

Current Application of Controlled Degradation Processes in Polymer Modification and Functionalization

Ahmad Mohamad Gumel,¹ M. Suffian M. Annuar,¹ Thorsten Heidelberg²

¹Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

²Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence to: M. S. M. Annuar (E-mail: suffian_annuar@um.edu.my)

ABSTRACT: Ecological concerns over the accumulation of polymeric waste material and the demand for functionalized polymers in specialty applications have promoted extensive research on different controlled degradation processes and their use. The production of functionalized or modified polymers by conventional synthetic routes is expensive and time consuming. However, advances in degradation technology have become an enabling factor in the production of modified polymers and their functionalization. Mild irradiation, ozonization, and enzymatic routes are among the processes that have been explored for polymer modification. Biopolymers, such as chitosan, hyaluronic acids, and polyhydroxyalkanoates, are known to be suitable for a diverse number of applications, ranging from biomedical to organic-electronics. At the same time, their high molecular weight, crystallinity, and shelf degradability limit their utility. Controlled degradation processes can be used to prepare these types of polymers with reasonably low molecular weights and to generate radical species that help to stabilize these polymers or to initiate further beneficial reactions. In this article, we review the application of controlled degradation processes for polymer modification and functionalization. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3079–3088, 2013

KEYWORDS: applications; biodegradable; biopolymers and renewable polymers; degradation; functionalization of polymers

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INTRODUCTION

Polymers are being increasingly used for more and more diverse purposes; they are particularly important in food, cosmetics, and biomedical applications.^{1–3} The rise in the utilization of polymers has health and (often negative) ecological implications, especially from biomedical and environmental perspectives. The demand for the control of the precise delivery targets for therapeutic drugs and the capability of polymeric drug carriers to release their drugs on an independent timescale is growing; polymeric waste disposal can cause severe environmental pollution when they are poorly degradable materials. Both of these warrant an intense research exploration into controlled degradation processes for polymer functionalization and modification. The recent momentum in the use of biodegradable polymers over nondegradable ones is among the measures taken toward environmental friendliness and an increase in the sophistication of biomedical applications. However, at present, most of these biodegradable polymers lack many of the attributes of their nondegradable counterparts. These issues are further compounded by the fact that the production of tailor-made or functionalized biodegradable polymers may be costly because of difficult synthetic steps that are often required for their

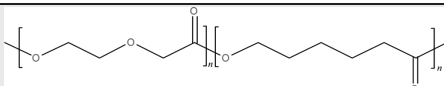
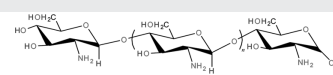
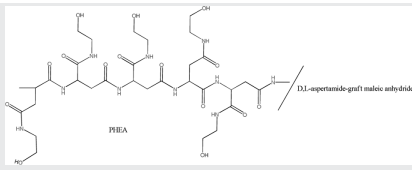
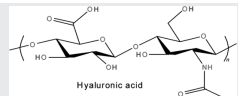
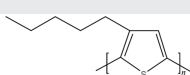
production. Although several approaches to the development of simpler and more cost-effective means to improve the quality of these biodegradable polymers, including dual biosynthesis⁴ and blending,⁵ have been reported, additional options need to be explored. In view of this, researchers have turned to the use of the opposite route of degradation processes to either improve the degradability of these important polymers or to customize the process for the production of specialty polymers for niche applications. Among recently reported methods have been the use of high-energy radiation,⁶ ozonization,⁷ ultrasonic irradiation,⁸ microwave irradiation,⁹ oxidation,^{10,11} biodegradation,¹² and photodegradation.¹³

In this article, we review current research approaches in the application of controlled degradation processes as alternative and viable routes toward enhanced polymer degradation, modification, and functionalization. In most cases, the mechanisms and biochemistry of the degradation process are also presented.

USE OF BIODEGRADATION AND ORGANOMODIFIERS

Biodegradation is known to be an effective method of completely removing degradable polymers and their constituents

Table I. Application of Controlled Degradation Processes for Polymer Degradation and/or Modification

Degradation method	Degradation agent	Polymer	Application	Reference
Selective enzymatic degradation	<i>Pseudomonas lipase</i>		Multifunctional polymers	23
Radiation induced partial degradation	γ	 $M_w = 10 \times 10^3$ to 2×10^3 kDa.	Plant growth promoters	50
Radiation induced graft polymerization	γ	 PHEA	Pulsatile protein release	54
Polymerization				
Ozonization	Ozone	 Hyaluronic acid $M_w = 1535\text{--}87$ kDa.	Antioxidant and wound healing activities	7
Ozonization	Ozone		Improved electroconductivity	61 and 62

from the environment.¹⁴ Several approaches have been developed that either employ the use of enzymes^{12,15,16} or microbial consortia^{17–19} to affect polymer degradation and modification. The metabolic degradation mechanism of polymers has been reported to use several enzymes, such as dehydrogenases, hydrolases, and oxidases, whereas the process is mostly based on either hydroxyl group oxidation to yield ketones or the hydrolysis of the carbonyl structure followed by the final mineralization of the components. The hydroxyl group oxidation is reported to be based on one of two steps, either the oxidation of one adjacent hydroxyl group to yield monoketone structure or the oxidation of two adjacent hydroxyl groups to form β -diketones structures.²⁰

