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Perspective

An old polymer class revisited: Versatile, degradable, non-alternating polyketones

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SUMMARY

Commercial plastics are essential to our society; however, they persist in the environment due to their chemical inertness. Plastic pollution causes serious environmental problems, necessitating new, sustainable strategies to break them down. Developing degradable materials that will decompose in the environment is of immense interest. However, these materials must also be of commercial relevance, and easily degradable polymers often do not display the necessary physical properties. This perspective will highlight one of these polymer classes: non-alternating polyketones. Historical perspective on the original synthesis and recent advances for synthesizing these materials highlight the longstanding interest in these polymers. Additionally, post-polymerization modifications and photodegradation studies will provide context for the potential applications of these interesting polymers.

THE BIGGER PICTURE

Challenges and opportunities:

- The ongoing research into photodegradable plastics holds immense significance in addressing the pervasive environmental crisis caused by conventional persistent plastics. By developing plastics that break down under light, the aim is to substantially reduce plastic pollution and its detrimental impact on ecosystems, wildlife, and human health.
- Access to these materials is limited by the methods available for synthesis and polymer sequence design. Development of new synthetic methods and catalysts will broaden the types of degradable materials.
- The longer-term ambition of this line of research is to revolutionize global plastic consumption patterns, promoting the widespread adoption of environmentally friendly materials. Although the immediate impact might be gradual, the potential long-term effects on society are profound, offering a sustainable solution to mitigate plastic pollution and pave the way for a cleaner, healthier planet.

INTRODUCTION

Over the last century, plastics have changed our daily lives, becoming integral to our modern society.[1] However, strategies to valorize these materials at end-of-life remain limited. Recent numbers reported by the Organisation for Economic Co-operation and Development Global Plastics Outlook Database stated that plastic production hit 460 million tonnes in 2019 and continues to grow. Additionally, two-thirds of the plastic waste generated is from materials less than 5 years old.[1] Waste management for plastics in 2019 included disposal through a landfill (49%), incineration (19%), and recycling (9%). Unfortunately, the other 22% of plastic waste was found to be mismanaged, ending up in uncontrolled waste sites, burned in unauthorized pits, or dumped into aquatic waterways. Due to the relative inertness of most commercial plastics, these materials persist in the environment for hundreds of years.[2]

Plastics, or polymers, are long-chain molecules comprising a sequence of repeating monomer units. The properties, function, and environmental degradability or recyclability of plastics depend on the structure and sequence of the monomers or comonomers.[3–10] Although most polymers are inert, with all-carbon backbones, degradable polymers bear reactive main-chain functional groups that can be cleaved to yield oligomers, which can then enter faster degradation pathways.[4,9–12] Polyketones are of immense interest because they contain carbon-oxygen bonds that can absorb radiation energy provided by light to promote photodegradation.[13–17] Specifically, polyketones are inherently photodegradable via Norrish cleavage reactions to cleave the polymer backbone.[15,18,19] Although these polymers have a long history, perfectly alternating polyketones have been the main focus. Unfortunately, they display vastly different properties from commercial polymers, making adoption challenging. They typically exhibit higher melting

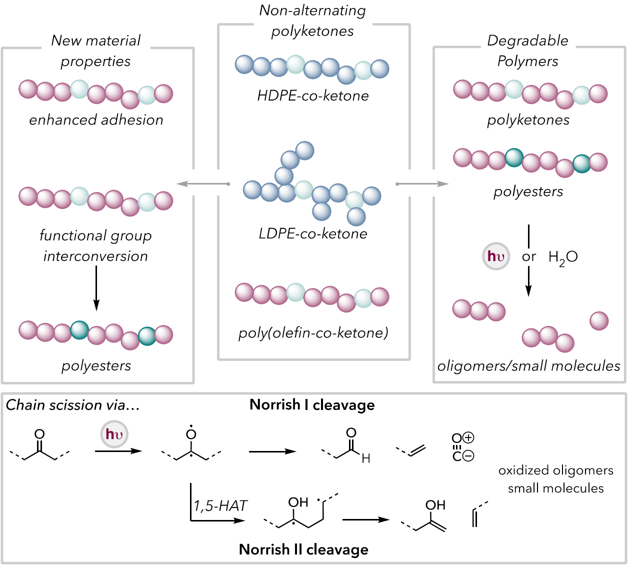

Figure 1. Diverse properties and degradability derived from non-alternating polyketones

temperatures making melt processing (major processing method for commercial polymers) difficult/impractical. The permeability properties are also changed, opening applications for membranes or resistant material packaging. Only recently has the focus shifted to non-alternating polyketones, which are still photodegradable but maintain similar physical properties, affording a drop-in replacement for existing commercial materials (Figure 1).

