STUDY ON BIODEGRADABLE AROMATIC/ALIPHATIC COPOLYESTERS

Yiwang Chen[*], Licheng Tan, Lie Chen, Yan Yang and Xiaofeng Wang

Institute of Polymer Materials, School of Materials Science and Engineering,
Nanchang University, Nanchang 330031, People's Republic of China.
E-mail: ywchen@ncu.edu.cn

Abstract - Progress on biodegradable aromatic/aliphatic copolyesters based on aliphatic and aromatic diacids, diols and ester monomers was reviewed. The aromatic/aliphatic copolyesters combined excellent mechanical properties with biodegradability. Physical properties and biodegradability of copolyesters varied with chain length of the aliphatic polyester segment and atacticity of copolyesters. The processability of copolyesters could be improved significantly after incorporating a stiff chain segment through copolymerization of aliphatic polyesters with an aromatic liquid crystal element. The aromatic/aliphatic copolyesters as a new type of biodegradable materials could replace some general plastics in certain applications, namely biomedical and environmental friendly fields.
Keywords: Aromatic/aliphatic copolyester; Biodegradation; Polycondensation; Polyester.

INTRODUCTION

In the world today, increasing volumes of plastics are manufactured and used for various applications because of their versatility and ability to be mass-produced. However, they usually do not naturally decompose, and they are considered to cause some environmental problems. Hydrolytic and enzymatic degradation of the polymeric backbone was investigated to reduce the ecological problems related to plastic recycling. In addition, such an investigation was also directed toward biomedical application of polymeric materials because there is a significant potentiality of polymers as drug-releasing implants, as bioabsorbable surgical sutures, or as the absorbable component in selectively biodegradable vascular grafts (Kumar et al., 1986; Vaiionpaa et al., 1989; Zhang et al., 1993). Various synthetic biodegradable and biocompatible polymers have been developed to meet certain specific requirements for such kinds of biomaterials. There are numerous studies to understand the relationships between the structure, morphology, mechanical properties, degradability, and processability to meet various requirements in other aspects of reconstructive surgery (Younes and Cohn, 1987; Li et al., 1990). Except for the critical influence of the chemical constitution, any alternation in crystallinity and morphology would result in a big change of degradation behaviors of polymers since the general degradation mechanism is of hydrolytic nature and proceeds through the two phases in those semicrystalline polymers. However, most conventional biodegradable polymers based on aliphatic polyesters, such as poly(glyco1ic acid) (PGA), usually have a lower T_g and a higher T_m, so their performance and processability could not sometimes match the requirements, even though they have quite good biodegradability.

For this reason, many scientists have worked to develop new biodegradable polymers; some of these biodegradable polymers have been commercialized. A wide variety of chemical or physical strategies, including the copolymerization, polymer blend, and

---
*To whom correspondence should be addressed

composite or cross-linking networks, have been explored to match individual requirements (Zhu et al., 1990; Storey et al., 1993; Simone et al., 1992). Blending and copolymerization techniques have been tried to obtain biodegradable polymers with improved properties (Yoshie et al., 1995; Gonsalves et al., 1992; Kim et al., 1995). Modified starch was blended with low-density polyethylene as a substitute for nonbiodegradable packaging films. Poly(hydroxybutyrate) (PHB) and poly(lactic acid) (PLA) were also blended with commercial polymers to cover their mechanical weaknesses. The blend of two or more polyester components can be changed into either block or random copolyesters depending upon the degree of the transesterification reaction at an elevated temperature in the presence of an adequate catalyst (Montando et al., 1992). Using this method, the segment of biodegradable polyesters can be introduced into nonbiodegradable polyesters, and the average sequence length of each unit can be controlled. However, the high price and weak properties of these polymers prevent them from being used in diverse applications.

Aromatic polyesters have excellent physical and mechanical properties compared to aliphatic polyesters, but their strong resistance to bacterial or fungal attack results in low degradability under the environmental conditions. Poly(ethylene terephthalate) (PET), a linear thermoplastic polyester, known as one of the major synthetic fibers, has become an important commercial material including various applications, such as, soft-drink bottles, photographic films, recording audio and video tapes, films for good packaging, and insulating material for capacitors. Currently, the overall world consumption of PET amounts to about 13 million tons. In view of such a large consumption, the effective utilization of PET waste is of considerable commercial and technological significance.

On the other hand, aliphatic polyesters have attracted many workers' research interest for biodegradable polymers, and several research studies have been reported. Poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), poly(L-lactide), and poly(hydroxybutyrate) are typical examples of biodegradable polymers. However, aliphatic polyesters have poor physical and mechanical properties.

Therefore, in developing biodegradable polymers, it is important to design polymers having both satisfactory mechanical properties and biodegradability. Aiming at this target, some researchers attempted to synthesize copolyesters consisting of aliphatic and aromatic units. The scope of this review is a comprehensive summary of all research efforts on the synthesis and design of biodegradable aromatic/aliphatic copolyesters. The author will attempt to arrange a structural classification of biodegradable aromatic/aliphatic copolyesters in terms of the liquid-crystallinity, such as biodegradable non-liquid-crystalline aromatic/aliphatic copolyesters and biodegradable liquid-crystalline aromatic/aliphatic copolyesters. In addition, the currently available results about the biological degradation of polymers containing aromatic constituents will be reviewed and conclusively evaluated.

Biodegradable Non-Liquid-Crystalline Aromatic/ Aliphatic Copolyesters

In 1954, to reduce the crystallinity of poly(ethylene terephthalate) and increase the hydrophilicity to improve dyeability with hydrophilic dyes, biodegradable copolyesters PEO/PET, as shown in Figure 1, were synthesized from polyethylene oxide (PEO) and poly(ethylene terephthalate) (PET) (Coleman, 1954). The copolyester PEO/PET was observed to degrade when implanted into biological tissue. With increasing PEO contents to produce surfaces of increasing energy, zero interfacial energy between an implant and the adjacent biological connective tissue in sheep was produced. The collagenous capsule formed around the implant approached the implant surface ever more closely as the PEO content increased. It was observed that the implants were unstable and fragmented over an 8 week period in subcutaneous tissue (Gilding and Reed, 1979). PEO/PET copolymers were synthesized by transesterification from di(2-hydroxyethyl) terephthalate (DET) monomer and poly(ethylene glycol) PEG using antimony trioxide (Sb_2O_3) and phosphoric acid as catalysts (Reed and Gilding, 1981). The biodegradability and biocompatibility of the copolyesters *in vitro* and *in vivo* were studied.

A series of poly(ether/ester)s derived from dimethyl terephthalate, 1,4-butanediol, 2-butyne-1,4-diol and α-hydro-ω-hydroxypoly(oxyethylene) was synthesized using $Ti(OC_4H_9)_4$ as catalyst (Gogeva and Fakirov, 1990). Data from differential scanning calorimetry suggested a three-phase structure, two amorphous and one crystalline one. Small-angle X-ray studies of the annealed samples revealed a strong tendency to phase separation with increasing annealing temperature. PEGT/PBT was synthesized from dimethyl terephthalate, 1,4-butanediol and α-hydro-ω-hydroxypoly(oxyethylene) (PEG) (Fakirov and Gogeva, 1990). PEGT/PBT block copoly(ether

ester)s were prepared by a two-step polymerization in the presence of titanium tetrabutoxide as catalyst and Irganox 1330 as antioxidant, as shown in Figure 2. The transesterification of PEG, dimethyl terephthalate (DMT) and 1,4-butanediol was carried out under a nitrogen atmosphere at 180°C. After 2 h, the pressure was slowly decreased from 1000 to 0.1 mbar to allow polycondensation. Simultaneously, the temperature was increased from 180 to 240°C. The

differential scanning calorimetry measurements suggested the existence of a three-phase morphology, two amorphous phases for both polyether and polyester segments, and a crystalline phase for the polyester segment. The tensile parameters of the studied polymers were similar to those of available commercial products (Polyactive®) based on poly(butylenes terephthalate) and poly (tetrahydrofuran) (Fakirov and Gogeva, 1990).
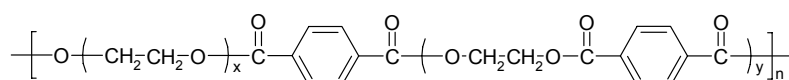

