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Chapter 1

Green Polymer Chemistry: Biocatalysis and Biomaterials[‡]

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[‡]Names of products are necessary to report factually on available data;
however, the USDA neither guarantees nor warrants the standards of the
products, and the use of the name USDA implies no approval of the products
to the exclusion of others that may also be suitable.

This overview briefly surveys the practice of green chemistry in polymer science. Eight related themes can be discerned from the current research activities: 1) biocatalysis, 2) bio-based building blocks and agricultural products, 3) degradable polymers, 4) recycling of polymer products and catalysts, 5) energy generation or minimization during use, 6) optimal molecular design and activity, 7) benign solvents, and 8) improved synthesis to achieve atom economy, reaction efficiency, and reduced toxicity. All of these areas are experiencing an increase in research activity with the development of new tools and technologies. Examples are given of recent developments in green chemistry with a focus on biocatalysis and biobased materials.

Introduction

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances (1). Sustainability refers to the development that meets the needs of the present without compromising the ability of future generations to meet their own needs (2). In the past few years these concepts have caught on and have become popular topics for research. Several books and review articles have appeared in the past few years (3–6).

In the polymer area, there is also increasing interest in green chemistry. This is evident by many recent symposia organized on this topic at national ACS meetings. In our view, developments in green polymer chemistry can be roughly grouped into the following eight related themes. These eight themes also agree well with most of the themes described in recent articles and books on green chemistry (3–6).

- 1) Greener catalysts (e.g., biocatalysts such as enzymes and whole cells)
- 2) Diverse feedstock base (especially agricultural products and biobased building blocks)
- 3) Degradable polymers and waste minimization
- 4) Recycling of polymer products and catalysts (e.g., biological recycling)
- 5) Energy generation or minimization of use
- 6) Optimal molecular design and activity
- 7) Benign solvents (e.g., water, ionic liquids, or reactions without solvents)
- 8) Improved syntheses and processes (e.g., atom economy, reaction efficiency, toxicity reduction)

In this article, we provide an overview of green polymer chemistry, with a particular emphasis on biocatalysis (7, 8) and biobased materials (9, 10). Examples are taken from the recent literature, especially articles in this symposium volume (11–39) and the preprints (40–62) from the international symposium on “Biocatalysis in Polymer Science” at the ACS national meeting in Washington, DC in August 2009.

Green Polymer Chemistry - The Eightfold Path

Biocatalysts

Biocatalysis is an up-and-coming field that has attracted the attention and participation of many researchers. Several reviews (7) and books (8) are available on biocatalysis. This current symposium volume documents important new research that uses biocatalysis and biobased materials as tools to describe practical and developing strategies to implement green chemistry practices. A total of 22 articles (and 17 symposium preprints) describe biocatalysis and biotransformations. Among these papers, 31 articles focus on cell-free enzyme catalysts and 8 utilize whole-cell catalysts to accomplish biotransformations.

Biobased Materials

Interest in biobased materials (9, 10) appears to be increasing proportionally with increases or increased volatility of crude oil prices. There is also general recognition that the resources of the world are limited, and *sustainability* has become a rallying point for many organizations and industries participating in chemical product development. Thus, there is growing interest in using readily renewable materials as ingredients for commercial products or raw materials for synthesis and polymerization. In this book, 14 articles deal with biobased raw materials or products. In addition, 11 symposium preprints focus on this topic.

Degradable Polymers and Waste Minimization

One advantage of agricultural raw materials and bio-based building blocks is that they are potentially biodegradable and have less negative environmental impact. In addition to the potential economic benefits, the use of agricultural by-products minimizes waste and mitigates disposal problems. Biocatalysis is helpful in this effort because enzyme-catalysts often catalyzed reactions of natural substrates at high rates. Many biobased products are biodegradable, and hydrolytic enzymes are critically important for the break down of biomass to usable building blocks for fermentation processes. Four of the articles in this book deal specifically with polymer degradation and hydrolysis (20, 34–36). In addition, most of the polymers described in this book (polyesters, polyamides, polypeptides, polysaccharides) are biodegradable or potentially biodegradable.

Recycling

Another advantage of agricultural raw materials and bio-based building blocks is that they can often be recycled. Some resulting polymers that are biodegradable can undergo biological recycling by which they are converted to biomass, CO₂, CH₄ (anaerobic conditions) and water. Recycling is also important for biocatalysts in order to decrease process cost; this is one of the reasons for the use of immobilized enzymes. Several examples of immobilized enzymes appear in this book (*vide infra*). A popular enzyme used thus far is Novozym® 435 lipase from Novozymes A/S, which is an immobilized lipase from *Candida antarctica*.