Recognizing that polyketones are still a valuable class of polymer to explore, renewed efforts of the last two decades have focused on polymerization strategies to obtain non-alternating polyketones. Lower ketone incorporations have been of primary interest, ensuring the polymer remains degradable via Norrish cleavages but remains processable under commercial processing conditions. This perspective will highlight recent contributions in this area, including monomer design, post-polymerization modifications, catalyst development, and inclusion of new C1 monomers. Exploration into four main areas of research, including (1) catalyst development, (2) new synthetic methods, (3) post-polymerization modifications, and (4) (photo)degradation studies of these materials, has brought new life to an old polymer class.

SYNTHESIS VIA MONOMER DESIGN OR POST-POLYMERIZATION MODIFICATIONS

A common way to install regular functionality into a polymer backbone is through the design and polymerization of ketone-containing monomers. This strategy relies on commonly used polymerization methods while dictating the amount of incorporation through homopolymerization or copolymerization with a similarly unfunctionalized monomer. Alternatively, reactive groups can be installed on unfunctionalized homopolymers in a post-polymerization functionalization strategy. This enables the functionalization or upcycling of existing polymers to enable new functions and degradability. Both approaches have proven effective for installing ketones into the backbone of polyolefins, rendering the polymers degradable while imbuing new material properties.[20]

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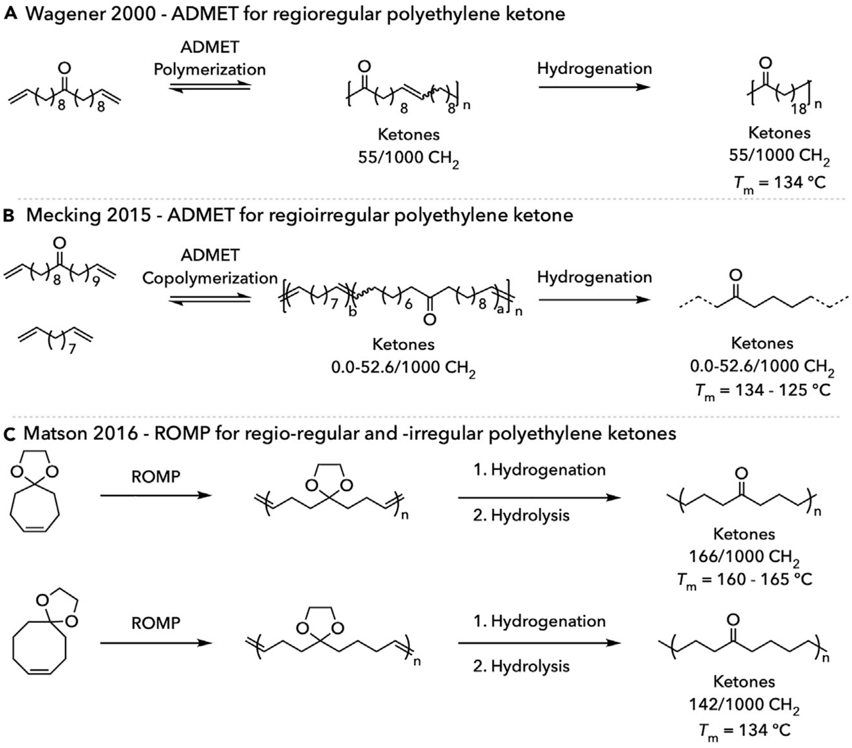


Figure 2. Polymerization of "ketone"-containing monomers

(A) ADMET of ketone containing diene.

(B) ADMET of ketone and diene comonomers.

(C) ROMP of cycloheptene and cyclooctene derviatives.

Adapted with permission from Watson and Wagener,[21] Ortmann et al.,[22] and Arrington et al.[23] Copyright 2001, 2015, and 2016 American Chemical Society.