Figure 1: The chemical structure of PEO/PET copolyester
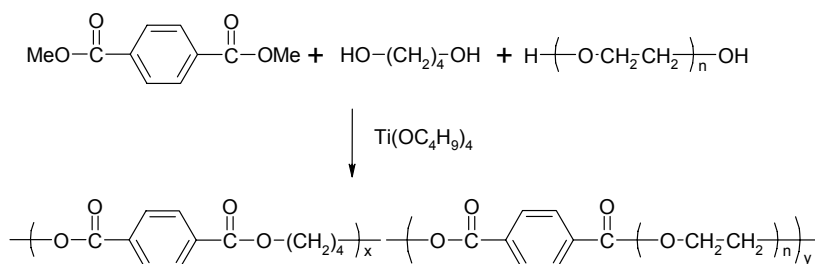

Figure 2: The synthetic scheme of PEGT/PBT block copoly(ether ester)s

First developed for textile applications (Hoeschele, 1976), PEGT/PBT copolymers have been shown to possess interesting physical properties for medical use as well (Wagener, 1982). In vitro, epidermal keratinocytes, dermal fibroblasts (Beumer et al., 1993), skeletal muscle cells and chondrocytes (Papadaki et al., 2001) showed good adhesion and proliferation on PEGT/PBT copolymer films. *In vivo* no adverse tissue reactions were observed after subcutaneous implantation in rats (Bakker et al.,1990; Beumer et al., 1994). Degradation of PEGT/PBT segmented copolymers *in vivo* has also been reported (Beumer. et al., 1994). *In vivo*, two degradation pathways of these copolymers are expected to take place. The first route involves hydrolysis of ester bonds in the PBT part or of ester bonds connecting PEG segments and terephthalate units. The influence of copolymer composition on the physical properties and the degradation behavior of thermoplastic elastomers based on poly(ethylene oxide) and poly(butylenes terephthalate) segments

was investigated (Deschamps et al., 2001). PEGT/PBT copolymers are microphase separated. Phase separation in the system is enhanced by increasing the molecular weight of the starting poly(ethylene glycol) (PEG) or by increasing the PBT content. The mechanical properties, swelling characteristics and degradation rates of the copolymers are influenced by the phase separation. The *in vitro* degradation of PEGT/PBT copolymers occurs via hydrolysis and oxidation. In both cases, degradation is more rapid for copolymers with high contents of PEO. Deterioration of copolymer films takes place when the films are exposed to light in the absence of antioxidant. In preventing oxidation under daylight conditions, Irganox 1330 turned out to be a more efficient antioxidant for the copolymers than vitamin E.

Poly(butylene terephthalate)/poly(ε-caprolactone) copolyesters were prepared by blending poly(butylene terephthalate) (PBT) and poly(ε-caprolactone) (PCL), followed transesterification at

257°C (Ma et al., 1997). A series of ethylene terephthalate ε-caprolactone copolyesters with different hard segment contents were synthesized, as shown in Figure 3 (Ma et al., 1998). First, dimethyl terephthalate (DMT), ethylene glycol (EG), and Zn(OAC)$_2$ were added into a nitrogen-purged reaction vessel, and the reactant mixture was heated to 170-220°C to process with transesterification and condensation. Then, ε-caprolactone (CL) monomer and Sb(OAC)$_3$ were added, thus carrying on ring-opening polymerization of the CL monomer (initiated by hydroxyl-terminated low-molecular-weight PET with the remaining EG) for about 2 h at the temperature of 170-180°C in an N$_2$ atmosphere. The last step was the condensation at a high degree of vacuum (<0.1 mmHg) at 260-270°C to ensure more complete conversion of monomer materials. The analysis by high-field ^{1}H NMR revealed that the transesterification between ethylene terephthalate and caprolactone segments during synthesis was unavoidable, so the copolyesters were segmented copolyesters with certain random properties, as shown by the specific chemical and sequence

structure and as conformed by their crystallization behavior.

Biodegradable copolyesters having aromatic rings (C$_6$H$_5$, C$_6$H$_5$CH$_2$) as side-chain residues, e.g., L-lactic acid (LA)/DL-mandelic acid (MA) and LA/L-3-phenyllactic acid (PheLA), were synthesized by direct copolycondensation without catalyst at 200°C (Figure 4) (Fukuzaki et al., 1990). The *in vivo* degradation pattern changed from a typical parabolic-type to an S-type with increasing aromatic hydroxyacid content in the copolyester and molecular weight of the copolyester.

A higher molecular weight processable polyester with bisphenol A terephthalate/isophthalate moieties and lactide moieties was prepared (Figure 5) (Haderlein et al., 1997). The combination of aliphatic and aromatic moieties was a promising concept for processable polyesters with potential sites for physiological degradation and improved mechanical properties. The molecular structure of the copolyesters prepared by melt condensation via an acid chloride route and incorporation of the lactide moieties by transesterification of an oligolactide was confirmed.
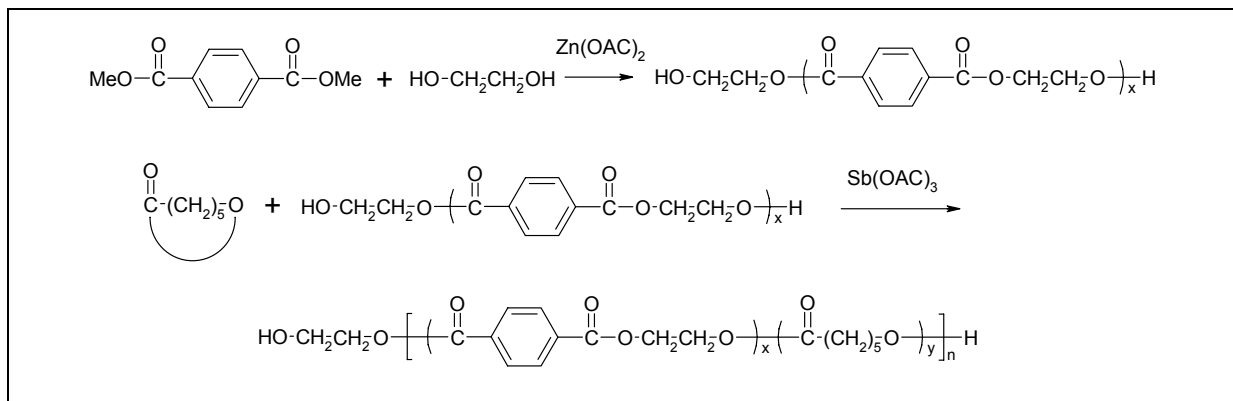

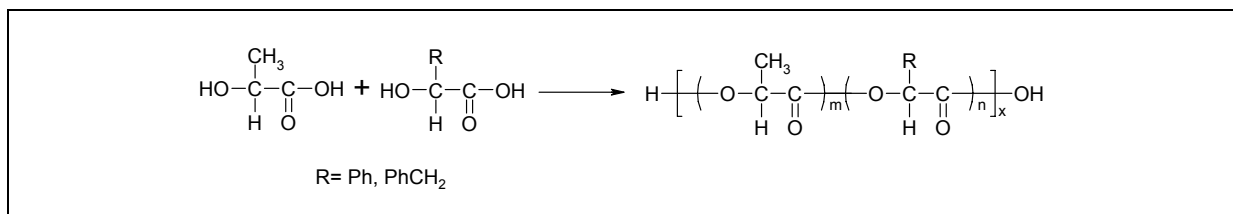
Figure 3: The synthetic scheme of PBT/PCL copolyesters

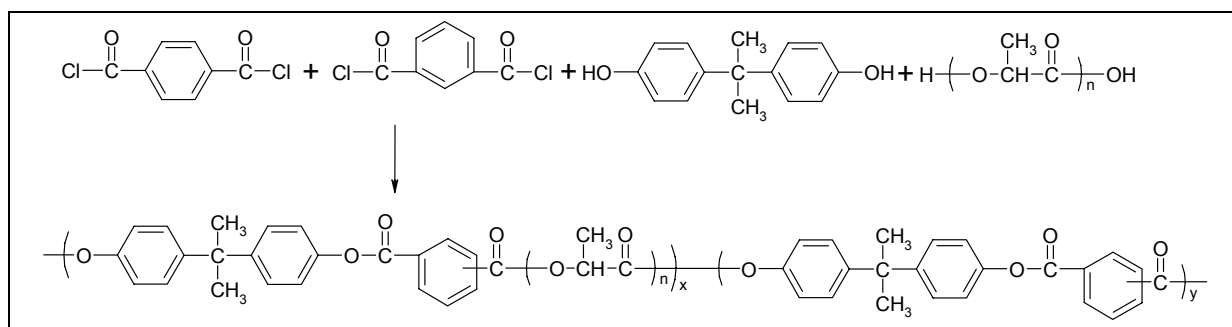**Figure 4:** The chemical structure of LA/PheLA copolyesters

Figure 5: The copolyester based on bisphenol A terephthalate/isophthalate and lactide

Poly(ethylene-1,4-cyclohexanedimethylene arylate) (arylate = terephthalate or naphthalate) copolyesters, as shown in Figure 6, were synthesized from bis(hydroxyethyl)arylate and bis (hydroxymethyl-cyclohexane)arylate by the melt polycondensation in the presence of metallic catalysts under nitrogen atmosphere for 4 h at a temperature of 245°C, followed by polymerization under 2 mm Hg for 50 min at a temperature of 290°C (Sun and Wang, 1999).

