

## Enzymatic Synthesis of Bio based Polyesters and Polyamides

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### Perspective

Now-a-days, "green" is a popular issue nearly everywhere, from stores to colleges to enterprises, and attaining green status has become a common goal. However, as a public stereotype, polymers are often seen as not being "green," being linked with huge energy use and serious environmental concerns (for example, the "Plastic Soup"). Green polymers should include three components: (1) green raw materials, catalysts, and solvents; (2) eco-friendly synthesis processes; and (3) sustainable polymers with a low carbon footprint, such as bio degradable polymers or polymers that can be recycled or disposed of with minimal environmental impact. Many beneficial green features may be accomplished by using bio based monomers in enzymatic polymerizations. Bio based monomers and enzyme catalysts, for example, are renewable resources generated from biomass feedstocks; enzymatic polymerizations are clean and energy-saving processes; and no hazardous residuals contaminate the final products. The synthesis of renewable polymers by enzymatic polymerizations of bio based monomers presents an opportunity for green polymers and a future sustainable polymer industry, which will eventually play an important part in creating and maintaining a bio based and sustainable society.

### Introduction to polymer, polyester and polyamides

Polymers are one of the most significant materials that humanity is exploiting and developing, and they play a vital and pervasive role in our modern lives. They are big molecules or macromolecules made up of a huge number of tiny molecular fragments known as repeating units. They are widely used in the production of plastics, rubbers, textiles, coatings, adhesives, foams, and speciality polymers. Polymers are classed as either natural or synthetic based on their origin. Natural polymers are formed in nature by in vivo processes in which biocatalysts, often enzymes, are unavoidably involved. Natural polymers are present in all living creatures, including plants, animals, and humans. Natural polymers include, to mention a few, lignocellulose, starch, protein, DNA, RNA, and polyhydroxyalkanoates (PHAs). With the exception of lignocellulose, the structures of natural polymers are often well-defined. Polymerization of petrol-based compounds with basic structures is a popular method of producing synthetic polymers. Chemical catalysts, particularly metal catalysts, are commonly employed in the production of synthetic polymers.

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Numerous synthetic polymers, such as phenol-formaldehyde resins, polyolefin, polyvinyl chloride, polystyrene, polyesters and polyamides, have been developed as a result of the booming petrochemical industry and the concomitant availability of cheap petroleum oils, as well as the well establishment and advancement of polymerization techniques.

Polyesters are polymers in which the monomer units are bonded together by ester groups. Polyesters include naturally occurring polyesters such as cutin, shellac, and poly(hydroxybutyrate) (PHB), as well as many synthetic polyesters such as poly(butylene succinate) (PBS), poly(lactic acid) (PLA), polyethylene terephthalate(PET), polybutylene terephthalate (PBT), and poly(4-hydroxybenzoate-co-6-hydroxynaphthalene-2-carboxylic acid) (V Polyesters are categorised as aliphatic, semi-aromatic, or aromatic based on the chemical makeup of their main chain. The majority of known aliphatic polyesters might be synthesised as biobased polymers, since the bulk of their starting monomers can be created from biomass feedstocks. Aliphatic polyesters are also bio degradable materials that may be recycled, disposed of, composted, or burned with minimal environmental effect. Aromatic polyesters are high-performance thermoplastics with good mechanical characteristics and great thermal stability and chemical resistance. Aromatic polyesters have a wide range of uses in the mechanical, chemical, electrical, aerospace, and car sectors. However, because of their very stiff structures, aromatic polyesters have low solubility even in strong solvents and are difficult to handle.

Polyamides are polymers with amide bonds connecting the monomeric components. Naturally occurring polyamides, such as proteins, and manufactured polyamides, such as polycaprolactam (nylon 6 or PA 6), poly(hexamethylene adipamide) (nylon 6,6 or PA 6,6), poly(hexamethylene terephthamide) (PA 6,T), and

poly(p-phenylene terephthamide), are examples of polyamides. Polyamides, like polyesters, are divided into three kinds based on the chemical makeup of the main chain: aliphatic, semi-aromatic, and aromatic polyamides. Semi-aromatic polyamides have both aliphatic and aromatic fragments in their main chain. ASTM D5336 defines polyphthalamides (PPAs), a kind of semi-aromatic polyamide, as “polyamides in which at least 55 mol percent of the carboxylic acid component of the repeating unit in the polymer chain is composed of a mixture of terephthalic acid (TPA) and isophthalic acid (IPA).”

### Enzyme-catalysed polyamide synthesis

The most promising alternatives are biobased polymers, which are described as “sustainable materials for which at least a part of the polymer comprises of elements generated from renewable basic resources.” In general, biobased polymers can be produced in three ways: (1) pristine natural polymers or chemical or physical modifications of natural polymers; (2) manufactured biobased polymers from a mixture of biobased molecules with similar functionalities converted from biomass feedstocks; and (3) synthesis of biobased polymers through polymerization of biobased monomers with tailored functionalities. The use of biobased monomers with tailored structures in polymer synthesis is the most promising approach to biobased polymers, as it can lead to not only sustainable alternatives to petrol-based counterparts with similar or identical structures, but also novel green polymers that cannot be produced from petrol-based monomers. However, as previously said, this is the most expensive option of the three.

Enzymatic polymerization is a new alternative method for producing polymeric materials that can compete with current chemical synthesis and physical modification approaches. Enzymatic polymerization also gives a tremendous chance for accessing new macromolecules that are not accessible via traditional methods. Furthermore, with moderate synthetic

conditions and renewable non-toxic enzyme catalysts, enzymatic polymerization is viewed as an efficient approach to minimise reliance on fossil resources and address the polymer industry's high material consumption and pollution concerns. Lipases, proteases, and other enzymes can catalyse the creation of amide bonds and are thus ideal enzymes for in vitro polyamide synthesis. Lipase-catalyzed polyamide synthesis, like biocatalytic polyester synthesis, can be accomplished in three ways: (1) step-growth polycondensation of diacid/diesters and diamines or -amino carboxylic acids/esters; (2) ring-opening polymerization of lactams; and (3) a hybrid of step-growth polycondensation and ring-opening polymerization.

In biocatalytic polyamide synthesis, two main types of elemental reactions are typically used: directly amidation and transamidation (aminolysis). Lipase-catalyzed polymerization of polyamides has received little attention. This might be due to two factors: (1) polyamides' high  $T_m$ , and (2) polyamides' low solubility in common organic solvents. On the one hand, polyamides such as nylons and TPA-based polyamides are semi-crystalline polymers that typically have melting points exceeding 100°C. Lipases' catalytic reactivity is considerably reduced at such high temperatures owing to protein denaturation and deactivation. Many polyamides, on the other hand, can only be dissolved in aggressive solvents such as formic acid, concentrated  $H_2SO_4$ , and trifluoroacetic acid, in which lipases cannot act. Nonetheless, certain oligoamides and polyamides may be effectively synthesised via lipase-catalyzed polymerization.

The majority of enzymatic polymerization research is still focused on the use of "conventional" monomers generated from fossil fuels. Because of increased awareness of energy security and environmental contamination, as well as increased interest in the creation of new polymeric materials, the use of biobased monomers in enzymatic polymerization has become an interesting issue in both academic and industry circles.