Polymerization of ketone-containing monomers

Design and polymerization of ketone-containing monomers have been used to generate polyketones with controlled insertion of ketone functionality.[12,21–25] Olefin metathesis via acyclic diene metathesis (ADMET) or ring-opening methathesis polymerization (ROMP) are facile methods for designing specialty polymers from monomers with embedded ketones that are not the functional group directly involved in the polymerization. Wagener and coworkers initially showed that ketone-containing diene monomers could be polymerized via ADMET, followed by hydrogenation to afford regioregular non-alternating polyethylene ketone (Figure 2A).[21] Later, Mecking and coworkers used a similar strategy to randomly copolymerize a ketone-containing diene and unfunctionalized diene with the resultant polymer containing up to 52.6 ketones per 1,000 CH_2 units (Figure 2B).[22] Upon hydrogenation, a polyethylene-like polymer with in-chain ketones was obtained. The authors observed decreasing melting temperatures (T_m°C) from 134 to 125 with increasing amounts of ketone. However, the authors also note the comparison with Wagener's earlier work, which displayed a higher T_m of 134°C for 55 ketones per 1,000 CH_2 units, which may be attributed to the regioregularity of the single monomer approach.

Similarly, Matson and coworkers used a 7-membered acetal monomer as a masked ketone in a ROMP to afford polymer (Figure 2C).[12,23] Hydrogenation to saturate the alkene-containing backbone and subsequent hydrolysis of the acetal afforded a regioregular polyketone. With three times the number of ketones per 1,000 CH_2 units and a feature of the regioregular arrangement along the backbone, this polymer displayed a much higher T_m of 160°C–165 °C. Interestingly, using an 8-membered acetal monomer and proceeding through the same protocol afforded a regioirregular polyethylene-like ketone polymer. Although maintaining a high number of ketone units, a much lower T_m was observed at 130 °C–133 °C, consistent with Mecking's earlier study. The spacing between and the number of ketone units strongly impacts the ability of the polymer chains to crystallize. Although the polarity of the ketone groups can enhance the melting temperature, frequency and regularity have a profound impact. Li and Matson have further explored this monomer strategy by adding other monomers and post-polymerization modifications to further expand the degradability and properties of the polyketone polymers.[12,24]

C–H oxidation of polymer backbones

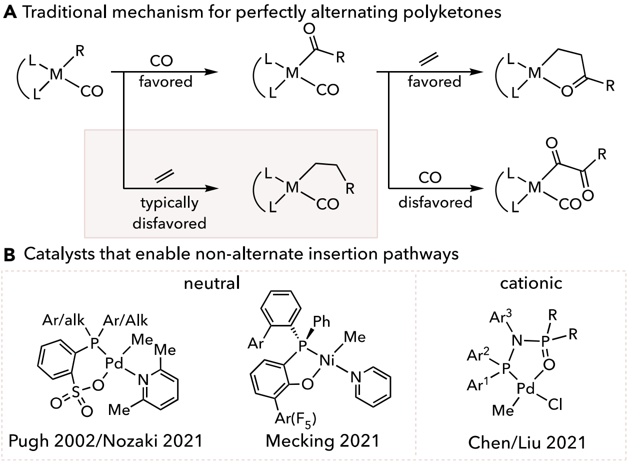
Photooxidative degradation is a common pathway for polyolefin degradation in the environment. This process usually occurs via a C–H abstraction event from the polymer backbone, and subsequent trapping with oxygen can result in oxidative chain cleavage. However, direct C–H oxidation without chain cleavage can install the ketone functionality.[26–28] This can be performed on post-consumer waste to upcycle the polymer. Hartwig and coworkers showed oxidation of several types of polyethylene (low density polyethylene [LDPE], high-density polyethylene [HDPE], and linear low-density polyethylene [LLDPE]) using a nickel catalyst and mCPBA as the terminal oxidant.[26] This strategy afforded functionalized polyethylene (ketones, alcohols, halides, esters) in up to 5 functionalities per 100 monomer units with minimal chain cleavage. However, this chemistry suffered from modest selectivity for hydroxylation and ketone formation. They then developed an oxidation protocol using a ruthenium porphyrin catalyst with a pyridine *N*-oxide oxidant.[28] Applied to several types of polyethylene, they found a nearly 1:1 ratio of ketones to alcohols with up to 4 mol % functionalization. Interestingly, they observed a decrease in T_m from 110°C to 101°C for LDPE with 0 and 3.8 mol % functionalization, respectively. These results are consistent with polyethylene-*co*-vinyl ether copolymers or independently synthesized polyethylene with alcohol functional groups. Upon mechanical testing, the authors found improved adhesive properties, consistent with improved surface wetting and further confirmed with water contact angles. Applying C–H oxidation of polyethylene on polymer waste enables polymer upcycling and access to new material properties.