Biodegradable polyesters typically contain a high fraction of aliphatic ester groups because, for electronic reasons, derivatives of aliphatic carboxylic acids are several orders of magnitude more electrophilic than analogous derivatives of aromatic carboxylic acids. Therefore, polyesters derived from aromatic dicarboxylic acids are much less electrophilic and, thus, far less sensitive to hydrolysis than aliphatic polyesters, as evidenced by the stability of poly(ethylene terephthalate) (PET)-based textile fibers to washing or acid rain (Gilding and Reed, 1979). However, aromatic polyesters may possess higher melting temperature (T_m's) and better mechanical properties. Therefore, it is an attractive challenge to synthesize semialiphatic/semiaromatic copolyesters and determine if it is possible to optimize the properties in the direction of a satisfactory rate of biodegradation while retaining good mechanical properties. In this connection, it should be mentioned that BASF AG offers biodegradable copolyesters prepared by the transesterification of poly(butylenes terephthalate) (PBT) with adipic acid and 1,4-butane diol (Ecoflex[®]) (Witt et al., 1999; Witt et al., 1999). Random copolyesters of terephthalic acid (TA), aliphatic carboxylic acids (ADAs), and alkane diols are mainly or totally amorphous [with low glass-transition temperatures (T_g's)] and, thus, of limited usefulness as engineering plastics. Higher degrees of crystallinity and higher melting temperatures require longer blocks of PBT than those typical for random

sequences, but longer blocks of PBT are unfavorable for a satisfactory hydrolytic biodegradation. This situation prompted the study of the synthesis and crystallization behavior of copolyesters with alternating sequences of TA, ADAs, and 1,2-ethane diol or 1,4-butane diol. Alternating copolyesters of terephthalic acid, aliphatic dicarboxylic acids, and alkane diols, as shown in Figure 7, were prepared by the polycondensation of silylated bis(4-hydroxybutyl)terephthalate or silylated bis(4-hydroxyethyl)terephthalate with various aliphatic dicarboxylic acid dichlorides (Shaik et al., 2001). Silylation gave satisfactory molecular weights. The resulting copolyesters showed significantly higher rates of crystallization.

PTS/PBT copolyester with high molecular weight was synthesized from dimethyl succinate, dimethyl terephthalate, and butanediol by a conventional polycondensation technique (Zhang et al., 2002). The copolyester was blended with starch. The biodegradation of copolyesters and the blends of the copolyester and starch were traced using soil-burial and CO_2 release tests. The results show that the blends have good biodegradability. Biodegradable aliphatic-aromatic random copolyesters PBCST were synthesized by polycondensation from succinic acid (SA), dimethylterephthalate (DMT), 1,4-butanediol (BD), and 1,4-cyclohexane dimethanol (CHDM) in the presence of titanium tetraisopropoxide as catalyst (Ki and Park, 2001). The melting temperature decreased gradually as more CHDM was added, and no melting temperature was observed when more than 20% of CHDM was used. The introduction of CHDM improved the transparency of the samples even though it deteriorated the mechanical properties slightly. In the hydrolytic degradation, the samples having more succinic units in their main chain showed better degradability. Furthermore, the copolyesters containing much CHDM showed faster hydrolytic degradation because of their rich amorphous phase.

Poly(ethylene terephthalate)/copoly(succinic anhydride/ethylene oxide) copolymers, (PET/PES copolymers) were synthesized by the transreaction between poly(ethylene terephthalate) and copoly (succinic anhydride/ethylene oxide) (Figure 8) (Maeda et al., 2000). Most of the copolymers obtained were random copolymers. In the copolymers having high PET content, the melting points, due to the PET segment, were observed, although the fusion heats of the copolymers were small. The enzymatic hydrolyzability by a lipase from *Rhizopus arrhizus* and biodegradability by activated sludge of the copolymers decreased with an increase in PET content. When the sequence length of succinic acid unit in the copolymer was below 2, the hydrolyzability of the copolymers decreased considerably. The tensile strengths of the cast films prepared from the copolymers increased with an increase in PET content, whereas the elongations at break decreased.
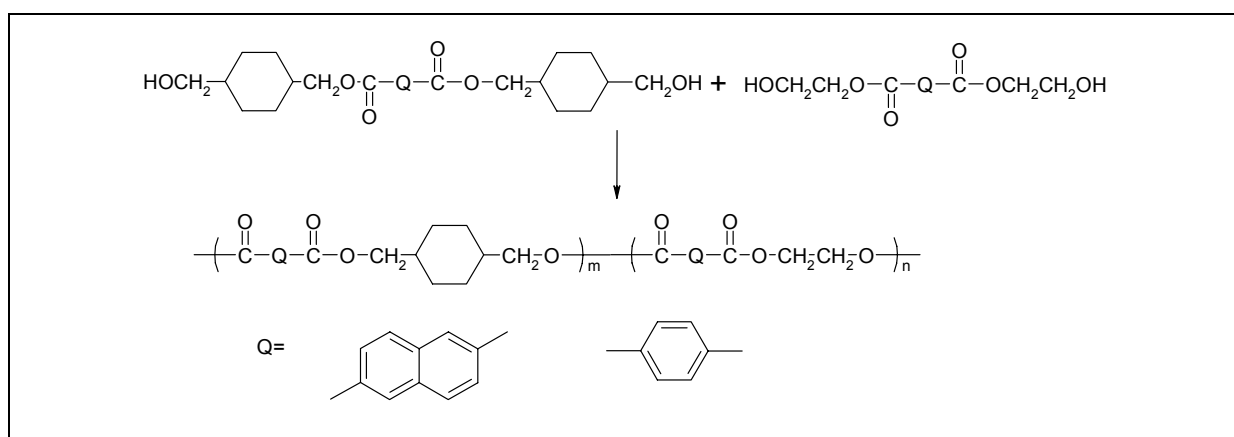

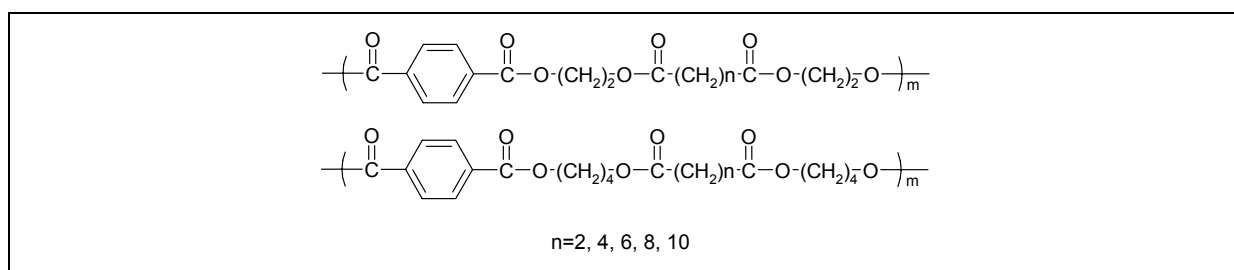**Figure 6:** The synthetic scheme of poly(ethylene-1,4-cyclohexanedimethylene arylate)s

Figure 7: Alternating copolyesters based on terephthalic acid, aliphatic dicarboxylic acids, and alkane diols
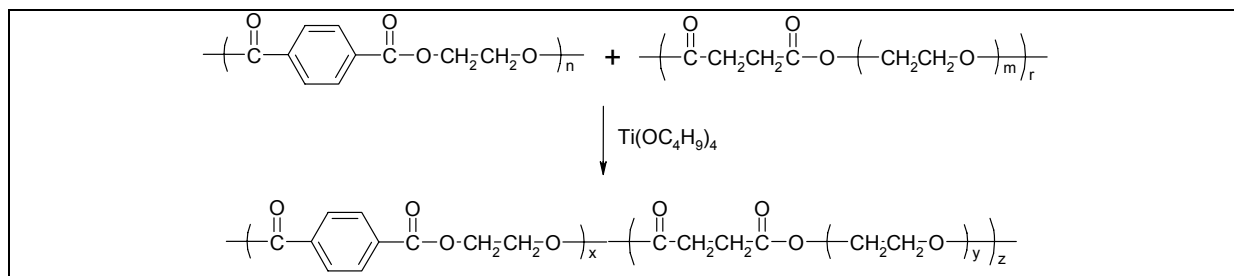

Figure 8: The synthetic scheme of PET/PES copolymers

A study of the microstructure of the copolyesters formed in the exchange reactions that occur during the melt mixing of poly(ethylene adipate) (PEA) and poly(ethylene terephthalate) (PET) was reported (Montaudo et al., 1992). Poly(butylenes adipate-co-succinate) (PBAS), an aliphatic polyester, is known for its excellent biodegradability, but its physical and mechanical properties are poor. To improve the physical properties, stiff aromatic rings were added to PBAS through transesterification with poly(ethylene terephthalate) (PET). The transesterification reaction was carried out at 280°C without a catalyst (Kim et al., 2004). A reduction of the melting temperature was observed for the copolyesters. The biodegradability of the copolyesters depends on the number of terephthalate units.