Extensive research on a plethora of microbial enzymes that are normally involved in polymer degradation has been reported recently.^{16–18} For example, controlling the rate of silk-based polymeric material degradation is vital to its potential use in biomedical applications, such as drug delivery and tissue engineering scaffolding. Recently, Pritchard et al.²¹ reported the use of protease type XIV and ethylenediamine tetraacetic acid (EDTA) as biocontrolling switches to control the *in vitro* degradation of silk-based drug-carrier devices. The researchers observed the effects of the protease concentration on accelerating degradation and the use of EDTA on reducing the rates of degradation and controlling drug release from silk-based biomaterials. They reported an increased rate of proteolysis with increasing protease concentration; this resulted in an increased

dye release from silk carriers. On the other hand, the release of EDTA from the silk carriers inhibited proteolysis, which in turn controlled the proteolytic rate and, hence, the drug release.

The important step in polymer degradation, especially that of polyhydroxyalkanoate, is the degradation of the polymeric lamellar crystal.^{12,22} It has been reported that in most cases, the extracellular enzymes, such as polymerases and hydrolases secreted by the microbial consortia, are responsible for polymer biodegradation. Kulkarni et al.²³ reported the selective enzymatic degradation of a block copolymer [polycaprolactone-*b*-poly(*p*-dioxanone)] with *Pseudomonas lipase* (Table I). The researchers reported that after they subjected the material to 200 h of enzymatic degradation, the poly(*p*-dioxanone) copolymer part was completely stable and not tampered with, whereas the degradation affected the polycaprolactone (PCL) part. They demonstrated that degradation properties of multifunctional polymers could be manipulated and controlled with selective enzymatic degradation; this results in unique polymers with specific properties for specialized applications. They further reported that the degree of enzymatic degradation relies heavily on the apparent enzyme penetration depth and the initial molecular weight of the block copolymer; a suggestion substantiated further by Numata et al.¹² and Tanuma et al.²⁴ In addition, the chemical structure,^{12,25} molecular branches,¹² and degree of acetylation²⁶ are among the parameters suggested to exert influence on the enzymatic degradation of polymeric

materials. Recently, the controlled enzymatic degradation of PCL was reported with a polymer-embedded *Candida antarctica* lipase B solution (1.6%) in both continuous fluid exchange flow and controlled humidity chamber processes.²⁷ With 20 mM potassium phosphate buffer at pH 7.1 and a flow rate of 0.2 mL/min, researchers were able to achieve a polymer weight loss of about 85% in 3 days, an increase that was more greater in the process without the flow, where a bulk weight loss of 70% within 9 days of incubation was observed. The researchers suggested that the increase in the degradation rate under the flow conditions could be attributed to the more efficient removal of the degradation products that could act as competitive inhibitors. However, they observed a slower decrease in the polymer weight loss (70% in 7 days) as the flow rate was further increased to 0.5 mL/min; they attributed this to the negative influence of the increased flow rate on the enzyme stability.²⁷ When studying the rate of enzymatic degradation at controlled relative humidities (RHs) of 20, 75, and 95% with the same polymer-embedded 1.6% *C. antarctica* lipase B, researchers observed an insignificant polymer weight loss in the 20% RH condition.²⁷ However, at 75 and 95% RH, the polymer film was observed to exhibit weight losses of 25 and 58% after 28 days of incubation, respectively. The application of this controlled enzymatic degradation of polymeric materials under controlled humidity conditions could be an advantage in applications where the unique degradation properties of enzyme-embedded biodegradable films are exploited for the release of active materials such as fragrances, flavors, and therapeutic agents.

The biodegradation of waterborne polyurethane was reported to be enhanced by the incorporation of vinyl trimethoxysilane modified starch.²⁸ When the chemically hybridized polymer was incubated with 10% modified starch in an α -amylase solution for 10 days, a maximum weight loss of 15% and a decrease in the tensile strength of 60% were observed. This result was reported to be much bigger than that of the polymer containing the unmodified starch (5% weight loss and \sim 17% tensile strength decrease). Extracellular poly(hydroxybutyrate depolymerase) purified from *Ralstonia pickettii* T1 was used to degrade a film of poly[(R)-3-hydroxybutyrate-co-4-hydroxybutyrate] that was prepared by uniaxial cold-drawing from an amorphous polymer at a temperature just below the glass transition.²⁹ In this type of polymer, the researchers observed the degradation rate to range from 0.14 to 0.67 mg cm⁻² h⁻¹, depending on the polymer mechanical structure. The degree of enzymatic degradation was observed to increase with increasing draw ratio and 4-hydroxybutyric acid (4HB) content; this was mostly attributed to the decrease in the polymer crystallinity. They further reported that the enzyme preferably attacked the β form over the α form; this was attributed to the lower steric hindrance against the ester bonds in the planar zigzag conformation of the β form as compared to the α -form helical conformation.²⁹ The controlled enzymatic degradation of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) was studied with commercial lipases,¹⁶ wherein the researchers employed the use of nonregio-specific Amano lipase AK and 1,3-regiospecific Novozym lipopan BG to control the degradation of Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB-co-4HB) from 400 kDa to low-molecular-weight polymers of 1–5 kDa within 72 h to

make it suitable as a drug-release device. In another study, the use of a nonspecific protease (pronase) to catalyze the controlled degradation of CaCO₃-templated capsules that were prepared via layer-by-layer deposition techniques was reported.³⁰ The researchers showed that by either increasing the number of biodegradable layers in the capsules or inserting a synthetic polyelectrolyte of poly(allylamine hydrochloride) (PAH) and poly(sodium-4-styrene sulfonate) (PSS) to form multicompartiment polyelectrolyte multilayer capsules (Figure 1), the pronase-induced degradation of the capsules could be slowed down on the order of hours, and this resulted in the controlled detachment of subcompartments of multicompartiment capsules, with the potential for intracellular delivery or *in vivo* applications. Furthermore, the degradation rate was observed to increase with increasing pronase concentration.³⁰