COPOLYMERIZATION WITH C1 MONOMERS

In contrast to the polymerization of ketone-containing monomers or post-polymerization C–H oxidation, copolymerization with the C1 monomer carbon monoxide (CO) directly installs the ketone into the polymer backbone. It is attractive due to its availability and low cost.[14,16,29] Until recently, most copolymers synthesized using CO resulted in perfect alternation with the comonomer, dramatically enhancing the thermomechanical properties. However, developing drop-in, degradable replacements for commercial polymers requires new strategies that lower the CO incorporation.[30]

Transition-metal catalyzed copolymerization with CO

Transition-metal-mediated coordination polymerization is an important method for large-scale commercial polyolefin production.[31] This strategy was long used in the synthesis of linear, perfectly alternating polyketones.[29,32,33] By nature of the mechanism, the highly favored alternating insertion of the carbonyl followed by the C2 component necessitates the formation of perfectly alternating polyketone structures (Figure 3A).[34] Beautiful works in catalyst development by Nozaki, Sen, Brookhart, and Drent afforded regio- and stereocontrol and included copolymerization with polar monomers.[34–37] Shell Chemical commercialized these copolymers in 1996 but


A Traditional mechanism for perfectly alternating polyketones

B Catalysts that enable non-alternate insertion pathways

Figure 3. Transition metal insertion coplymerization of CO and ethylene

(A) traditional mechanism favoring alteration.

(B) bespoke catalysts disfavoring CO coordination relative to the C2 comonomer. Cationic or neutral refers to the active species during polymerization.

Adapted from Nozaki and Hiyama. [34] Copyright 1999, with permission from Elsevier.

discontinued production in 2000 due to processing difficulties brought on by limited solubility and high melt processing temperatures ($T_m \sim 260°C$). The induced dipole effect from the carbonyl units caused these less desirable properties.[23] Therefore, decreasing the carbonyl content by synthesizing non-alternating polyketones became crucial, requiring new advances in catalyst design.

Through steric and electronic catalyst redesign, the incorporation of CO has been tuned to attain low amounts of CO in milder reaction conditions (lower pressures) (Figure 3B). In 2002, Drent and coworkers first disclosed a neutral Pd(II) complex with asymmetric chelating ligands that copolymerized ethylene and CO in a non-alternating fashion where two or more ethylenes are inserted subsequently into the polyketone chain (Figure 3B).[38] By using a more electron-donating isopropyl group on the P-O ligand, Drent could generate copolymers with as much as 18.3% non-alternating ethylene insertions beginning with a 2:3 mol ratio of ethylene to CO. Although Drent did not report CO incorporation percentages, Nozaki and coworkers recently employed this reported catalyst using metal carbonyls as a source of CO to achieve low and isolated carbonyls into linear ethylene/CO copolymers.[39] They achieved as low as 0.14%–0.83% CO incorporation with >99:1 selectivity for non-alternating insertions using this protocol. Alternatively, in 2023, two separate reports combined electrochemical or photochemical and organometallic catalysts to engender carbon dioxide (CO_2)-derived polyketones.[40,41] Using a unique reactor design, they were able to integrate the two catalyst systems to simultaneously reduce CO_2 to CO and copolymerize under pressure of ethylene to generate alternating and non-alternating polyketones. They found that the molecular weights (MWs) and CO incorporation could be varied by applied current density and the organometallic catalyst, demonstrating the use of a traditional cationic Pd catalyst for perfectly alternating structures and the neutral catalyst reported by Drent in 2002. Challenges of this method include low catalyst activity at room temperature and low conversion of ethylene.