Reactive blending at 290°C of a series of mixtures of poly(ethylene terephthalate) (PET) and poly(1,4-butylene succinate) (PBS) led to the formation of block PET/PBS copolyesters (Kint et al., 2003). The block lengths of the resulting copolymers decreased with the severity of the treatment. The T_g, T_m and crystallinity of the copolymers decreased as the content in PBS and the degree of randomness increased. The elastic modulus and tensile strength of the copolymers decreased with the content of PBS, whereas, on the contrary, the elongation at break increased. The PET/PBS copolymers exhibited a pronounced hydrolytic degradability, which increased with the content in 1,4-butylene succinic units. Hydrolysis mainly occurred on the aliphatic ester groups.

A copolyester, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) (PBEST), was synthesized via direct polycondensation from three prepolymers of butylenes succinate, ethylene succinate and ethylene terephthalate (ET) (Deng et al., 2004). Compared to poly(butylene succinate-co-ethylene succinate) (PBES), PBEST has improved thermal properties such as higher T_m due to the incorporation of poly(ethylene terephthalate) units into the main chains of copolyesters, but very low crystallization speeds. The degradation test of copolyesters in a compost condition shows that the degradability of PBEST is a function of content of ET.

Poly(bis(hydroxyethyl)terephthalate-ethyl ortho-phosphorylate/terephthaloyl chloride) (Politerefate[TM]), as shown in Figure 9, was synthesized by introducing phosphoester into poly(ethylene terephthalate), and was applied in nerve guide conduit engineering and drug delivery (Wang et al., 2001; Zhao et al., 2003).
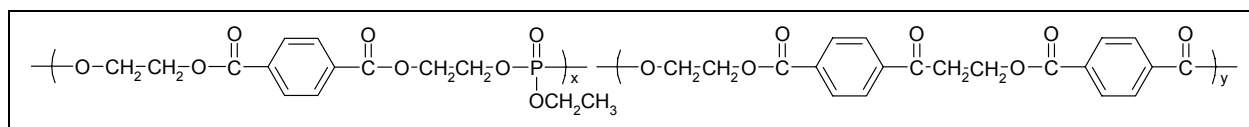

Figure 9: The chemical structure of Politerefate[TM]

Poly(ethylene terephthalate) (PET) was successfully modified by using biodegradable poly(lactic acid)(PLA) by solvent copolymerization, the weight loss of the products after hydrolytic degradation being up to 48.72% after 28 days in phosphate buffer solution of pH 7.2 at 60°C (Acar et al., 2006). Poly(vinyl chloride) (PVC) modified with biodegradable aliphatic polyester has a higher dehydrochlorination temperature and better thermooxidative stability (Andricic et al., 2006). Biodegradable ideal random copolymer poly(butylene adipate-co-terephthalate) (PBAT), with 44 mol% butylene terephthalate (BT), was melt-spun into fibers with take-up velocities up to 5 km/min. PBAT fiber showed well-developed PBT-like crystal structure, while its melting temperature (ca. 121°C) was over 100°C lower than that of PBT. Based on the quantitative analyses on the lattice spacing, the crystallinity and fraction of crystallizable BT sequences, the crystal structure of PBAT was characterized to be formed by mixed-crystallization of BT and butylene adipate (BA) units, where BA units were incorporated into the BT lattice. This mixed-crystal structure was found to undergo PBT-like reversible crystal modification with the application and removal of tensile stress. This crystal modification was found to occur in higher strain regions compared with that of PBT fibers (Shi et al., 2005; Shi et al., 2006).

New investigations of the effect of comonomer sequential structure on the thermal and crystallization behaviors and biodegradability have been implemented for biodegradable poly(butylene succinate-co-butylene terephthalate) (PBST). It was demonstrated that the synthesized copolyesters have random comonomer sequential structures with thermal and crystallization properties strongly dependent on their comonomer molar compositions (Li et al., 2006).

A series of biodegradable aliphatic/aromatic copolyesters, poly(butylene terephthalate)-co-

poly(butylene cyclohexanedicarboxylate)-b-poly (ethylene glycol) (PTCG), were prepared by a two-step melt polycondensation method. The decrease in mechanical strength was observed with an increase in poly(butylene cyclohexanedicarboxylate) (PBC) molar fraction. DSC results showed one melting point and two glass transition temperatures in all samples, and the melting temperature was found to go down gradually as more cyclohexanedicarboxylic acid (CHDA) was added. During the *in vitro* and *in vivo* degradation processes, erosion of the surface was dominant, as evidenced by scanning electron microscopic observations. The copolyesters containing many CHDA units had higher water uptake and faster degradation due to the much richer amorphous phase within them (Li et al., 2006).

Polymer blends of poly(tetramethylene succinate) (PTMS) and poly(butylene terephthalate) (PBT) were prepared by melt mixing. Transesterification reactions between both polyesters were promoted by the addition of zinc acetate as a catalyst. The process of transesterification is strongly influenced by the amount of catalyst and the initial blend composition. The copolymer structure changes from a block structure to a more random distribution of units along the chain. The block length decreases slightly with increasing amount of catalyst. The blends processed without catalyst are heterogeneous and show very poor mechanical properties due to their two-phase morphology. The impact strength of the blends could be markedly improved by the transesterification reaction (Wojciech et al., 2006).

Biodegradable Liquid-Crystalline Aromatic/ Aliphatic Copolyesters

Liquid crystalline (LC) polymer was developed to combine high mechanical and thermal properties with excellent processability. Several kinds of polymers like KEVLAR or VECTRA represent clear examples in this direction. For liquid crystalline polymers (most of them also belong to the polyester family), it is well-known that they usually possess excellent processability and self-reinforced mechanical strength due to the unique morphology of the highly oriented macromolecules (Ober et al., 1984).

However, based on previous knowledge, there is no synthetic biodegradable polymer that exhibits thermotropic behavior, although some synthetic polypeptides like poly(γ-benzyl L-glutamate) and cellulose derivatives are lyotropic. Therefore, current research is aimed at exploring the possibility of developing an easily-processable, biodegradable,

and/or biocompatible polymer with enhanced mechanical properties. The efforts for such a high-performance biodegradable polymer mainly involve molecular design and synthesis strategy. Accordingly, the expected biodegradable thermotropic liquid crystalline polymers should be composed of some aromatic polyester units as mesogenic segments and some aliphatic polyester units as both flexible spacer and biodegradable sites.

The polycondensation of glycolic acid (GA) and *p*-hydroxybenzoic acid (PHBA) did decrease the melting temperature of the copolyesters and also made them thermotropic (Figure 10) (Jin et al., 1994). However, owing to the poor copolycondensability of aliphatic α-hydroxy acid with the aromatic ones, its degree of polymerization is usually quite limited.

The alternative approach of polymerizing diethyl biphenyldicarboxylate and aliphatic diol with glycolic acid or polylactide failed to produce a very high molecular weight copolymer with satisfactory mechanical properties (Figure 11) (Jin et al., 1993). In this case, a higher polymerization temperature had been employed to increase the molecular weight of the growing chains. However, severe thermal decomposition could not be avoided.

