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# Studies on the enzymatic hydrolysis of polyesters. II. Aliphatic–aromatic copolyesters

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**Abstract**

The dependence of the enzymatic degradation of aliphatic–aromatic copolyesters on the polymer structure has been investigated. A number of defined model copolyesters containing terephthalate units as aromatic component were synthesized. The model polymers included random copolyesters, block copolyesters and also strictly alternating copolyesters, which were made from especially synthesized and purified pre-building blocks. The biodegradability was evaluated applying a laboratory degradation test under well-defined conditions with a lipase from *Pseudomonas* sp.

It could clearly be proven that the selectivity of the lipase concerning the aliphatic or aromatic environment near the ester bonds is not the predominant factor controlling the biodegradability of the copolyesters. As already described for aliphatic homo polyesters the biodegradation rate of the copolyesters is mainly controlled by the chain mobility of the polymers, being correlated with the difference between the melting point of the polyester and the degradation temperature. The presence of longer aliphatic domains, e.g., in block copolyesters does not facilitate the hydrolytic attack by the lipase, but longer aromatic sequences, which control the melting point of the crystalline regions, reduce the biodegradation rate. The concept of chain mobility seems to be a quite universal way to describe and predict the biodegradation rate of synthetic polyesters, independent on their composition or microstructure.


*Keywords:* Biodegradable polymers; Aliphatic–aromatic copolyesters; Lipase; Hydrolysis

## 1. Introduction

Plastics have been developed as versatile materials with excellent properties for many applications. However, in some cases the high persistence of plastics in the environment is regarded as a problem (e.g. increasing plastic waste) and attempts have been made to make plastics controlled susceptible to microbes – to design biodegradable plastics. Besides some natural polymers (e.g. PHB) mainly synthetic aliphatic polyesters were used in the past to produce biodegradable plastics (e.g. poly(ε-caprolactone), PCL).

The degradation of polyesters by microorganisms is initiated by extracellular hydrolases, which are secreted by the organisms to reduce the molar mass of the polymeric substrate and to make it bioavailable. While for the natural polyhydroxyalkanoates (PHB, etc.) a special group of extracellular hydrolases has been developed by nature (called polyhydroxy-depolymerases) [1], it was first demonstrated by Tokiwa and Suzuki that synthetic polyesters also can be attacked by hydrolases (lipases) [2]. A number of other investigations

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on the degradation of synthetic polyesters by hydrolases have been published up to now. There is strong evidence, that microbial biodegradation of synthetic polyesters in nature is also initially caused by hydrolases secreted from the microorganisms. For PCL, polyester-degrading microorganisms were isolated and the corresponding extracellular enzymes were identified as hydrolases (cutinases, lipases) [3–7]. For aliphatic–aromatic copolyesters a thermophilic actinomycete (*Thermobifida fusca*) recently could be isolated and the degrading enzyme was characterized to be also a lipase-like hydrolase [8,9]. Other publications also confirmed that such copolyesters can be attacked by lipases [10–13].

To understand the differences in biodegradability of polyesters of different structure many controlling factors, such as molar mass, hydrophobicity/hydrophilicity or selectivity of the enzymes concerning the microstructure of the ester bond vicinity have been discussed in the literature [14,15]

Very early Tokiwa et al. found a correlation of the enzymatic degradability of various aliphatic polyesters with their melting point, but a detailed interpretation of this observation was not given at that time [16]. Recently, we could demonstrate that the dominating effect controlling biodegradability of aliphatic polyesters is the mobility of the polymer chains, which is correlated with the difference of the melting temperature of the crystalline fraction of the polyester and the temperature at which the degradation takes place [17].

While the biological susceptibility of many aliphatic polyesters has been known for many years, aromatic polyesters such as polyethylene terephthalate (PET) or polybutylene terephthalate are regarded as non-biodegradable [18]. Due to the fact, that many biodegradable aliphatic polyesters, e.g. poly(ε-caprolactone) (PCL), exhibit only limited properties which are important for many applications (e.g. PCL has a melting temperature of only approx. 60 °C), the attempt was made to combine the biodegradability of aliphatic polyesters with the good material performance of aromatic polyesters in novel aliphatic–aromatic copolyesters [19–21]. Equivalent commercial materials are already available at the market, e.g. under the trade name Ecoflex® (BASF, Germany).

With regard to the high commercial potential of aliphatic–aromatic copolyesters and their interesting properties, the question arose, if the concept of the chain mobility controlling the biodegradability is also applicable to copolyesters. These polymers exhibit a much more complex micro-structure, since the presence of different monomers cause domains of different structural characteristics side by side in one polymer chain. For the investigation presented here, a number of defined and well characterized aliphatic–aromatic copolyesters (based on terephthalic acid as aromatic component) were synthesized and applied in laboratory degradation tests of high reproducibility using a lipase as biological active agent.

## 2. Material and methods

### 2.1. Enzymes

For the degradation experiments a commercially available lipase from *Pseudomonas* sp. (PsL) was used (Sigma, Germany). The enzyme formulation (53.6% protein content) was dissolved in 0.9% NaCl solution to a concentration of 4 mg/cm$^3$ and stored at −20 °C.

### 2.2. Polymers

#### 2.2.1. Aliphatic polyesters

Aliphatic polyesters were synthesized as described by Witt et al. [22] from 1,4-butanediol and the corresponding dicarboxylic acids using *p*-toluene sulfonic acid as catalyst or, if available, from the dicarboxylic dimethyl esters with tetra-isopropyl orthotitanate/triphenyl phosphate as catalyst.

#### 2.2.2. Random aliphatic–aromatic copolyesters

Random copolyesters were synthesized by melt polycondensation from terephthalic acid dimethyl ester, the corresponding aliphatic dicarboxylic acid methyl ester and 1,4-butanediol (equimolar to the aromatic dicarboxylic acid components) using tetra-isopropyl orthotitanate/triphenyl phosphate (0.02 weight% each) as catalysts. 1,4-Butanediol was used in a 5% molar excess which was evaporated during the condensation process.

#### 2.2.3. Alternating aliphatic–aromatic copolyesters

Alternating copolyesters were synthesized from aliphatic dicarboxylic acids and aromatic oligoester diols by solution polycondensation in toluene at 111 °C using 1 weight% *p*-toluene sulphonic acid as catalyst. The aromatic oligoester diol (0.0258 mol) and the aliphatic dicarboxylic acid (0.0258 mol) were dissolved together with the catalyst in 70 ml toluene heated to boiling temperature. The water formed during the esterification was trapped in a water separator. The remaining 10% of the reaction water was extracted from the mixture by using molecular sieve in an extractor. The reaction time was 12–18 h. The product was then purified by precipitation in a 10-fold amount of methanol and dried at 30 °C under vacuum.

To produce the alternating polyester $BTX_{altern.}$ 50:50 the oligoester diol BTB and for $BTX_{altern.}$ 33:67 the oligoester diol BTBTB were used as pre-monomers along with different aliphatic dicarboxylic acids.