Later, Chen and Liu systematically studied the effect of strong electron-donating ligands of a cationic Pd catalyst that they had previously reported as a versatile ligand platform for copolymerizing ethylene with other polar monomers.[42] The electronically asymmetric diphosphazane monoxide (PNPO) ligand featured a strongly σ donating phosphine moiety and a weakly σ donating phosphine oxide moiety that allowed for ethylene and CO copolymerization to generate non-alternating copolymers with as low as 39% with 24.2% extra ethylene insertions at a 20:1 ethylene:CO feed ratio.

Using neutral Pd complexes with anionic phosphine-sulfonate ligands previously reported by Pugh, Sen, and coworkers further studied the effect of monomer feed ratios to obtain copolymers with a wide range of CO incorporations.[38,43] Under 9:1 ethylene:CO feed ratios, they obtained copolymers with 6% ketone incorporation.[38] Importantly, Sen subsequently revealed calculations of the thermodynamic parameters that suggest the neutral Pd complexes have small differences in binding affinities for ethylene and CO and that the rate of decarbonylation played a larger role in the degree of non-alternation.[43] Interestingly, the traditional cationic palladium complexes were found to have higher decarbonylation rates. By contrast, the neutral complex disfavored the formation of Pd-O chelates by coordinating the carbonyl group on the growing polymer chain (Figure 3A). As a result, ethylene coordination to the metal and subsequent insertion are facilitated.

In 2021, Mecking and coworkers introduced a neutral nickel (II) catalyst inspired by the precedent of neutral transition metal catalysts that show a lessened preference for binding CO.[44] In this report, they achieved 0.3% ketone incorporation with 79% isolated carbonyls and no alternating motifs at a 0.2 mol % CO feed ratio and demonstrated that the thermomechanical properties of these copolymers were like that of HDPE.[45] Later, Mecking and Baur used this system to terpolymerize methyl acrylate (MA) and CO with ethylene to generate linear polyethylene with isolated carbonyls and polar ester side-chain units.[46] They note that the solid-state structure of PE is retained, and although the catalyst activity is not adversely affected by polar comonomer, the MW is determined by chain transfer events after acrylate insertion.

Ultimately, these approaches are plagued by the limitation of use with polar vinyl monomers, restricting their application as commercial materials, and carbonyl clustering, which is not ideal for accessing effective degradable pathways. This non-alternating copolymerization strategy is suitable for achieving linear copolymers but is only feasible with ethylene as a comonomer.

Free-radical or controlled radical copolymerization with CO

An alternative to transition-metal-catalyzed copolymerization, free-radical polymerization uses the reactivity of the propagating radicals to tune the incorporation. Using radical methods results in less control over the structure and stereoregularity but allows the use of monomers with polar functional groups. The first polyketones were synthesized via free-radical polymerization at high temperatures (250°C) and extreme pressures (400 bar) of ethylene and CO, initiated by di-(tert-butyl) peroxide.[32,33] These copolymers were patented in 1941 by Farbenfabriken Bayer and in 1950 by DuPont. These methods obtained less than 50% carbonyl incorporation throughout the polymer and produced low-MW liquids to crystalline solids with poor physical properties.

Few developments in free-radical copolymerization with CO had been reported until 2020, when Mecking and coworkers produced and thoroughly characterized low-density polyethylene with in-chain ketones using free-radical copolymerization of ethylene and CO.[47] Extensive structural characterization showed the copolymer

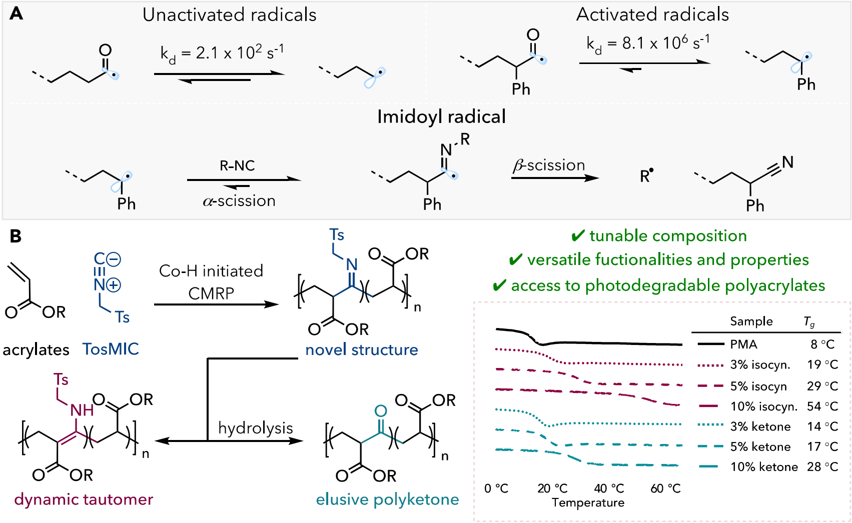


Figure 4. Radical copolymerization of isocyanides in place of carbon monoxide to access non-alternating polyketones

(A) unfavorable propoagation with CO compared to isocyanides.