In addition to extracellular and *in vitro* enzymatic degradation, whole-cell microbial polymer degradation has been reported.^{20,31} Poly(vinyl alcohol) (PVA) is considered to be an excellent compatible polymer blend with other polyhydroxyalkanoates because of its water solubility, biodegradability, and diverse applications. Jecu et al.³² observed the degradation of poly(vinyl alcohol) by fungal strains belonging to genera of *Aspergillus*, *Monillia*, *Penicillium*, *Aureobasidium*, and *Trichoderma*. The researchers observed that of all the species tested, *Aspergillus niger* came out to be the best at degrading the PVA composite, with the degree of degradation largely depending on the media and polymer compositions. A higher degradation (\geq 60%) of a copolymer of sucrose polyesters was also reported with *A. niger*.³³ The increasing demand for soft wood, especially in current infrastructural developments, has been a point of ecological concern. It has been suggested that a polymer composite of fast-growing herbs, such as kenaf, grass, palm oil leaves, and bamboo, could serve as an alternative to wood.³⁴ A biocomposite polymer of polylactide and *Hibiscus cannabinus* (kenaf) was said to have a similar properties to that of particle-board and, as such, has been considered as a softwood alternative.³⁵ Recently, mycelia of *Pleurotus ostreatus* immobilized on calcium alginate beads was used by Hidayat and Tachibana³⁵ to degrade a composite polymer of polylactide and kenaf fiber; they achieved a 48% degradation after 6 months as compared an 84% fiber degradation in a noncomposite. They reported that the degradation of the PLA/kenaf composite by *P. ostreatus* mycelia occurred via oxidation and caused the rupture of hydroxyl groups and the formation of carboxylic acid groups.

In contrast to eukaryotic fungal species, several bacterial genera, such as *Bacillus*, *Comamonas*, *Pseudomonas*, *Staphylococcus*, and *Streptococcus*, are among those that have been used in polymer biodegradation.³¹ Schneider et al.³⁶ observed the effects of the oleic acid concentration on poly(3-hydroxybutyrate) (P3HB) biodegradation produced by *Cupriavidus necator*. They observed that the polymer crystallinity decreased with increasing oleic acid concentration in the feed; this increased the degradability of the produced polymer.

The presence of impurities, organomodifiers, and plasticizers have been reported to affect the biodegradability of polymers. Researchers reported the use of organomodifiers such as clay to manipulate the polymer degradability and stability. Clay

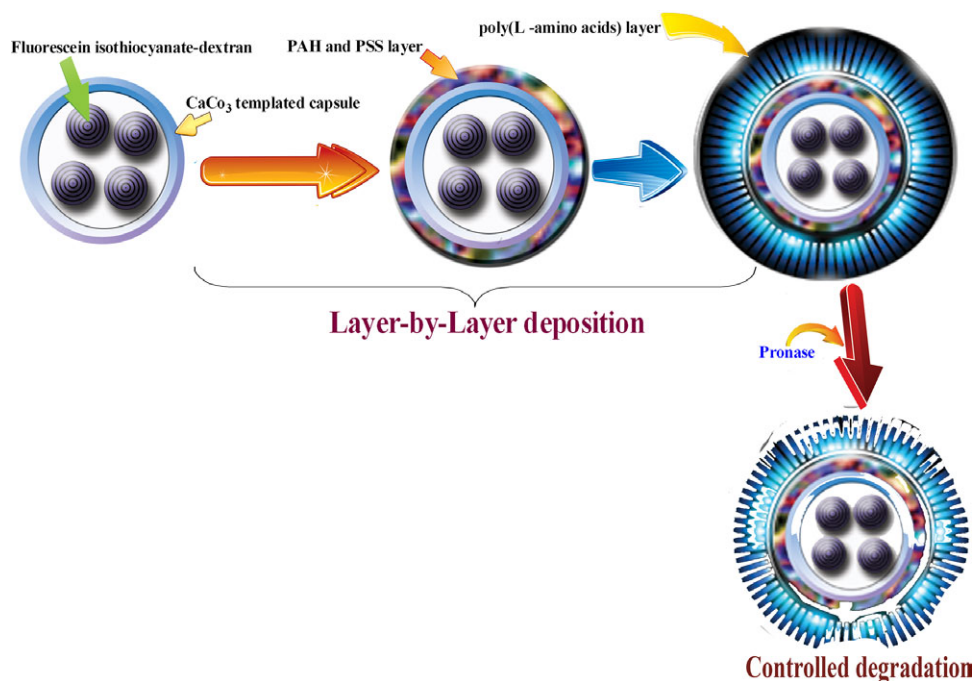


Figure 1. Controlled enzymatic degradation of the multilayer capsule in drug-delivery devices. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nanoparticles were reported to modulate the biodegradability of gluten-based agromaterials³⁷ and result in a degree of degradation as high as 92%. Heteroaromatic ring derivatives were used to control the degree of degradation in polypropylene.³⁸ The researchers reported that the degradation rate was highly influenced by the electron density of the C=C bond in the heteroaromatic derivatives. Low-electron-density heteroaromatic derivatives such as 2-(furan-2-ylmethylene) malononitrile were found to restrict the β scission of polypropylene macroradicals by converting them to stable-resonance macroradicals. In comparison, changing the aromatic rings with high-electron-density derivatives such as 2-cyano-3-(pyrrole-2-yl)-2-propionic acid ethyl ester resulted in a high degradation rate.³⁸

