

Synthesis of poly(alkylene succinate) biodegradable polyesters I. Mathematical modelling of the esterification reaction

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Received 19 January 2006; received in revised form 13 April 2006; accepted 13 April 2006

Available online 18 May 2006

Abstract

Synthesis of three biodegradable aliphatic polyesters, namely poly(ethylene succinate), poly(propylene succinate) and poly(butylene succinate) is presented using the appropriate diols and succinic acid in the presence of tetrabutoxytitanium as catalyst. A theoretical mathematical model for the esterification reaction, based on the functional group approach, is developed and applied successfully in the simulation of all experimental data. Values for the kinetic rate constants are proposed for different catalyst molar ratios and comonomer chemical structure. It was found that the presence of the metal catalyst used leads to a poor activity of self-catalyzed acid and the main kinetic rate constant of the esterification reaction correlates well with the square root of the catalyst concentration. Different glycols do not influence much the number average degree of polymerization (NADP) values of the oligomers produced, even though they slightly affect esterification rates in the order BG > PG > EG. In contrast, these values are affected by the amount of catalyst, with larger catalyst molar ratio giving polymer with bigger average molecular weight. These results were verified from measurements of the final polyester average molecular weight obtained at different polycondensation temperatures. Finally, from theoretical simulation results it was found that although higher initial ratios of glycol to succinic acid are useful to increase the esterification rate, they lower the NADP of the oligomers formed at a fixed conversion of acid end groups.

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Keywords: Aliphatic polyesters; Biodegradable polymers; Mathematical modelling

1. Introduction

In recent years, biodegradable polymers have attracted considerable attention as green materials and biomaterials in pharmaceutical, medical and biomedical engineering applications, including drug delivery systems, artificial implants and functional materials in tissue engineering. Among synthetic polymers, aliphatic polyesters have attracted considerable attention as they combine the features of biodegradability, biocompatibility and physical or chemical properties comparable with many traditional and non-biodegradable polymers such as low-density polyethylene (LDPE) and polypropylene (PP). Biodegradable final products made from these polymers find a variety of end-uses especially as films for packaging and in agricultural applications [1–3].

Carothers first studied the synthesis of aliphatic polyesters by polycondensation reactions of diols with different

dicarboxylic acids or their esters back in 1930s [4]. However, the low melting points of the most produced polyesters in combinations with the difficulty to obtain high molecular weight materials, has prevented their usage for long-time. High molecular weight polyesters are an essential request for producing materials with appropriate processability and acceptant mechanical properties capable for producing fibers, bottles, films etc. Techniques like solid-state polycondensation that used in other polyesters like poly(ethylene terephthalate) (PET) are not possible to be implementing due to the low melting point of aliphatic polyesters, which makes very difficult the removal of by-products formed during polycondensation [5].

In polyester preparation, it is known that reaction kinetics are mostly affected by the monomer(s) chemical structure, type and amount of catalyst used, polymerization temperature and reaction time [6–9]. However, an extensive and more detailed study about synthesis of aliphatic polyesters and the dependence of molecular weight on several parameters has not been reported so far in the literature. To this direction, three polyesters of succinic acid were prepared by using ethylene, propylene and butylene glycols by the two-stage melt polycondensation method, esterification and polycondensation.

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The advantage of these polyesters is that despite of their low melting point they have very high thermal stability (decomposition temperature higher than 400 °C), which is similar to aromatic polyesters [10–12]. Comparative biodegradability studies, as well as the crystallization and melting behavior of the three polyesters, namely, poly(ethylene succinate) (PESu), poly(propylene succinate) (PPSu) and poly(butylene succinate) (PBSu) have already been carried out in our laboratory [8,13]. It should be noticed that PPSu synthesis has been reported only recently [14] due to difficulties encountered in the production of one of its comonomers (1,3-propanediol) in sufficient quantity and purity. Thus, available literature data about its synthesis and characterization are limited [8].