(B) Three distinct polymer structures achieved through copolymerization and corresponding thermal properties.

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maintained desirable low carbonyl content within branched polyethylene (the majority of branching occurred in α-position to ketones) through temperature, solvent, and pressure modifications. They found that dispersion copolymerization led to a 5-fold increased branching density compared with solution copolymerization methods due to transfer reactions at the high local polymer concentration in the compartmented aqueous polymerization. Ultimately, the solubility of CO as a gas and the rate of decarbonylation make CO challenging to use in FRP. Furthermore, the control over the architecture will be limited due to the uncontrolled nature of the polymerization.

Mecking and coworkers recently reported a controlled polymerization method to copolymerize ethylene and CO using cobalt-mediated radical polymerization (CMRP).[48] In this report, an organocobalt species was generated to initiate and control the synthesis of non-alternating polyketones. The researchers found that the polymerization rate was enhanced in the presence of CO, which they propose stabilizes the cobalt complex by coordinating as a Lewis base. Notably, 2-methylene-1,3-dioxepane was terpolymerized with CO and ethylene. However, CO incorporation only occurred after ethylene addition. The MWs achieved were modest (∼5 kg/mol). Still, they noted that the polymer architecture was more controlled than ethylene homopolymerization under similar conditions with fewer termination events from ß-H transfer.

Controlled radical copolymerization with isocyanides

Although radical copolymerizations with CO and ethylene have successfully introduced predictable, low levels of incorporation, this strategy has not been broadly employed with other monomers. This limitation is likely due to the enhanced rate of decarbonylation, making it more challenging to introduce CO (Figure 4A).[15,32,33] Recently, we reported that isocyanides can be used as isoelectronic alternatives to CO in radical polymerizations (Figure 4B).[49] First, we showed that free-radical copolymerization of *p*-tosyl methyl isocyanide (TosMIC) with MA yielded a non-alternating poly(MA-*co*-TosMIC) copolymer.[50] Then, we implemented a novel cobalt-hydride (Co-H) initiated CMRP protocol as a complementary controlled radical copolymerization method.[51] The degree of incorporation was adjusted by changing the initial concentrations of the monomers. After examining the polymer microstructure, the imine was first revealed as the isolable kinetic product. Because of the proximity of the ester moiety to the imine, the backbone is favorably tautomerized to the β-enamine ester. Upon hydrolysis, the non-alternating polyketone microstructure can be accessed. Notably, the incorporation of the isocyanide dramatically affected the thermomechanical properties, while more modest increases were found upon hydrolysis. This approach enabled the flexible tuning of various structures and properties using a single copolymerization process.

DEGRADATION VIA PHOTOLYSIS AND POST-POLYMERIZATION MODIFICATIONS

Adding ketone units in polymers can offer a wide range of functional handles for various properties and modifications, thus expanding the versatility of these materials. One way to achieve this is by using the ketone units to derivatize the polymer, allowing for the installation of functional groups and introducing distinct properties. This process can increase the waste polyolefin value and facilitate the recycling of these materials. Therefore, these copolymers may serve as more environmentally friendly alternative plastics than the analogous homopolymers.

Traditional photodegradation pathways for polyketones

In 1935, Norrish discovered that ketones became photoexcited upon irradiation with UV light and underwent interesting transformations.[18,52] The carbonyl goes through a π^* or π to π^* transition into a triplet excited state. This results in homolysis of the C–O double bond, which then causes sp^3 rehybridization of the oxygen and carbon orbitals. This can result in a Norrish type I or II process upon relaxation. Norrish type I processes result in the corresponding alkyl and acyl radicals. By contrast, Norrish type II processes describe intermolecular rearrangement from γ-hydrogen abstraction, resulting in the corresponding ketone and alkene.

