringer Ingelheim, Germany) was crystallized from distilled 2-propanol and sublimed (10^{-3}mbar, 85 °C). N-hexanol (HA) (99%, Aldrich) and ethylene glycol (EG) (99.8%, Aldrich) were stored over molecular sieves and vacuum distilled before use. Benzyl alcohol (BA) (99.8%, Aldrich) was distilled before use. Tin(II) octoate (2-ethylhexanoate, Sn(Oct)$_2$) (92.5–100%, Aldrich) was purified by high-vacuum distillation at 140 °C/3×10^{-3}mbar and directly distributed into thin-walled ampoules equipped with break-seals and then sealed off and stored at −12 °C. Glycolic acid (GA) (99%, Aldrich), 2,2-bis(hydroxymethyl)propionic acid (BHPA) (98%, Aldrich), trifluoromethanesulfonic acid (98%, Aldrich), succinic anhydride (SA) (99%, Aldrich), 1,4-diazobicyclo [2.2.2]octane (DABCO) (99%, Aldrich) were used as received. Tetrahydrofuran (THF) (99%. POCH) was kept for several days over KOH pellets, filtered off, refluxed over Na metal, distilled, degassed, and stored over a liquid Na/K alloy. Dichloromethane (99%, POCH) was dried over calcium hydride and distilled. Methanol (pure, Chempur) was used as received.

2.2. Synthesis of polylactides by cationic ring-opening polymerization
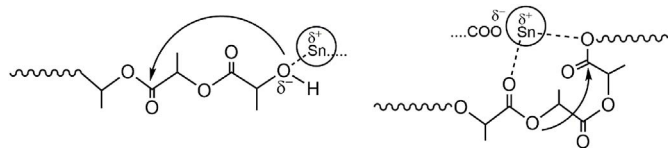
L,L–lactide (3.0 g, 20.8 mmol) was placed in Shlenk tube equipped with stirring bar and closed with a rubber septum. The tube was degassed in vacuum, charged with argon and 7 mL of dichloromethane was added via syringe followed by an addition of an initiator (HA, EG) (0.6 mmol) after the dissolution of lactide. The solid initiators (GA, BHPA) were added together with lactide before tube closing. Subsequently, triflic acid (8.0 μl, 0.09 mmol) was added via syringe and polymerization process was carried out for 24 h at room temperature. The polymer solution was precipitated into cold methanol, washed with methanol, filtered and dried in vacuum. All polymers were characterized by ^{1}H NMR and size exclusion chromatography (SEC).

2.3. Synthesis of polylactide by coordination ring-opening polymerization

Benzyl alcohol initiated PLA was synthesized by the coordination polymerization of L-lactide in THF at 80 °C using BA as the initiator and tin octoate as a catalyst according to the method previously described [10]. Briefly, Sn(Oct)$_2$ (0.01 g, 0.025 mmol in dry THF solution), L-lactide (4.08 g, 28.36 mmol) and BA (0.11 g, 1.0 mmol)were transferred under vacuum into breakseals and sealed after freezing in liquid nitrogen. Breaksealswere connected with the reaction glass vessel and the vessel was filled with 15 ml of dry THF. Breakseals were broken and all components were mixed at room temperature. An ampoule containing reacting mixture was placed into a thermostat (80 °C). The resulting polymer was precipitated into methanol, separated by filtration and washed several times with methanol.

2.4. Transformation of hydroxyl end-groups of PLA into carboxyl end-groups

Hydroxyl groups containing PLAs: BHPA-PLA and EG-PLA were esterified using 1.3 excess of SA and 1.3 excess of DABCO in respect to