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# Synthesis, characterization and thermal degradation mechanism of three poly(alkylene adipate)s: Comparative study

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**Abstract**

Three high molecular weight aliphatic polyesters derived from adipic acid and the appropriate diol – poly(ethylene adipate) (PEAd), poly(propylene adipate) (PPAd) and poly(butylene adipate) (PBAd) – were prepared by two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. Intrinsic viscosities, GPC, DSC, NMR and carboxylic end-group measurements were used for their characterization. Mechanical properties of the prepared polyesters showed that PPAd has similar tensile strength to low-density polyethylene while PEAd and PBAd are much higher. From TGA analysis it was found that PEAd and PPAd have lower thermal stability than poly (butylene adipate) (PBAd). The decomposition kinetic parameters of all polyesters were calculated while the activation energies were estimated using the Ozawa, Flynn and Wall (OFW) and Friedman methods. Thermal degradation of PEAd was found to be satisfactorily described by one mechanism, with activation energy 153 kJ/mol, while that of PPAd and PBAd by two mechanisms having different activation energies: the first corresponding to a small mass loss with activation energies 121 and 185 kJ/mol for PPAd and PBAd, respectively, while the second is attributed to the main decomposition mechanism, where substantial mass loss takes place, with activation energies 157 and 217 kJ/mol, respectively.


*Keywords:* Biodegradable polymer; Poly(alkylene adipate)s; Thermal degradation; Thermogravimetry

## 1. Introduction

Environmental pollution by synthetic polymers, especially in developed countries, is continuously increasing to dangerous proportions and for this reason there is a growing demand for biodegradable polymers as a solution to solid waste management. 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 gained considerable attention as they combine features of biodegradability, biocompatibility and present 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 [1–7].

Aliphatic polyesters, derived from aliphatic diols and dicarboxylic acids, are considered to be the most preferable among a number of biodegradable polymers for ecological reasons due to their good balance between physical properties and cost. Carothers first studied the synthesis of aliphatic polyesters by polycondensation reactions of diols with different dicarboxylic acids or their esters, in the 1930s [8]. However, the low melting point temperatures of most produced polyesters, in combination with the difficulty of obtaining high molecular weight materials, has prevented their usage for a long time. High molecular weight polyesters are an essential

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request for the production of materials with appropriate processability and acceptable mechanical properties, like fibres, bottles, films, etc. Techniques like solid-state polycondensation that are used for aromatic polyesters, e.g. poly(ethylene terephthalate) (PET), cannot be implemented due to the low melting points of aliphatic polyesters, which render the removal of by-products formed during polycondensation very difficult [9].

In our previous study a theoretical mathematical model for the esterification reaction of aliphatic acids with different diols, based on the functional group approach, has been developed and applied successfully to predict the reaction kinetics in aliphatic polyesters like poly(alkylene succinate)s [10]. It was found that high molecular weight aliphatic polyesters can be prepared using the appropriate amount of metal catalyst and monomer molar ratio. The metal catalyst used (tetrabutyl titanate) leads to a poor activity of self-catalysed acid and the main kinetic rate constant of the esterification reaction correlates well with the square root of the catalyst concentration. Moreover, different glycols do not significantly influence the number average degree of polymerization values of the oligomers produced during the esterification step, as it was found that it can have a slight effect on esterification rates in the order BG > PG > EG (butylene glycol, propylene glycol, ethylene glycol). On the contrary, these values are affected by the amount of catalyst used, a larger catalyst molar ratio leading to a polymer with a larger average molecular weight. Additionally, the polycondensation temperature is a critical parameter regarding the molecular weight achieved as well as the thermal stability of the final polyester [11].

In the present work three aliphatic polyesters, namely poly(ethylene adipate) (PEAd), poly(propylene adipate) (PPAd) and poly(butylene adipate) (PBAd) were synthesized in order to examine comparatively their molecular properties and their kinetic decomposition parameters. The polyester PPAd is prepared for the first time and characterized due to the difficulty of producing 1,3-propanediol in the past with high purity, capable of polymerization. Additionally, their crystallization and melting behavior, from the amorphous phase and for a specific rate, were registered. Although PEAd and PBAd, which are commercially available nowadays, have been studied extensively concerning their biodegradability and miscibility with other polymers [12–15] as well as their crystallization thermokinetics [16–20], there is no reported work so far in the literature about their thermal decomposition, while limited relative work has been reported for PBAd ionomers [14]. Consequently the present study is focused mainly on the thermal decomposition of these polyesters and on the evaluation of their decomposition mechanism.

### 1.1. Kinetic methods

Kinetic information can be extracted from dynamic experiments by means of various methods. For non-isothermal measurements at constant heating rate $\beta = dT/dt$, that is:

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

where $f(\alpha)$ is a function of the conversion depending on the mechanism of the degradation reaction, $\alpha$ being the degree of conversion of the mass loss, $A$ the pre-exponential factor, $E$ the activation energy, $T$ the absolute temperature, and $R$ the gas constant.

The activation energy $E$ can be calculated by various methods. In the present work two well established methods are used. The first method, the isoconversional method of Ozawa, Flynn and Wall (OFW) [21,22] is in fact, a "model free" method which assumes that the conversion function $f(\alpha)$ does not change with the alteration of the heating rate for all values of $\alpha$. It involves measuring of the temperatures corresponding to fixed values of $\alpha$ from experiments at different heating rates $\beta$. Therefore, plotting $\ln(\beta)$ against $1/T$ in the form of

$$\ln(\beta) = \ln[Af(\alpha)/(d\alpha/dT)] - E/RT \quad (2)$$

should give straight lines and their slopes are directly proportional to the activation energies ($-E/R$). If the determined activation energy is the same for the various values of $\alpha$, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of $E$ with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [23]. These complications are significant, especially in the case when the total reaction involves competitive mechanisms.

The second method is also an isoconversional one. Friedman [24] proposed the use of the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature, in the form of

$$\ln(d\alpha/dT) = \ln(A/\beta) + \ln(f(\alpha)) - E/RT \quad (3)$$

It is obvious from Eq. (2) that if the function $f(\alpha)$ is constant for a particular value of $\alpha$, then the sum $\ln(f(\alpha)) + \ln A/\beta$ is also constant. By plotting $\ln(d\alpha/dT)$ against $1/T$, the value of $-E/R$ for a given value of $\alpha$ can be directly obtained. Using this equation, it is possible to obtain values for $E$ over a wide range of conversions.

## 2. Experimental

### 2.1. Materials

Adipic acid (AdA) (purum 99+%) was purchased from Aldrich Chemical Co. 1,3-Propanediol (1,3-PDA) (CAS number: 504-63-2, purity: > 99.7%) was kindly supplied by Du Pont de Nemours Co. Ethylene glycol (EG) (purum 99%) and butylene glycol (BG) (purum 99%) were purchased from Aldrich Chemical Co. Tetrabutyl titanate (TBT), used as catalyst, was of analytical grade and was purchased from Aldrich Chemical Co. Polyphosphoric acid (PPA) used as a heat