Energy Generation and Minimization of Use

An active area of research is biofuels, and many review articles are available (63, 64). First generation products have largely been based on biotransformation of sugars and starch. The second-generation products, based on lignocelluloses conversion to sugars, are still under development. Biocatalysis is compatible with energy savings because their use often involves lower reaction temperatures and, therefore, lower energy input (e.g., refs. (27, 48)). The reactive extrusion technique is another process methodology that can decrease energy use (38, 39).

Molecular Design and Activity

In polymer science, structure-property and structure-activity correlations are often employed as part of synthetic design, and many articles on synthesis in this book inherently incorporated this feature. In biochemistry, a good example of molecular design is the development via protein engineering of protein variants that are optimized for a particular activity or characteristic (e.g. thermal stability). For example, Kiick (40) used *in vivo* methods to produce resilin, and McChalicher and Srienc (50) used site-specific mutagenesis for the synthase that produces poly(hydroxyalkanoate)s. In a different way, Ito et al (18) used molecular recognition to optimize biological activity of aptamers. Li et al (29) used biopathway engineering to produce lipopolysaccharides and their analogs.

Benign Solvents

A highly desirable goal of green chemistry is to replace organic solvents in chemical reactions with water. Biocatalytic reactions are highly suited for this. In fact, all whole-cell biotransformations and many enzymatic reactions in this book are performed in aqueous media. An alternative is to carry out the reaction without any solvents, as exemplified by several articles in this book.

Improved Syntheses and Processes

Optimization of experimental parameters in synthesis and process improvement during scale-up and commercialization are part of the work that synthetic scientists and engineers do. Biocatalysis certainly brings a new dimension to reactions and processes. Biocatalytic reactions often involve fewer by-products and less (or no) toxic chemical reagents. Several new or improved synthetic and process methodologies are described in the following sections. In addition, it is noteworthy that Matos et al (52) used microwave energy to assist in lipase-catalyzed polymerization, and Fishman et al (15) used microwave for extraction. Wang et al (38, 39) used reactive extrusion to facilitate polymer modification reactions.

From the foregoing discussion, it is clear that *biocatalysis* and *biobased materials* are major contributors to current research and development activities in green polymer chemistry. Active researchers in these fields have been working with different polymers, different biocatalysts, and different strategies. For convenience, the rest of this review is divided into eight sections: 1) Novel Biobased Materials, 2) New or Improved Biocatalysts, 3) Synthesis of Polyesters and Polycarbonates, 4) Synthesis of Polyamides and Polypeptides, 5) Synthesis and Modification of Polysaccharides, 6) Biocatalytic Redox Polymerizations, 7) Enzymatic Hydrolysis and Degradation, and 8) Grafting and Functionalization Reactions.

Novel Biobased Materials

As noted earlier, biobased materials constitute one of the most active research areas today. These include polypeptides/proteins, carbohydrates, lipids/triglycerides, microbial polyesters, plant fibers, and many others.

Polypeptides/Proteins

An active area of research is to use polypeptides and proteins for various applications. Kiick (40) worked with resilin, the insect energy storage protein that shows useful mechanical properties. This work involved incorporation of unnatural amino acids to produce biomaterials for possible use in engineering the vocal folds (more commonly known as vocal cords). Liu et al (12) carried out biofabrication based on enzyme-catalyzed coupling and crosslinking of pre-formed biopolymers for potential use as medical adhesives. Renggli and Bruns (11) reviewed polymer-protein hybrid materials and their use as biomaterials and biocatalytic polymers. Zhang and Chen (13) made novel blends of soy proteins and biodegradable thermoplastics, which exhibit excellent mechanical properties. Jong (57) made composites from rubber and soy protein modified with phthalic anhydride and found they provide a significant reinforcement effect. Venkateshan and Sun (14) made urea-soy protein composites and characterized their thermodynamic behavior and structural changes.

Polysaccharides

DeAngelis (30) and Schwach-Abdellaoui et al (31) both worked with glycoaminoglycans, which are useful in drug delivery, implantable gels, and cell scaffolds. Li et al (29) carried out extensive work in *in vitro* biosynthesis of O-polysaccharides and *in vivo* production of liposaccharides. Bulone et al (48) described a low-energy biosynthetic approach for the production of high-strength nanopaper from compartmentalized bacterial cellulose fibers. Fishman et al (15) extracted polysaccharides from sugar beet pulp and extensively characterized the resulting fractions.