High molecular weight main-chain thermotropic liquid crystalline terpolyesters with a biodegradable property based on *p*-hydroxybenzoic acid (PHBA), glycolic acid (GA), and the bridge comonomer 4-hydroxycinnamic acid (PHCA) were synthesized via a one-step melt copolycondensation process (Figure 12) (Jin et al., 1995). PHCA is selected as the comonomer with PHBA and GA to balance the liquid crystallinity and biodegradability for development of a biodegradable liquid crystalline copolyester. Another consideration for the use of PHCA as comonomer is that the double bond in the cinnamyl group could be used as the potential reactive site for a second-stage cross-linking reaction to produce an LC network. A random sequence distribution of the comonomeric units along the polymeric chains was produced. A single glass transition temperature at about 82°C and a broad endothermic transition with a maximum at 150°C were discerned. The nematic liquid crystallinity was confirmed from the characteristic textures under optical polarizing microscopy. The hydrophilicity was greatly improved due to the incorporation of GA segments. The copolymer degraded via a simple hydrolysis of the ester bonds of GA-rich segments, and the aromatic counterpart could also be involved in the hydrolysis. These degradations occurred predominantly in the amorphous or less aligned regions.
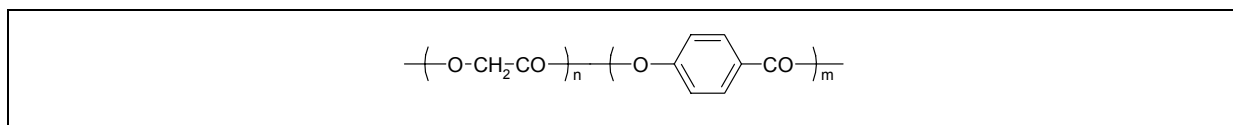
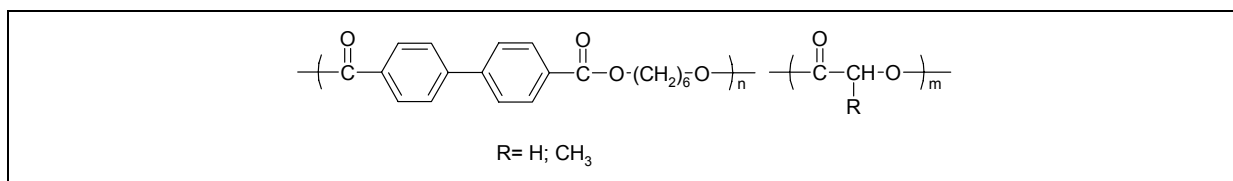**Figure 10:** The copolyester based on glycolic acid and *p*-hydroxybenzoic acid

R= H; CH$_3$

Figure 11: The copolyesters obtained from diethyl biphenyldicarboxylate
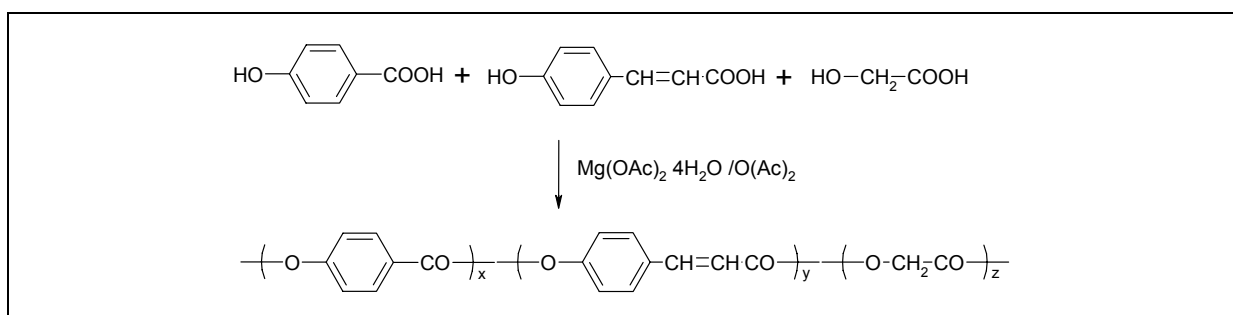and aliphatic diol with glycolic acid or polylactide

Figure 12: The copolyester based on *p*-hydroxybenzoic acid, glycolic acid and 4-hydroxycinnamic acid

The fact that aliphatic polyesters possess relatively flexible aliphatic main chains has the consequence that the glass transition temperatures (T_g's) are relatively low (-60 to 60°C) and that, in order to use the biodegradable polylactones as engineering plastics, it may be useful to find polymers and methods that allow their mechanical reinforcement. A strategy was designed for the mechanical reinforcement of biodegradable polyesters based on aromatic liquid-crystalline polyesters. The thermotropic character is advantageous to allow easy processing from the melt (i.e., low melt viscosity) and to obtain mechanical strengths. Biodegradable liquid-crystalline copolyesters made up of natural nontoxic monomers such as β-(4-hydroxyphenyl)propionic acid and 4-hydroxybenzoic acid were synthesized (Kricheldorf et al., 1998).

Liquid crystalline copolyester of 3-(4-hydroxyphenyl)propionic acid (HPPA) of natural origin with 4-hydroxybenzoic acid (HBA) was synthesized by direct acidolytic polycondensation of the pure acetoxy derivatives of the monomers (Figure 13) (Prasad et al., 2001). The HPPA/HBA

50:50 copolyester showed birefringence with nematic Schlieren texture above 220°C with melt processability. The degradation observed at 30°C and pH 7 was 0.7 wt%, in the case of HPPA/HBA 50:50 copolyester after 340 hrs.

High molecular weight liquid crystalline copolyesters were obtained by polycondensation of phenylterephthaloyl dichloride and 2,2'-dimethyl-4,4'-dihydroxybiphenyl with oligolactides (Figure 14) (Haderlein et al., 1999; Chen et al., 2004). In spite of a significant content of lactide moieties of the copolyesters, their films and fibers were characterized by exceptional mechanical properties. Initial experiments indicated excellent biocompatibility based on cell seeding experiments and microscopic evidence. Their hydrolytic and enzymatic degradation was investigated in detail.

Melt-processable liquid-crystalline terpolyesters of 4-hydroxyphenylacetic acid and 3-(4-hydroxyphenyl) propionic acid with terephthalic acid and 2,6-naphthalene diol were synthesized by one-step acidolysis melt polycondensation followed by postpolymerization (Figure 15) (Prasad and Pillai,

2002). Considerable enzymatic degradation was also observed with porcine pancreas lipase/buffer solutions in comparison with *Candida rugosa* lipase after 60 days.

A series of thermotropic liquid crystalline polyesters was prepared from a diacyl chloride derivative of 4,4'-(terephthaloyldioxy)-di-4-phenylpropionic acid and glycols with a different number of methylene groups that incorporate aliphatic-aliphatic ester linkages in the main chain (Figure 16) (Nagata and Nakae, 2001). The effects of the number of methylene groups on the thermal properties and *in vitro* degradations were examined.
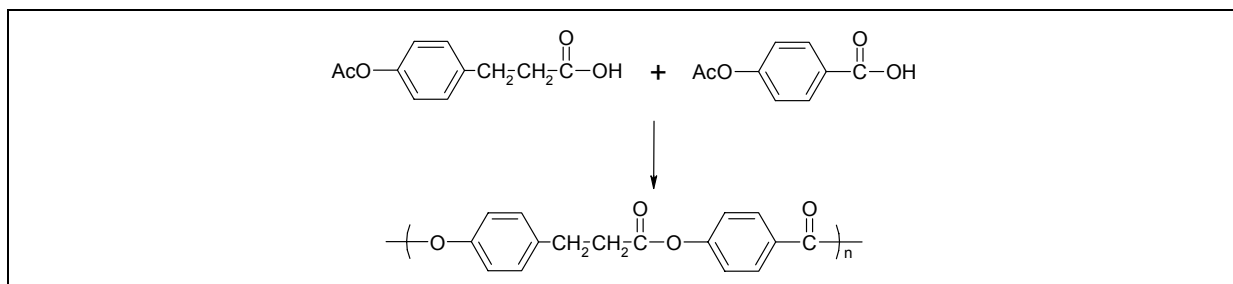

Figure 13: A liquid crystalline copolyester from 3-(4-hydroxyphenyl)propionic acid of natural origin with 4-hydroxybenzoic acid
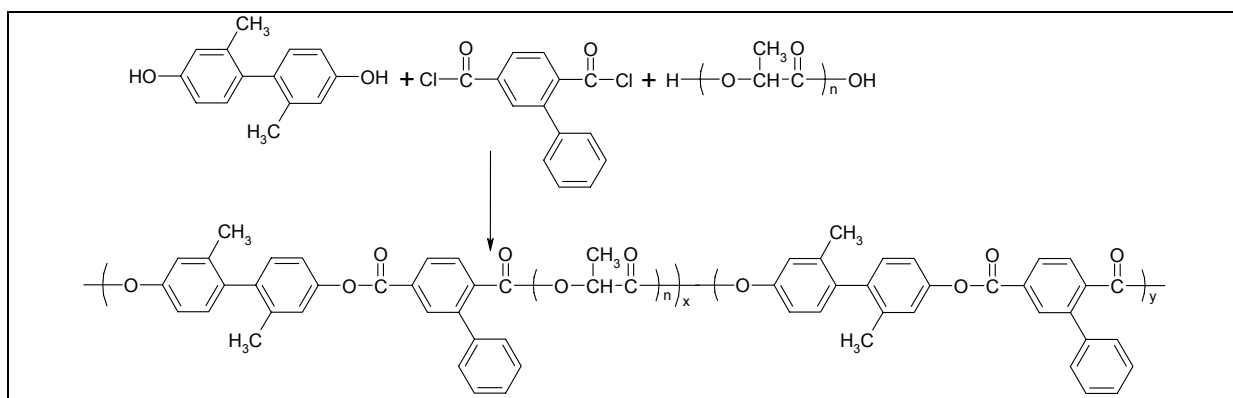