HIGH-ENERGY RADIATION

High-energy radiation has been proven to be a useful tool in polymer degradation and/or the manipulation of the physicochemical structure of many industrially important polymers.^{39,40} For instance, high-energy radiation has been applied to cause chain scission and branching in polypropylene.⁴¹ High-melt-strength polypropylene grains were synthesized by Oliani et al.⁴² using γ radiation. The same radiation was also shown to degrade poly(lactide-co-glycolide) (PLGA).⁴⁰ It has also been used to enhance the electric conductivity of polymer electrolytes⁴³ and polyaniline-[poly(vinylidene chloride)-co-(vinyl acetate)] blends.⁴⁴ An electron beam was employed to degrade PLGA by chain scission;⁴⁵ it has also been reported to have been used to achieve controlled surface degradation in biodegradable polymers.^{39,46} Carbon ion beams were reported to modify the physicochemical structures of both poly(allyl diglycol) carbonate and poly(ethylene terephthalate) polymer films.⁴⁷ An informative review of the effects of irradiation on controlled

drug-delivery and release systems was compiled by Ražem and Katušin-Ražem.⁴⁸

Galovic et al.⁴⁹ studied the effect of γ radiation on polyethylenes of different densities with temperature-modulated differential scanning calorimetry. The researchers observed increases in the crystallinity and stability of the polymer at radiation doses up to 200 kGy; beyond this value, decreases in these parameters were observed. They suggested that the low radiation favored polymer macromolecular breakage over crosslinking, which in turn led to an increased perfection of the crystals because of the alleviation of tension at the sites of the lamellae surfaces where the molecules entered the lattice. On the other hand, the high radiation doses favored the increase in the macromolecular surface free energy that induced crosslinking at the lateral grain boundaries and resulted in a lower crystallinity because of lattice distortion and expansion.⁴⁹ El-Sawy et al.⁵⁰ employed γ radiation to degrade chitosan with a molecular weight of about 10×10^3 kDa into water-soluble chitosan with an average molecular weight of less than 2×10^3 kDa and that was suitable for use as a growth promoter in agricultural fields (Table I). Using initiators such as ammonium persulfate and hydrogen peroxide, the researchers showed that the degree of degradation depended not only on the radiation dose but also on the concentration of the initiator. Technically, by modulating the radiation dose and initiator concentration, one can achieve a specific oligomeric chitosan polymer. The production of high-performance carbon fibers mostly depends on the precursors, among which polyacrylonitrile (PAN) is the most important. Unfortunately, the use of PAN as a precursor involves peroxidation to achieve the oligomerization of the nitrile groups to form a ladder chain structure, which improves the thermal stability of the fibers. The conventional method is time consuming, requires

the use of chemicals, and is a highly exothermic process.⁶ Gamma radiation has recently been reported to induce the formation of free radicals and crosslinking in PAN fibers and improve both the thermal stability and cyclization (oligomerization) efficiency of the fibers.^{6,51}

Polymer ion-beam irradiation liberates hydrogen and other volatile gasses that are suggested to influence the formation of free radicals and unsaturation; this in turn improves the polymer dielectric constant and conductivity. Singh et al.⁵² employed this phenomenon to improve the electrical conductivity of copper-doped poly(methyl methacrylate) for applications in organoelectronic components. High-energy radiation was used to induce graft polymerization (Table I) because of its simplicity, and it requires no catalyst or additives over the conventional methods and, hence, results in an almost pure product.⁵³ Recently, the mild condition of γ radiation was used to crosslink poly(*N*-2-hydroxyethyl)-DL-aspartamide with maleic anhydride to produce a functionalized hydrogel that was used as a drug-delivery device by the encapsulation and pulsatile release of proteins.⁵⁴

Lotfy⁵⁵ studied the controlled degradation of low-molecular-weight dextrin in the presence of γ irradiation (5–100 kGy). Using both electron spin resonance and X-ray diffraction spectra, the researchers reported the dextrin to undergo oxidative degradation at the crystalline regions of the amylopectin chains. Furthermore, they revealed that the polymer weight loss of the irradiated sample occurred at lower temperatures compared to that of the unirradiated samples; this resulted in oligomeric dextrin components with melting temperatures that decreased with increasing irradiation dose.⁵⁵

Flocculation is an efficient and cost-effective process for water treatment; polymers are popularly used as flocculating agents because of their ability to destabilize colloidal suspensions.⁵⁶ Ironically, the biodegradability of natural polymers reduces their shelf life in this process, whereas synthetic polymers are costly and nonbiodegradable. In view of this, γ radiation was used as a cost-effective route to produce a novel flocculant by the grafting of 2-methacryloyloxyethyl trimethyl ammonium chloride onto chitosan; this resulted in a copolymer with high cationic properties that was able to treat water over a wide range of pHs.⁵⁶