Moreover, concerning the theoretical modelling of the polyesterification reaction, although it is well-known for about 50 years since the work of Flory [15], the models published in literature on the direct esterification for the poly(alkylene succinates) production are very limited. In fact, to our knowledge, only one work dealing with modelling of the PBSu reaction has been published [16]. The Flory's self-catalyzed reaction model was used for unanalyzed reactions, together with a new complex model suitable for catalyzed esterification. The ability of the diacid used to act as a self-catalyst was addressed there [16]. Therefore, the aim of this work is to develop a theoretical mathematical model to predict the kinetics of the esterification reaction of the three poly(alkylene succinates) (PESu, PPSu and PBSu). The model is based on the functional group analysis, which had originally developed for the PET synthesis by Kang et al. [17,18] and extended by our group in the production of poly(propylene terephthalate) [19]. The effect of the catalyst molar ratio, monomer chemical structure and glycol/acid molar ratio on the esterification kinetics is elucidated. Finally, some results on the effect of the polycondensation temperature on the average molecular weight of the polyesters produced are presented.

2. Experimental

2.1. Materials

Succinic acid (purum 99%), ethylene glycol (purum 99%) and butylene glycol (purum 99%) were purchased from Aldrich Chemical Co. 1,3-Propanediol (CAS Number: 504-63-2, Purity: >99,7%) was kindly supplied by Du Pont de Nemours Co. Tetrabutoxy-titanium (TBT) used as catalyst was analytical grade and purchased from Aldrich Chemical Co. Polyphosphoric acid (PPA) used as heat stabilizer was supplied from Fluka. All other materials and solvents used for the analytical methods were of analytical grade.

2.2. Synthesis of polyesters

Synthesis of aliphatic polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [19]. In brief, the proper amount of succinic acid (0.55 mol) and appropriate

glycols (ethylene glycol, 1,3-propanediol and butylene glycol) in a molar ratio 1/1.1 and the catalyst TBT (3×10^{-4} mol TBT/mol SA) were charged into the reaction tube of the polycondensation apparatus [20]. TBT was selected as a proper catalyst leading to high reaction rates as it was observed in poly(propylene terephthalate) esterification [19]. The apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture was heated at 190 °C under argon atmosphere and stirring at a constant speed (500 rpm) was applied. This first step (esterification) is considered to complete after the collection of almost the theoretical amount of H₂O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. In order to ensure that all glycol vaporized totally returned to the reactor, in the side condenser a closed tube was used containing water, as it was described in the apparatus used by Günther and Zachmann [21]. This tube acts as a stopper, entrapping the glycol while the volatile water can pass and be removed from the reactor.

In the case of PPSu two additional catalyst concentrations, namely 1.5×10^{-4} and 6×10^{-4} mol TBT/mol SA were used in order to study the effect of catalyst amount on esterification and polycondensation reactions.

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol SA), which is believed that prevents side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period time of about 30 min, to avoid excessive foaming and to minimise oligomer sublimation, which is a potential problem during the melt polycondensation. For each polyester prepared several polycondensation temperatures were used such as 140, 170, 200, 230 and 250 °C while stirring speed was slowly increased to 720 rpm. The polycondensation reaction time was always kept constant at 1 h and afterwards the polyesters maintained at room temperature in order to be cooled.

2.3. Measurements

2.3.1. Intrinsic viscosity

Intrinsic viscosity $[\eta]$ measurements were performed, by using an Ubbelohde viscometer at 25 °C in chloroform. All polyesters were dissolved at room temperature in order to prepare solutions 1 wt% and filtered through a disposable membrane filter 0.2 μm (Teflon). Intrinsic viscosity was calculated after the Solomon–Ciuta equation [22]

$$[\eta] = \left[2 \left\{ \frac{t/t_0}{\ln(t/t_0)} - 1 \right\} \right]^{1/2} / c \quad (1)$$

where c is the concentration of the solution; t , the flow time of solution and t_0 the flow time of pure solvent.

2.3.2. Gel permeation chromatography (GPC)

GPC analysis was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastraygel (10^3 , 10^4 , 10^5 Å) columns in series. CHCl₃ was used as the eluent (1 ml/min) and the measurements were

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