Figure 14: Copolyester obtained from phenylterephthaloyl dichloride and 2,2'-dimethyl-4,4'-dihydroxybiphenyl with oligolactides
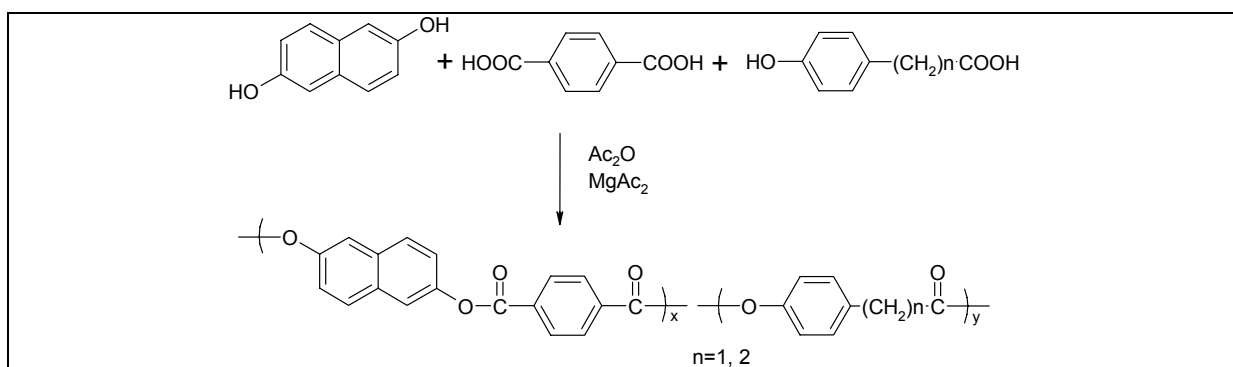

Figure 15: The copolyester based on 3-(4-hydroxyphenyl)propionic acid with terephthalic acid and 2,6-naphthalene diol
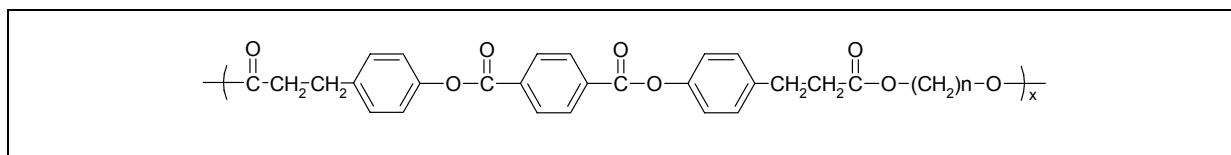
Figure 16: The copolyesters from 4,4'-(terephthaloyldioxy)-di-4-phenylpropionic acid and glycols

Degradation of Aromatic/Aliphatic Copolyesters

Polymers that undergo a controlled biological degradation by micro-organisms have became of remarkable interest during the last years. Composting for instance could thereby be established as an alternative waste management system for parts of the plastic waste. Within this group of innovative polymers, polyesters play a predominant role, due to their potentially hydrolyzable ester bonds. While aromatic polyesters such as poly(ethylene terephthalate) exhibit excellent material properties but proved to be almost resistant to microbial attack, many aliphatic polyesters turned out to be biodegradable but lacking in properties important for applications. To combine good material properties with biodegradability, aliphatic–aromatic copolyesters have been developed as biodegradable polymers for many years.

The biodegradability of polymers is influenced not only by the chemical structure of the polymers, especially the presence of functional groups and hydrophilicity–hydrophobicity balance, but also by the ordered structure such as crystallinity, orientation, and other morphological properties. The degree of crystallinity was known to be one of the major rate-determining factors of the biodegradability of polymers in the condition that the biodegradation starts in the amorphous regions and then continues into the crystalline regions.

In most cases, the primary biological attack is an enzymatically catalysed hydrolysis of ester, amide or urethane bonds in the polymers. This first step of depolymerization is a surface erosion process (enzymes can not penetrate into the polymer bulk) that leads to water-soluble intermediates, which then can be assimilated by microbial cells and thereby metabolized. However, in many cases, the term "biodegradation" is also used if the primary degradation step is caused by a hydrolysis, which is not catalysed by enzymes, but the depolymerization intermediates are then finally metabolized by micro-organisms or reabsorbed by the body, in the case of medical applications.

Since aromatic polyesters were found to be resistant to hydrolysis under mild conditions many attempts were made to increase their hydrolytic susceptibility by introducing aliphatic components into the aromatic polyester chains (Kint and Muňoz-Guerra, 1999). Tokiwa and Suzuki prepared copolyesters by a transesterification reaction between poly(butylenes terephthalate) or poly(ethylene isophthalate) and PCL and then studied their hydrolyzability by exposing them to *Rhizopus delemar* lipase (Tokiwa and Suzuki, 1981). Witt *et al*. have also studied copolyesters prepared by the polycondensation of aliphatic and aromatic monomers (Witt et al., 1995). Reed and Gilding have investigated the biodegradability of PET copolymers consisting of 50–70 wt % PEG of molecular weight (M_w) 1500 as biodegradable elastomer (Reed and Gilding, 1981). Nagata *et al*. have studied the enzymatic degradation of PET copolymers with aliphatic dicarboxylic acids and/or PEG (Nagata et al., 1997).

Early investigations on the biologically-induced degradation of aliphatic–aromatic copolyesters came to the conclusion, that a significant degradation can be observed only at relative low fractions of aromatic component (Tokiwa and Suzuki, 1981; Tokiwa et al., 1990; Jun et al., 1994). However, this statistical copolyester contains aromatic ester-sequences (sequences of terephthalic acid and 1,4-butanediol not interrupted by adipic acids) of different length in the amount of several percent of the total material mass (Witt et al., 1996). Because long aromatic sequences (e.g., pure aromatic polyesters like PBT) are known to be biologically persistent, even from such respirometric tests, the possibility that aromatic oligomers would remain undegraded in the compost cannot be entirely excluded.

The degradability of the aromatic oligomers did not decrease continuously with the length of the sequence, but oligomers containing one or two terephthalate units were degraded and metabolized rapidly, while in these experiments longer aromatic sequences remained almost unaffected. This was interpreted in correlation to the solubility and, thus, the availability of the oligomers of different length for intracellular processes, indicating that no effective extracellular enzymes were present to cleave the aromatic ester bonds. However, in

compost at elevated temperatures longer aromatic oligomers also disappeared, probably due to chemical hydrolysis. Up to now, it is not clear if any enzymes existthat are able to cleave principally ester bonds between two terephthalic acids; probably chemical hydrolysis plays a role in the breakdown of these oligomeric intermediates.

Independent of the degradation mechanisms, it has been proven that aromatic oligomers formed during the depolymerization of the aliphatic–aromatic copolyester do not accumulate under the conditions present during a composting process and no acute ecotoxic effect results from these intermediates. Aliphatic–aromatic copolyesters combine the properties of materials such as PET or PBT with the biodegradability often found for aliphatic polyesters and, thus, are of great practical and commercial relevance. From the environmental point of view, the aromatic components are not necessarily to be regarded as problematic. However, only limited knowledge about the detailed mechanisms of the enzymatic attack on the different structures present in the copolyesters are available up to now. For the design of new and improved materials and the evaluation of the degradation behavior under other environmental conditions, work has to be done to elucidate the degradation mechanism of these interesting groups of biodegradable polymers.

CONCLUSIONS

Aromatic/aliphatic copolyesters combine the biodegradability and biocompatibility of aliphatic polyesters with the physical properties and thermal properties of aromatic polyesters. They will be playing an important role in improving human healthy and in maintaining an ecologically friendly environment. In spite of the limited knowledge about the detailed biodegradation mechanisms and properties of the different structures present in the copolyesters available up to now, future work should be concerned with the following aspects. Most aromatic/aliphatic copolyesters are at the laboratory stage; exploration of new synthetic routes is required to lower the price of biodegradable materials with desirable physical properties. Due to limited knowledge on relationships of biodegradation mechanisms and aromatic sequences in aromatic/aliphatic copolyesters, design of new aromatic/aliphatic copolyesters and incorporation of the third component into the aromatic/aliphatic

copolyesters have to be done to expand the properties and to elucidate the relationships of the structures and properties of the aromatic/aliphatic copolyesters. For biomedical applications, a search for new materials is needed to improve physical properties while strictly controlling aromatic sequences in aromatic/aliphatic copolyesters.