Gamma-radiation graft polymerization was also applied in the preparation of a thermosensitive and pH-sensitive copolymer of polypropylene that was prepared by the grafting of *N*-isopropyl acrylamide and acrylic acid onto polypropylene films.⁵³ The researchers observed that the degree of grafting increased with increasing radiation dose to 20 kGy; above this value, the increase was insignificant, which they reported to be due to an increased free-radical concentration, which resulted in a high probability of radical recombination.⁵³ Previously, the γ -induced controlled release of clonazepam by the radiolysis of poly(D,L-lactide-co-glycolide)-loaded microspheres was investigated with matrix electron paramagnetic resonance spectroscopy in a vacuum temperature range of 77–298 K.⁵⁷ The researchers observed that increasing the radiation resulted in an increase in the generation of the drug-free radicals and reported the stabilization of the polymer matrix in the mixed system with respect to the radiation damage.⁵⁷

The tensile strength and stability of starch-based thermoplastic was enhanced by crosslinking with aromatic cinnamyl alcohol using electron-beam irradiation.⁵⁸ The macromolecular chain scission due to the electron-beam irradiation was observed to be counterbalanced by the induced interchain covalent linkage bridged by the cinnamyl alcohol, which led to a grafted polymer with superior properties.

OZONIZATION

Ozonization is among the most important aspects in polymer degradation as a result of atmospheric exposure. Under strained conditions, a nonresistance elastomer can be attacked by ozone concentrations as little as 1 ppb.⁵⁹ Polymer degradation by ozonolysis has been reported to occur mostly by the cleavage of bonds between sp^2 or sp carbon atoms in olefinic polymers.^{59,60} However, the sp^3 carbon-hydrogen bonds of polymers containing labile hydrogen atoms are also attacked but at much slower rates.⁵⁹ The ozonolysis mechanism is said to involve steps such as the cycloaddition of ozone to the olefinic double bond to form unstable molozonide (Figure 2), which is decomposed into carbonyl compounds and carbonyl oxide moieties via a cycloreversion process. Lastly, a stereoselective cycloaddition occurs as a result of the carbonyl oxide, which flips over with the nucleophilic oxyanion attacking the carbon atom of the carbonyl group, resulting in the formation of a peroxidic ozonolysis product.⁵⁹

Although reactive and degradative to polymers, ozone still finds applications in polymer modification. Hyaluronic acids, especially those of low molecular weight, have electron-scavenging antioxidant activities and promote excisional wound healing.⁷ Recently, ozone treatment was used to prepare low-molecular-weight hyaluronic acid.⁷ Using ozonization (Table I), the researchers reported a reduction in the native hyaluronic acid molecular weight as large as 94.3% (from 1535 to 87 kDa within 120 min at 40°C), and they further observed that the heterogeneous reaction between the gaseous-phase ozone and the hyaluronic acid solution affected the polydispersity of the polymer. Experimental parameters, such as the reaction temperature, ozone concentration, media pH, ionic strength, and agitation speed are among the factors that have been reported to influence the ozonization process.⁷

Ozonization has further been reported to be used in the production of organoconductive polymers. It has been reported to influence the electrical conductivity of poly(3-pentylthiophene) films because of the formation of charge-transfer complexes.⁶¹ However, the conductivity was observed to drop significantly with time as a result of the oxidative degradation of the polymer. In contrast to this observation, Nowaczyk et al.⁶² reported the use of ozonization to induce both permanent and temporary increases in the electrical specific conductivity of a gold-sandwiched poly(3-pentylthiophene) polymer. The researchers observed that a permanent increase in the conductivity could be induced by the ozonization effect on the polymer morphology, which resulted in the formation of polymer grains aggregates, due to grain boundary resistance on polymer expansion. Whereas a temporary increase in the conductivity was observed to be a result of induced *p*-doping by ozonization, which took