Lipids and Triglycerides

In their article, Lu and Larock (16) provided a good overview of their work on converting agricultural oils into plastics, rubbers, composites, coatings and adhesives. Zini, et al (41) reviewed their work on poly(sophorolipid) and its potential as a biomaterial. Lu, et al (44) produced new ω -hydroxy and ω -carboxy fatty acids as building blocks for functional polyesters.

Specialty Polymeric Materials

Dinu et al (17) made smart coatings by immobilizing enzymes on carbon nanotubes and incorporating them into latex paints. The resulting materials can detect and eliminate hazardous agents to combat chemical and biological agents.

Xue, et al (61) made poly(ester-urethanes) based on poly(ϵ -caprolactone) that exhibit shape-memory effect at body temperature. Rovira-Truitt and White (43) prepared poly(D,L-lactide)/tin-supported mesoporous nanocomposites by in-situ polymerization.

Biomaterials

Most of the above aforementioned materials can be used in medical and dental applications as *biomaterials*, e.g., tissue engineering, implants, molecular imprinting, stimuli responsive systems for drug delivery and biosensing. Moreover, the nucleic acid-based aptamer described by Ito et al (18) has potential use for biosensing, diagnostic, and therapeutics. In addition, most of the polyesters described in this book are biodegradable and also have potential use in medical applications. For example, polylactides and polyglycolides are well known bioresorbable polyesters used as sutures, stents, dialysis media, drug delivery devices and others.

New and Improved Biocatalysts

Not surprisingly, one of the active research areas of biocatalysis and biotransformation is the development of new and improved biocatalysts.

New or Improved Enzymes

Methods to improve protein activity, specificity, stability and other characteristics are rapidly developing both through high-throughput as well as information-rich small library strategies. An example was given by McChalicher and Srien (50) who modified the synthase to facilitate the synthesis of poly(hydroxyalkanoate) (PHA). Ito et al (18) described a different class of enzymes ("aptazymes") based on oligonucleotides, which bind to hemin (iron-containing porphyrin) and also show peroxidase activity.

Ganesh and Gross (34) embedded enzymes within a bioresorbable polymer matrix, thereby demonstrating a new concept by which the lifetime of existing bioresorbable materials can be "fine tuned." Gitsov et al (45) made enzyme-polymer complexes that form "nanosponges." Renggli and Bruns (11) also made enzyme-polymer hybrid materials. Schoffelen et al (19, 46) developed a method to introduce an azide group onto an enzyme, which allowed subsequent coupling via click chemistry to other structures such as a polymer or enzyme(s) to facilitate reactions that require multiple enzymes. Immobilized enzymes were also used by a large number of authors in this book.

Whole Cell Approaches

Whole cell approaches were used by Yu (21) and by Smith (47) to produce PHA. Li et al (29) conducted *in vitro* biosynthesis of O-polysaccharides and *in vivo* production of liposaccharides. Schwach-Abdellaoui et al (31) used

a transferred gene in *Bacillus subtilis* to produce hyaluronic acid through an advanced fermentation process. Bulone et al (48) produced cellulose nanofibrils via *Gluconacetobacter xylinus* in the presence of hydroethylcellulose. Lu et al (44) produced ω -hydroxy and ω -carboxy fatty acids by engineering a *Candida tropicalis* strain and the corresponding fermentation processes. Uses of ω -hydroxy and ω -carboxy fatty as biobased monomers for next-generation poly(hydroxyanoates) was discussed. In their review on Baeyer-Villiger biooxidation Lau et al (33) included whole cell approaches. In her article, Kawai (36) summarized microorganisms capable of degrading polylactic acid.

Syntheses of Polyesters and Polycarbonates

Many examples of biocatalytic routes to polyesters and polycarbonates are discussed in this book and corresponding symposium preprints. In order to facilitate accessing these contributions to the book, the specific polymers, biocatalysts and authors for each polymer system are summarized in the following Table 1.

Syntheses of Polyamides and Polypeptides

Resilin-like polypeptides were made via whole cell biocatalysis described by Kiick (40). Co-oligopeptides consisting of glutamate and leucine residues were prepared via protease catalysis by Li et al (42). Polyamides were synthesized via lipase catalysis by Gu et al (49), by Cheng and Gu (27), and by Loos et al (53). Palmans et al (53) used dynamic kinetic resolution method to form chiral esters and amides, which can potentially lead to chiral polyamides.