Polymer chemists quickly explored this unit's utility as a photodegradable unit in polymer backbones. Although polyolefin backbones are inert to chain scission, incorporating ketones would lead to lower MWs and enhanced degradation rates. Beginning in 1963, Guillet spent several decades examining polyketones, accomplishing many preliminary mechanistic and kinetic studies of the degradation rates and quantum yields of Norrish cleavage concerning the copolymer structures and crystallinity.[19,53,54] Photodegradation of polyketones was not revisited until recently in 2020 by Mecking.[47] First, the decomposition of copolymer films generated by free-radical polymerization (2%–10% ketone content, ~8–20 branches per 1,000 carbon atoms) was studied using UV light irradiation (350–400 nm) for a short timeframe (6 h). Overall, the films became brittle with loss of material properties, and the MWs decreased as the dispersities increased over time, with chain cleavage being promoted by the ketone groups. However, they noted that for copolymers with ≤6% ketone incorporation, portions of the MW of the film increased, implying crosslinking events may occur by the uncontrolled free-radical nature of Norrish reactions.

Subsequently, Mecking used the linear copolymer analog of low ketone composition (0.7%–2.3%) for a longer timeframe under conditions simulating natural sunlight (295–400 nm) at sea level in a marine- or limnic-like environment. Continuous weight

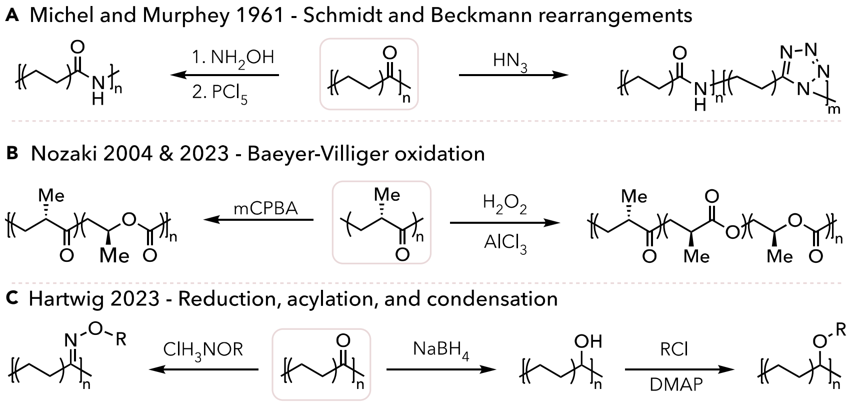

Figure 5. Diversification of polyketones to access other functionalities

(A) Introduction of non-alternating polyamides via rearrangement.

(B) Conversion of polyketones to polyesters.

(C) Multiple post-polymerization functionalizations of non-alternating polyketones.

loss and embrittlement were observed for all copolymers, which qualitatively increased with increasing ketone content, while the HDPE reference was unaffected. Importantly, photoinduced oxidation of the copolymers was observed, alluding to the promotion of further chain cleavage. In this way, the introduction of ketone groups can lead to continuous breakdown past the initial Norrish cleavage events. Nozaki then examined the photodegradability of linear copolymers with isolated carbonyls (0.41% and <0.02%) in powder form upon 275 nm light irradiation for 50 h.[39] The 0.41% ketone copolymer decreased significantly compared with the <0.02% ketone copolymer. These results highlight the capability of small amounts of ketone incorporation leading to dramatic MW loss.

Finally, our group demonstrated the degradation of polyacrylates with isocyanide incorporation in addition to the hydrolyzed ketone samples in solution at near-visible wavelengths (390 nm).[49] We found that degradation of the polyisocyanides was faster than that of polyketones, and chain scission amounts increased relative to their incorporation percentages. The enhanced degradation of the isocyanide copolymer could be attributed to the conjugation of the enamine ester, shifting the absorption to longer wavelengths, and increasing the strength of the absorption. Notably, both copolymer microstructures lent access to a photodegradable copolymer, whereas the parent homopolymer was stable under these conditions.