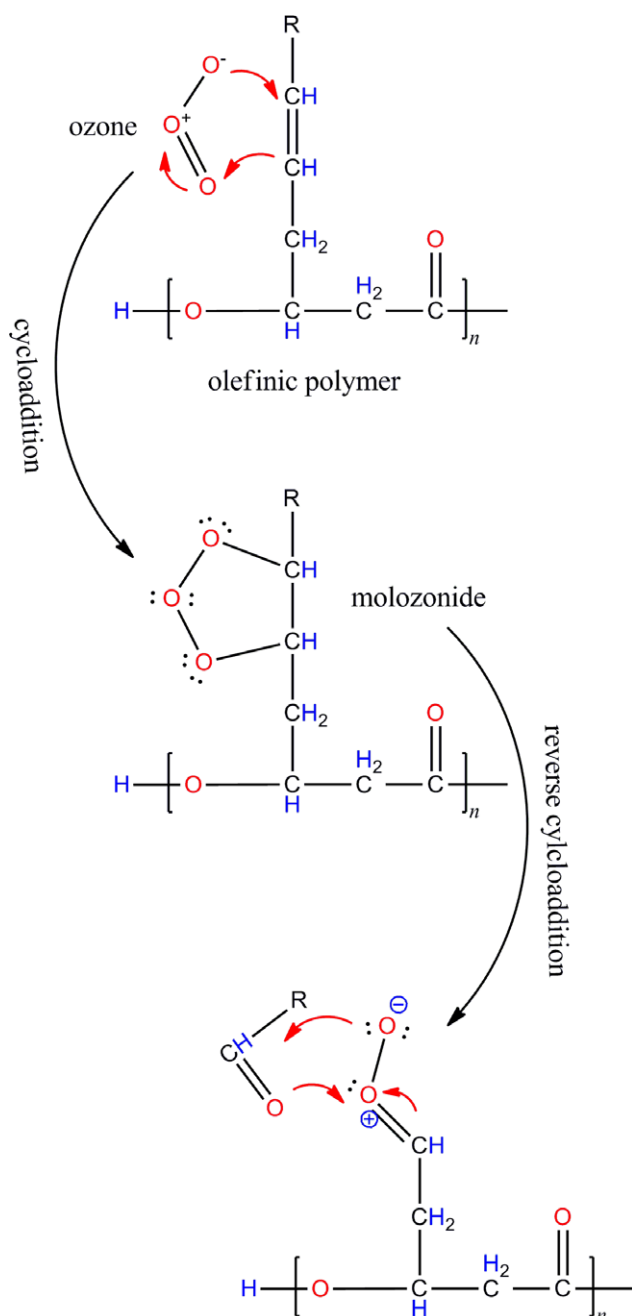


Figure 2. Mechanism of polymer ozonization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

place because the high electronegativity of the ozone readily captured electrons from the delocalized π orbitals in the polymer backbone to form charge-transfer complexes, which operated as excess charge carriers.⁶²

Polyethylene has been widely used in a number of industrial applications. Unfortunately, the polymer is characterized by poor dye adhesion to its surface, especially high-density polyethylene. Currently employed chemical surface modification methods, such as thermal oxidation and the use of strong electrical fields, are costly and time consuming. The surface functionalization of ultra-high-molecular-weight polyethylene with oxygen-bearing moieties was successfully achieved via ozoniza-

tion process with 10% ozone in oxygen under mild conditions.⁶³ In this process, the researchers reported that the ozonization mostly affected the amorphous phase of the polymer while preserving the crystalline phase. A similar report of polymer surface modification by ozonization was reported for styrenic triblock copolymers of elastomeric poly(ethylene-butylene) capped by polystyrene.⁶⁴ The researchers observed that prolonged exposure to ozone-induced crystallization and conferred a higher oxidative thermal stability to the polymer; this resulted in a qualitative polymer with a wide range of applications from organoelectronics to biopatterning.⁶⁴

PHOTODEGRADATION

The diverse applications of polymers in almost all aspects of human endeavors, ranging from spacecraft down to agricultural irrigation materials, has exposed applied polymers to adverse environmental conditions that warrant research concerning polymer degradation and stability. Although some of these polymers are biodegradable, environmental plastic wastes are usually thermally decomposed. The thermal degradation process is known to be costly and releases carcinogenic volatile gasses, and as such, the process is normally discouraged. The basis of polymer photolysis arises because of the presence of repeating carbonyl groups in polyesters, which results in photochemical cleavage by a Norrish-type reaction to degrade the polymer.^{65–67} The ability of light photons, such as UV and IR irradiation, to degrade polymers has previously been reported.^{65,68,69}

Previously, Tsuji et al.⁶⁹ studied the photodegradation of polylactide and polycaprolactone (PCL) for 200 h. They reported that UV radiation penetrated the polymer sample without a reduction in the intensity, regardless of the crystallinity or chemical structure, and degraded the polymer through a bulk erosion mechanism. However, they reported that the chemical structure adjacent to the carbonyl oxygen played a role in the photodegradability of the polymer. The effect of UV radiation on PHB was reported.⁷⁰ It was observed that in PHB, UV irradiation degraded the polymer by predominant chain scission into oligomers that could easily be functionalized (Figure 3) with lesser crosslinking reactions. The researchers further reported that when the UV irradiation was operated at temperatures higher than that of polymer's glass transition, the crystallinity increased as a result of the degraded molecules' mobility in the amorphous region, which tended to rearrange themselves by crystallization.⁷⁰ Klinger and Landfester⁷¹ observed the effect of UV-induced degradation on dual-stimuli poly(2-hydroxyethyl methacrylate-*co*-methacrylic acid) microgels. They reported the degradation rate to depend on parameters such as the media pH, intensity and wavelength of the applied irradiation, molecular structure of the crosslinking molecules, and overall molecular weight of the copolymer.

The control of protein adsorption onto a polymer surface is known to be a difficult challenge in biotechnological applications because of the strong adsorption that is irreversible and makes protein patterning almost impossible.⁷² It has been reported that polymer brushes of oligo(ethylene glycol) methacrylate showed an exceptional resistance to protein adsorption. Ahmad et al.⁷² used UV radiation at 244 nm to modify