Syntheses and Modifications of Polysaccharides

As noted earlier, DeAngelis (30) and Schwach-Abdellaoui et al (31) both produced glycoaminoglycans through cell-free enzyme and whole-cell approaches, respectively, and Bulone et al (48) produced bacterial cellulose through a whole-cell approach. Li et al (29) produced O-polysaccharides and liposaccharides through *in vitro* and *in vivo* biosynthesis. Fishman et al (15) made carboxymethylcellulose with materials obtained from sugar beet pulp. In addition, Biswas et al (56) grafted polyacrylamide onto starch using horseradish peroxidase as a catalyst.

Biocatalytic Redox Polymerizations

In their chapter, Bouldin et al (32) provided a good review of the use of oxidoreductase as a catalyst for the synthesis of electrically conducting polymers based on aniline, pyrrole, and thiophene. In a preprint (58), they reported a low-temperature, template-assisted polymerization of pyrrole using soybean oxidase in an aqueous solvent system. In another study,

Table 1. Examples of polyester and polycarbonate synthesis via biocatalysis

<i>Polymer^a</i>	<i>Biocatalyst^b</i>	<i>Authors</i>	<i>Ref.</i>
PHA	Whole cell	Yu	(21)
PHA	Whole cell with mutant enzyme	McChalicher, Srienc	(50)
PHA (Mirel™)	Whole cell	Smith	(47)
Functional polycarbonates	Lipase (N-435)	Bisht, Al-Azemi	(22)
Copolymers of PDL, caprolactone, valerolactone, dioxanone, trimethylenecarbonate	Lipase (N-435)	Scandola et al	(23)
Poly(PDL-co-glycolate)	Lipase (N-435)	Jiang, Liu	(24)
Polycaprolactone	Embedded N-435	Ganesh, Gross	(34)
Polyol polyesters	Lipase (N-435)	Gross, Sharma	(51)
Polycaprolactone	Lipase (N-435)	Matos et al	(52)
Chiral polyesters	Lipase (N-435)	Palmans et al	(53)
Poly(carbonate-co-ester), terpolymer	Lipase (N-435)	Jiang et al	(54)
Poly(carbonate-co-ester), diblock	Lipase (N-435)	Dai et al	(55)
Poly(PDL-co-butylene-co-succinate)	Lipase (N-435)	Mazzocchetti et al	(60)
Polycaprolactone-based poly(ester-urethanes)	Lipase (N-435)	Xue et al	(61)
Polycaprolactone diol	Immobilized lipase from <i>Y. lipolytica</i>	Barrera-Rivera et al	(25)
Polyester elastomer from 12-hydroxystearate, itaconate, and 1,4-butanediol	Immobilized lipase from <i>B. cepacia</i>	Yasuda et al	(26)
Polyesters	(Immobilized) Cutinase	Baker, Montclare	(20)

^a PHA = poly(hydroxyalkanoate), PDL = ω -pentadecalactone, ^b N-435 = Novozym® 435

Cruz-Silva et al (59) polymerized pyrrole using horseradish peroxidase/H₂O₂ and 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) as mediator.

Lau et al (33) provided a useful review on Baeyer-Villiger biooxidative transformations, covering both cell-free enzyme and whole-cell approaches. Liu et al (12) used a tyranosinase to conjugate pre-formed biopolymers.

Enzymatic Hydrolyses and Degradation

Ganesh and Gross (34) demonstrated the concept of controlled biomaterial lifetime by embedded Novozym® 435 lipase into poly(ϵ -caprolactone). By using different quantities of embedded enzyme in films, they controlled the degradation rate and tuned the lifetime of these biomaterials. Ronkvist et al (35) discovered surprisingly rapid enzymatic hydrolysis of poly(ethylene terephthalate) using cutinases. The ability of cutinases to carry out polymer hydrolysis and degradation was also noted by Baker and Montclare (20) in their review on cutinase. A good review was provided by Kawai (36) on poly(lactic acid)-degrading microorganisms and depolymerases. Some proteases were found to be specific to poly(L-lactic acid), but lipases active for poly(lactic acid) hydrolysis preferred degrading poly(D-lactic acid).

Grafting and Functionalization Reactions

Puskas and Sen (37) used the immobilized lipase-catalyst system Novozym 435 to catalyze methacrylation of hydroxyl functionalized polyisobutylene and polydimethylsiloxane as well as conjugation of thymine onto poly(ethylene glycol). Wang and Schertz (39) grafted poly(lactic acid) onto poly(hydroxyalkanoate) using a reactive extrusion process. Wang and He (38) modified poly(lactic acid) and poly(butylene succinate) with a diol or a functionalized alcohol via a catalyst, also using a reactive extrusion process. Moreover, as noted earlier, polyacrylamide was grafted onto starch using horseradish peroxidase by Biswas et al (56).

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