REFERENCE

Acar I., Kasgoz A., Ozgumus S. and Orbay M., Modification of Waste Poly(ethylene terephthalate) (PET) by Using Poly(L-lactic acid) (PLA) and Hydrolytic Stability, Polymer-Plastic Technology and Engineering, 45, 351 (2006).

Andricic B., Kovacic T. and Klaric I., Miscibility and Thermooxidative Degradation of Poly(vinyl chloride)/Biodegradable Aliphatic-Aromatic Copolyester Blends, Journal of Applied Polymer Science, 100, 2158 (2006).

Bakker D., van Blitterswijk C. A., Hesseling S. C., Koerten H.K., Kuijpers W. and Grote J.J., Biocompatibility of a Polyether Urethane, Polypropylene Oxide, and a Polyether Polyester Copolymer, Journal of Biomedical Materials Research, 24, 489 (1990).

Beumer G. J., van Blitterswijk C. A., Bakker D. and Ponec M., Cell-Seeding and in Vitro Biocompatibility Evaluation of Polymeric Matrices of PEO/PBT Copolymers and PLLA, Biomaterials, 14, 598 (1993).

Beumer G. J., van Blitterswijk C. A. and Ponec M., Seeding and in Vitro Biocompatibility Evaluation of Polymeric Matrixes of PEO/PET Copolymers and PLLA, Journal of Biomedical Materials Research, 28, 545 (1994)

Chen Y., Jia Z., Schaper A., Kristiansen M., Smith P., Wombacher R., Wendorff J. H. and Greiner A., Hydrolytic and Enzymatic Degradation of Liquid-Crystalline Aromatic/Aliphatic Copolyesters,

Biomacromolecules, 5, 11 (2004).

Cohn D. and Younes H., Biodegradable PEO/PLA Block Copolymers, Journal of Biomedical Materials Research, 22, 993 (1988).

Coleman D., Block copolymers: Copolymerization of Ethylene Terephthalate and Polyoxyethylene Glycols, Journal of Polymer Science, 14, 15 (1954).

Deng L. M., Wang Y. Z., Yang K. K., Wang X. L., Zhou Q. and Ding, S.D., A New Biodegrdable Copolyester Poly(butylenes succinate-co-ethylene terephthalate), Acta Materialia, 52, 5871(2004).

Deschamps A. A., Grijpma D. W. and Feijen G., Poly(ethylene oxide)/Poly(butylene terephthalate) Segmented Block Copolymers: The Effect of Copolymer Composition on Physical Properties and Degradation Behavior, Polymer, 42, 9335 (2001).

De Simone V., Magkio G., Palubo R. and Scardi V., Synthesis, Characterization, and Degradation of Block Polyesteramides Containing Poly(L-lactide) Segments, Journal of Applied Polymer Science, 46, 1813 (1992).

Fakirov S. and Gogeva T., Poly(ether/ester)s Based on Poly(butylene terephthalate) and Poly (ethylene glycol), Makromoleculare Chemie, 191, 603 (1990).

Fakirov S. and Gogeva T., Poly(ether/ester)s Based on Poly(tetramethylene terephthalate) and Poly(ethylene glycol), Makromoleculare Chemie, 191, 615 (1990).

Fukuzaki H., Yoshida M., Asano M., Kumakura M., Imasaka K., Nagai T., Mashimo T., Yuasa H., Imai K. and Yamanaka H., Synthesis of Biodegradable Copoly(L-lactic acid/aromatic hydroxy acids) with Relatively Low Molecular Weight, European Polymer Journal, 26, 1273 (1990).

Gogeva T. and Fakirov S., Poly(ether/ester)s Based on Poly(tetramethylene terephthalate) and Poly(ethylene glycol), Makromoleculare Chemie, 191, 2355 (1990).

Gilding D. K. and Reed A. M., Biodegradable Polymers for Use in Surgery-Poly(ethylene oxide)/Poly(ethylene terephthalate) (PEO/PET) Copolymers, Polymer, 20, 1454-1458 (1979).

Gonsalves K. E., Chen X. and Cameron J. A., Degradation of Nonalternating Poly(ester-amides), Macromolecules, 25, 3309 (1992).

Haderlein G., Schmidt C., Wendorff J. H. and Greiner A., Synthesis of Hydrolytically Degradable Aromatic Polyesters with Lactide Moieties, Polymers for Advanced Technologies, 8, 568 (1997).

Haderlein G., Petersen H., Schmidt C., Wendorff J.H., Schaper A., Jones D.B., Visjager J., Smith P. and Greiner A., Synthesis and Properties of Liquid Crystalline Aromatic Copolyesters with Lactide Moieties, Macromolecular Chemistry and Physics, 200, 2080 (1999).

Hoeschele G. K., Thermostabile Polyester-Block-Copolymere, US Patent 3 954 689 (1976).

Jin X.M., Carfagna C. and Nicolais L., International Workshop on Liquid Crystalline Polymers. Capri, Italy (1993).

Jin X. M., Carfagna C., Nicolais L. and Lanzetta R., Synthesis and Characterization of Potentially Biodegradable Thermotropic Polyesters Based on p-Hydroxybenzoic Acid and Glycolic Acid, Journal of Polymer Science, Part A: Polymer Chemistry, 32, 3115 (1994).

Jin X., Carfagna C., Nicolais L. and Lanzetta R., Synthesis, Characterization, and in Vitro Degradation of a Novel Thermotropic Ternary Copolyester Based on p-Hydroxybenzoic Acid, Glycolic Acid, and p-Hydroxycinnamic Acid, Macromolecules, 28, 4785 (1995).

Jun H. S., Kim B. O., Kim Y. C., Chang N. H. and Woo S. I., Synthesis of. Copolyesters Containing Poly(ethylene terephthalate) and Polycaprolactone Units and Their Susceptibility to Pseudomonas Lipase, Journal of Environmental Polymer Degradation, 2, 9 (1994).

Jun H. S., Kim B. O., Kim Y. C., Chang N. H. and Woo S.I., Synthesis of Copolyester containing poly(ethylene terephthalate) and poly(ε-Caprolactone) units, and its biodegradability, Studies in Polymer Science, 12, 498 (1994).

Kim S. W., Lim J. C., Kim D. J. and Seo K. H., Synthesis and Characteristics of Biodegradable Copolyesters from the Transesterification of Poly(butylene adipate-co-succinate) and Poly (ethylene terephthalate), Journal of Applied Polymer Science, 92, 3266 (2004).

Ki H. C. and Park O. O., Synthesis, Characterization and Biodegradability of the Biodegradable Aliphaticaromatic Random Copolyesters, Polymer, 42, 1849 (2001).

Kim Y. J., Lee H.M. and Park O. O., Processabilities and Mechanical Properties of Surlyn-treated Starch/LDPE Blends, Polymer Engineering and Science, 35, No. 20, 1652 (1995).

Kint D. and Muňoz-Guerra S., In a Review on the Potential Biodegradability of Poly(ethylene terephthalate), Polymer International, 44, 346 (1999).

Kint D. P. R., Alla A., Deloret, E., Campos J. L. and Muñoz-Guerra S., Synthesis, Characterization,

and Properties of Poly(ethylene terephthalate)/ Poly(1,4-butylene succinate) Block Copolymer, Polymer, 44, 1321 (2003).

Kricheldorf H. R., Wahlen L. and Stukenbrook T., Biodegradable Liquid-Crystalline Aromatic Polyesters, Macromolecular Symposium, 130, 261 (1998).

Kumar G. S., Biodegradable Polymer. Marcel Dekker Inc., New York (1986).

Li F.X., Xu X.J., Hao Q.H., Li Q.B., Yu J.Y. and Cao A.M., Effects of Comonomer Sequential Structure on Thermal and Crystallization Behaviors of Biodegradable Poly(butylene succinate-co-butylene terephthalate)s, Journal of Polymer Science, Part B: Polymer Physics, 44, 1635 (2006).

Li S. M., Garreau H. and Vert M., Structure-Property Relationships in the Case of Degradation of Massive Aliphatic Poly(hydroxy acids) in Aqueous Media, Journal of Materials Science Materials in Medicine, 1, 123 (1990).

Ma D., Xu X., Luo X. and Nishi T., Transesterification and Ringed Sphe Rulites in Blends of Butylene Terephthalate-Caprolactone Copolyester with Poly(ε-caprolactone), Polymer, 38, 1131 (1997).