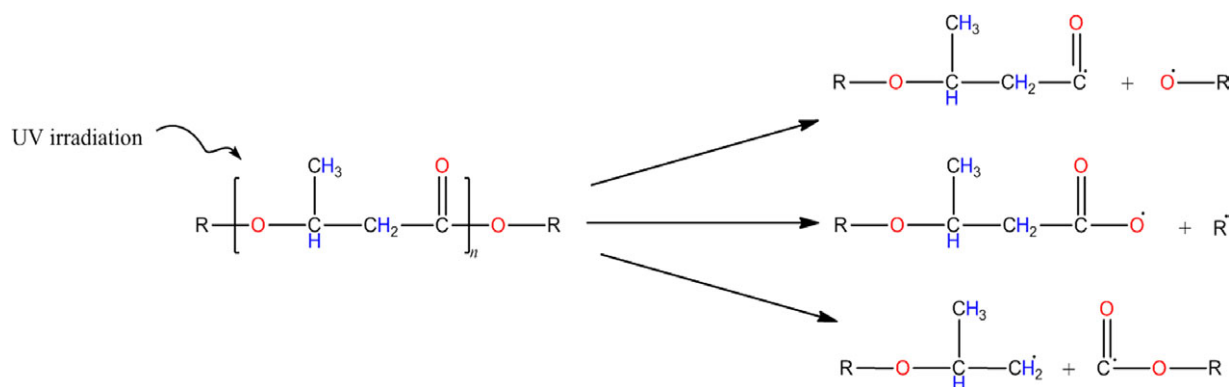


Figure 3. Schematic diagram of UV-induced progressive chain scission in PHB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

poly[oligo(ethylene glycol)] methacrylate under mild conditions to break the oligo(ethylene glycol) chain to aldehyde that covalently bound protein and enhanced the patterning process.

Low-molecular-weight chitosan has been reported to increase the postharvest quality of citrus and exhibit antimycotic, antibacterial, and anticarcinogenic activities.^{73–75} The deacetylation of chitin gives a chitosan of high molecular weight that has a low solubility in aqueous media, and this limits its industrial applications in many fields.⁷⁶ Recently, Yue et al.⁷⁶ reported the use of UV irradiation to induce accelerated degradation of chitosan during ozonolization to produce low-molecular-weight chitosan, which could be used in agrobases, biomedical, cosmetics, and food applications.

Silk fiber was reported to have a tensile strength of up to 4.5 GPa and an elasticity of about 35%; this makes it the toughest fiber known to man.⁷⁷ Silk fibroins are known to be surprisingly soluble in salt-containing aqueous, aqueous–organic, and organic solvents; unfortunately, the process is said to be time consuming. UV radiation was used to generate the silk fibroin in water within a shorter time to yield fibroin that was biocompatible and, at the same time, possessed remarkable physico-mechanical properties for use in diverse applications, such as surgical sutures, three-dimensional porous sponges, and microcapsules.⁷⁷

THERMOMECHANICAL AND OXIDATIVE DEGRADATION

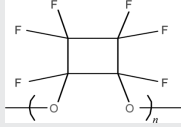
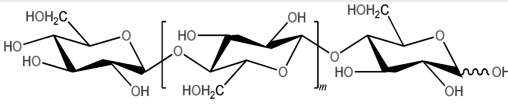
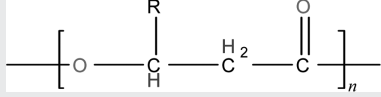
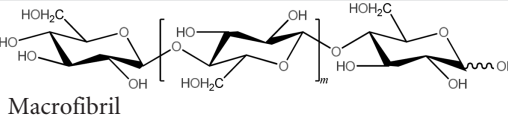
Polymeric physical and chemical structures are known to influence the thermomechanical properties of polymers. It has been reviewed earlier that mechanical action induces chemical changes in polymers.⁷⁸ Moreover, the fermentation of substrates, especially ammonium cations in polyhydroxyalkanoates, have been reported to greatly influence the thermomechanical degradation of polymers.^{79,80} Hydroxyalkanoic acids (HAs) are reported to have a wide range of industrial applications, such as metal corrosion inhibitors⁸¹ and antibacterial agents.⁸² These HAs are said to be chiral building blocks of several therapeutic drugs such as β -lactam, captopril, elaiophylin, and hydroxyacyl hydrazine in viscosin; and fungicides such as vermuculin and norpyrenophorin.⁸³ Conventionally, HAs are produced by the

acid/base hydrolysis or methanolysis of high-molecular-weight polyhydroxyalkanoates, a process that mostly results in traces of impurities within the final products. Thermal degradation is seen as an alternative process because of the generation of pure HA. Sin et al.⁸⁴ reported the use of moderately high temperatures (160–190°C) to produce oligomeric HAs from medium-chain-length polyhydroxyalkanoates. They proposed the degradation mechanism to occur via hydrolytic chain cleavage initiated at the $-\text{COO}-\text{CH}-\text{alkyl}$ group.⁸⁵ The researchers observed a loss of crystallinity when the PHA was heated at 180–190°C; ascribing the effects to the degradation of the polymer crystalline phase, which caused an increase in the mobility of the degraded polymeric units as the temperature approached the decomposition point.⁸⁴ In contrast to this observation, Sadi et al.⁷⁰ reported that an increased mobility of degraded polymeric molecules caused increased crystallinity because the molecules tended to rearrange themselves by crystallization.

Thermal degradation with microwave irradiation (Table II) to induce the controlled production of oligoesters (number-average molecular weight ≤ 1000 g/mol) in polyhydroxyalkanoates was recently reported.⁹ The researchers observed the process to be 100 times faster than the conventional thermal degradation process and to occur within a very short time (<15 min). They attributed the faster rate of degradation to be due to the generated highly efficient internal heating as a result of the direct coupling of microwave energy with the polar molecules; this led to the carboxyl–ester linkage.⁹ The researchers suggested that for effective control of the degradation rate, microwave power should be modulated with the application of simultaneous cooling.

The mechanical ultrasonic degradation of commercially important polymers, such as polystyrene, polybutadiene, polystyrene–butadiene, PAN–butadiene, and polystyrene–acrylonitrile was reported.⁸⁶ Pinheiro et al.⁸⁷ proposed that chain scission was a starting point in the thermomechanical degradation of longer chains of high-density polyethylene, where their higher probability of entanglements resulted in macroradicals that could be functionalized. However, they noticed that the chain scission mechanism was less prominent in the shorter chains as a result

Table II. Thermomechanical and Oxidative Degradation in Polymer Modification

Degradation method	Polymer	Application	Reference
Pulse ultrasonication		1,4-Diradical intermediate for polymer functionalization	88
Ultrasound fragmentation		Improved crystallinity for the biocomposite polymer	90
Microwave irradiation		Oligoesters for functionalization	9
TEMPO chemooxidative degradation	 <p>Macrofibril</p>	Surface-oxidized cellulosic nanofibril	11

of their mobility but was rather useful for grafting the macro-radicals and, thus, increased the molecular weight.⁸⁷

Recently, Klukovich et al.⁸⁸ studied the mechanical effects of pulsed ultrasound on perfluorocyclobutane polymers (Table II); this led to mechanically induced chain scission and molecular weight degradation via a stepwise mechanism with a 1,4-diradical intermediate. It yielded a polymer for localized functionalization and crosslinking.⁸⁸ The high crystallinity and extensive hydrogen bonding within the cellulosic polymer backbone conferred to it the advantage of being a natural fiber composite. However, because of the presence of an amorphous region in these naturally occurring celluloses, their tensile strength was highly limited. Hence, for the efficient application of these materials, a modification in the polymeric properties, especially the crystallinity, is needed. Goodwin et al.⁸⁹ reported the use of ultrasound irradiation to produce customized-molecular-weight pharmaceutical cellulosic ethers. The rate of degradation was observed to depend on the type of polymeric material and the irradiation time.⁸⁹ Recently, prolonged ultrasound fragmentation was reported to alter the crystallinity and molecular weight of cellulosic materials.⁹⁰ Using plant and bacterial cellulosic samples having a weight-average molecular weights of about 100 and 200 kDa, respectively, the researchers observed a continuous increase in the crystallinity index and a reduction in the molecular weight of the materials within 60 min of ultrasound irradiation to about 46 and 47 kDa, respectively. Pectin, which is a complex heteropolysaccharide commonly found in plant cell walls and middle lamella, has a wide application in the food and pharmaceutical industries as gelling, thickening, texturizing, stabilizing, and emulsifying agent.⁹¹ However, the strong resistance of pectin to degradation by other physicochemical processes, such as ultrasound irradiation and some me-

chanical degradation methods, limits its optimal utilization. Chen et al.⁹¹ reported the use of dynamic high-pressure microfluidization (DHPM) to induce controlled degradation in high-methoxyl pectin. The researchers observed a reduction of about 50% in molecular weight through the application of a DHPM of 80 MPa at pH 3.7, whereas an increase in the DHPM to 200 MPa at the same pH resulted in a molecular weight reduction of about 74%. However, a change in the pH to more acidic conditions appeared to highly influence the degradation. For instance, the application of 160 MPa of DHPM at pH 1.0 resulted in about an 89% degradation of the methoxyl pectin.⁹¹ This reduction in the pectin's average molecular weight with the treatments was attributed to the breakdown of the covalent bonds inside the polymer chain.

The chemooxidative degradation of cellulose microfibrils with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) radical derivatives and its analogous compounds were employed by Iwamoto et al.¹¹ to produce surface-oxidized cellulosic nanofibrils via hydromechanical treatment. When the oxidative effect of the TEMPO and its derivatives on wood cellulose surface oxidation were compared, researchers observed that both TEMPO and those analogous compounds of 4-acetamide and 4-methoxy derivatives showed an efficient catalytic surface oxidation of nanofibrils (>56%) compared to those of 4-hydroxyl and 4-oxo derivatives (<2%). The researchers reported that the observed differences in the catalytic efficiency among the TEMPO and its derivatives was probably due to their low redox potential, catalyst stability to media system, and affinity to cellulose type.

CONCLUSIONS

The demand for specific degradability traits and functionalized/modified polymers in niche applications, and the difficulty

encountered in their *de novo* preparations under conventional syntheses has brought about the current interest in polymer modification and functionalization via controlled degradation processes. A successful degradation program depends on the ability to exert a certain degree of control over major parameters such as the rate and selectivity/specificity. This can be achieved through the manipulation of the degradation environment, for example, the (bio)catalyst concentration, modulation of irradiation intensity, humidity, and pH, for a particular process. Preparation methods of polymers before degradation can also be used as means to affect another level of control; this may involve the tailoring of the composition of the polymer, degree of crystallinity in different parts of the polymer, molecular weight, functional groups, and so on. It is possible to achieve a specific degradation outcome through a combination of these distinct techniques. There is also an opportunity to combine tandem physicochemical and enzymatic degradation steps, and this opens up wider possibilities for modified products.

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