Ma D., Zhang G., Huang Z. and Luo X., Synthesis and Chain Structure of Ethylene Terephthalate - ε - Caprolactone Copolyester, Journal of Polymer Science, Part A: Polymer Chemistry, 36, 2961 (1998).

Maeda Y., Maeda T., Yamaguchi K., Kubota S., Nakayama A., Kawasaki N., Yamamoto N. and Aiba S., Synthesis and Characterization of Novel Biodegradable Copolyeater by Transreaction of Poly(ethylene terephthalate) with Copoly (succinic anhydride/ethylene oxide), Journal of Polymer Science, Part A: Polymer Chemistry, 38, 4478 (2000).

Montaudo G., Montaudo M. S., Scamporrino E. and Vitalini D., Mechanism of exchange in polyester, composition and microstructure of copolymers formed in the melt mixing process of poly(ethylene terephthalate and Poly(ethylene adipate), Macromolecules, 25, 5099 (1992).

Nagata M., Kiyotsukuri T., Minami S., Tsutsumi N. and Sakai W., Enzymatic Degradation of Poly(ethylene terephthalate) Copolymers with Aliphatic Dicarboxylic Acids and/or Poly (ethylene glycol), European Polymer Journal, 33, 1701 (1997).

Nagata M. and Nakae M., Synthesis, Characterization, and in Vitro Degradation of Thermotropic Polyesters and Copolyesters Based

on Terephthalic Acid, 3-(4-Hydroxyphenyl) Propionic Acid, and Glycols, Journal of Polymer Science, Part A: Polymer Chemistry, 39, 3043 (2001).

Ober C. K., Jin J. I. and Lenz R. W., Liquid Crystal Polymers with Flexible Spacers in the Main Chain, Advances in Polymer Science, 13, 103 (1984).

Papadaki M., Mahmood T., Gupta P., Claase M.B., Grijpma D.W., Riesle J., van Blitterswijk C.A. and Langer R., The Different Behaviors of Skeletal Muscle Cells and Chondrocytes on PEGT/PBT Clock Copolymers are Related to the Surface Properties of the Substrate, Journal of Biomedical Materials Research, 54, 47 (2001).

Prasad V. S., Pillai K. S. and Kricheldorf H. R., Biodegradable Liquid Crystalline Polyesters of Hydroxyphenylalkanoic Acids: Synthesis and in Vitro Degradation Studies of Poly[3-(4-oxyphenyl)-propionate-co-4-oxybenzoate], Journal of Macromolecular Science-Pure and Applied Chemistry, A38, 641 (2001).

Prasad V. S. and Pillai C. K. S., Synthesis, Characterization, and in Vitro Degradation of Liquid-Crystalline Terpolyesters of 4-Hydroxyphenylacetic Acid/3-(4-Hydroxyphenyl) Propionic Acid with Terephthalic Acid and 2,6-Naphthalene Diol, Journal of Polymer Science, Part A: Polymer Chemistry, 40, 1845 (2002).

Reed A. M. and Gilding D. K., Biodegradable Polymers for Use in Surgery-Poly(glycolic)/. Poly(lactic acid) Homo and Copolymers, 2: in Vitro Degradation, Polymer, 22, 499 (1981).

Shaik A. A., Richter M., Kricheldorf H. R. and Krüger R. P., New Polymer Synthesis. CIX. Biodegradable, Alternating Copolyesters of Terephthalic Acid, Aliphatic Dicarboxylic Acids, and Alkane Diols, Journal of Polymer Science, Part A: Polymer Chemistry, 39, 3371 (2001).

Shi X. Q., Aimi K., Ito H., Ando S. and Kikutani T, Characterization on Mixed-Crystal Structure of Poly(butylene terephthalate/succinate/adipate) Biodegradable Copolymer Fibers, Polymer, 46, 751 (2005).

Shi X. Q., Ito H. and Kikutani T, Characterization on Mixed-Crystal Structure and Properties of Poly (butylene adipate-co-terephthalate) Biodegradable Fibers, Polymer, 46, 11442 (2005).

Shi X. Q., Takasaki M., Ito H. and Kikutani T, Structural Development and Properties of Melt Spun Poly(butylene succinate) and Poly(butylene terephthalate-co-succinate-co-adipate) Biodegradable Fibers, Polymer Processing, XXI, 64 (2006).

Storey R.F., Warren S.C., Allison C.J., Wiggins J.S. and Puckett A.D., Synthesis of Bioabsorbable Networks from Methacrylate-Endcapped Polyesters, Polymer, 34, 4365 (1993).

Sun Y.M. and Wang C.S., Preparation and Properties of Poly(Ethylene-1,4-Cyclohexane dimethylene Naphthalate), European Polymer Journal, 35, 1087 (1999).

Tokiwa Y. and Suzuki T., Hydrolysis of Copolyesters Containing Aromatic and Aliphatic Ester Blocks by Lipase, Journal of Applied Polymer Science, 26, 441 (1981).

Tokiwa Y., Ando T., Suzuki T. and Takeda T., Biodegradation of Synthetic Polymers Containing Ester Bonds, Polymer Materials Science and Engineering, 62, 988 (1990).

Tokiwa Y., Ando, T., Suzuki, T. and Takeda T., Hydrolysis of polyesters by lipases, ACS Symposium Series, 433, 136 (1990).

Vaiionpaa S., Rokkanen P., Tormala P., Surgical Appilcations of Biodegradable Polymers in Human Tissue, Progress in Polymer Science, 14, 679 (1989).

Wagener K.B., Biocompatible copolymers, US Patent, 4 350 806, 1982.

Wang S., Wan A.C.A., Xu X., Gao S., Mao H.Q., Leong K.W. and Yu H., A New Nerve Guide Conduit Material Composed of a Biodegradable Poly(posphoester), Biomaterials, 22, 1157 (2001).

Wang L.C., Xie Z.G., Bi X.J., Wang X., Zhang A.Y., Chen Z.Q., Zhou J.Y. and Feng Z.G., Preparation and Characterization of Aliphatic/Aromatic Copolyesters Based on 1,4- Cyclohexanedicarboxylic Acid, Polymer Degradation and Stability, 91,2220 (2006).

Witt U., Müller R. J. and Deckwer W. D., New Biodegradable Polyester-Copolymers from Commodity Chemicals with Favourable Use Properties, Journal of Environmental Polymer Degradation, 3, 215 (1995).

Witt U., Müller R. J. and Deckwer W. D., Studies on Sequence Distribution of Aliphatic/Aromatic Copolyesters by High - Resolution ^{13}C Nuclear Magnetic Resonance Spectroscopy for Evaluation of Biodegradability, Makromolekulare Chemie, 197, 1525 (1996).

Witt U., Yamamato M., Seeliger V., Müller R.I. and Warzelhan V., Biodegradable Polymeric Materials- Not the Origin but the Chemical Structure Determines Biodegradability, Angewandte Chemie International Edition, 38, 1438 (1999).

Witt U., Yamamato M., Seeliger V., Müller R.I. and Warzelhan V., Biodegradation of aliphatic-aromatic copolyesters: Evaluation of the final biodegradability and ecotoxicological impact of biodegradation intermediates, Angewandte Chemie, 111, 540 (1999).

Wojiciech P., Jacek P. and Claudia K., Preparation and Characterization of copolyesters of Poly(tetramethylene succinate) and Poly(butylene terephthalate), Polimery, 51, No 5, 341 (2006).

Yoshie N., Azuma Y., Sakurai M. and Inoue Y., Crystalization and Compatibility of Poly(vinyl alcohol)/Poly(3-hydroxybutyrate) Blends: Ingluence of Blend Composition and Tacticity of Poly (vinyl alcohol), Journal of Applied Polymer Science, 56, 17 (1995).

Younes H. and Cohn D., Morphological Study of Biodegradable PEO/PLA Block Copolymers, Journal of Biomedical Materials Research, 21, 1301 (1987).

Zhang P., Huang F. and Wang B., Characterization of Biodegradable Aliphatic/Aromatic Copolyesters and Their Starch Blends, Polymer-Plastic Technology and Engineering, 41, 273 (2002).

Zhang X., Goosen M. F. A., Wyss U. P. and Picohora D., Biodergradable Polymers for Orthopedic Applications, Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics, C33, 81 (1993).

Zhao Z., Wang J., Mao H. Q. and Leong K. W., Polyphosphoesters in Drug and Gene Delivery, Advanced Drug Delivery Reviews, 55, 483 (2003).

Zhu K. J., Lin X. and Yang S L., Preparation, Characterization, and Properties of Polylactide-Poly(ethylene glycol) Cop.