Post-polymerization modifications for polymer transformation

The ketone functional group can be leveraged as a handle for several transformations, giving new life to polymers to be repurposed or transformed.[55] A seminal work in 1952 by Brubaker, Coffman, and Hoehn describes various transformations on polyketones.[32,33] They note the quantitative hydrogenation of ketones to alcohols using a copper chromite catalyst. Treating with excess hydrogen cyanide in the presence of potassium cyanide catalyst revealed a polycyanohydrin (80% conversion of carbonyls). Adding aqueous hydroxylamine led to the formation of polyoximes (78% conversion). Finally, they oxidatively degraded the copolymers with nitric acid to yield a mixture of dicarboxylic acids.

In 1961, Michel and Murphey at Dupont, followed by Iwakura and coworkers, performed Schmidt and Beckmann rearrangements on aliphatic and aromatic polyketones to generate polyamides (Figure 5A).[56,57] Partial conversion to polytetrazole was formed using an excess of hydrazoic acid, while a stoichiometric amount formed the polyamide. They noted lower conversion of the aromatic polyketones, and no significant degradation of the polymers was observed after the rearrangement. Then, the formation of polyoximes was studied by condensing hydroxylamine onto the polyketone with high conversion (>90%). Upon treatment with phosphorous pentachloride, the polyoxime underwent the Beckmann rearrangement determined by characteristics in the infrared spectrum similar to the polyamides formed from the Schmidt with no evidence for extensive chain degradation.

Polyesters are an attractive class of biodegradable polymers typically synthesized by polycondensation of long-chain difunctional monomers. Copolymerization with CO_2 would be a great way to catalytically incorporate ester units into polymers that have not yet been realized due to the inertness of CO_2 to radical chemistry and the inertness of metal carboxylates to olefin insertion. Another avenue that has been explored by the Nozaki group starting in 2004 employed *m*-chlorobenzoic acid (*m*CPBA) to perform partial Bayer-Villager oxidation of perfectly alternating, optically active poly(propylene-*co*-ketone)s to generate random poly(ketone/ester)s (12% ketone to ester conversion) (Figure 5B).[58] Commercial polyesters accessed via ring-opening polymerization, like poly(3-hydroxybutyrate) (P3HB) or poly(L-lactide) (PLLA), undergo efficient biodegradation. In this way, similar structures to well-studied polyesters are generated, and the copolymer's photodegradability in this study is replaced or joined by biodegradability. However, biodegradation was never examined due to the inability to separate the polymers from *m*CPBA.

Upon methanolysis, the MW of the oxidized copolymers was diminished and resulted in oligomeric ketones, suggesting random ester incorporation. It is noted that although the oxidation was assumed to be regioselective, the determination of stereochemistry was inconclusive. Other oxidative conditions were examined; magnesium monoperoxyphthalate (MMPP) was inert, while trifluoroperacetic acid with Na_2HPO_4 or $CaCO_3$ as a buffer converted roughly 8% of the ketone units to esters. However, it was observed that the acidic nature of the conditions led to undesired spiroketal formation from the cyclization of the ketone units, which were then protected from oxidation. After that, Mecking studied the thermomechanical properties of the keto-ester polymers compared with HDPE to determine their viability as degradable replacements and reported that the melting point depression correlates linearly to the amount of incorporated functional groups.[59] They found that the photodegradation corresponded to the keto content, as esters are less prone to Norrish-type reactions, and the methanolysis occurred to complete conversion similar to previous reports.

More recently, Nozaki used more mild oxidants (aqueous hydrogen peroxide) on *R*-iso, *S*-iso, and atactic poly(propylene-*co*-ketone)s.[60] The use of these stereoregular copolymers was examined, motivated by the stereoregularity-dependent enzymatic degradability. These conditions led to the formation of some isolable peroxide units. Notably, $AlCl_3$ was employed as a promoter to suppress peroxide formation. They achieved up to 35% conversion of the ketone to the ester with steretention and confirmed moderate biodegradability. In all these copolymers, regiocontrol of the ester formation was not successful; however, there was a preference for oxygen insertion on the more sterically hindered side (2:1).

Recently, Hartwig's group explored a few functional transformations of polyketones (Figure 5C).[27] In this work, the ketone was controllably reduced to alcohol groups using sodium borohydride, which they then acetylated with various alkyl chlorides. The reduced copolymer could also be reoxidized to the ketone using ruthenium or Cp* catalysts in the presence of base. Poly(oximes) could then be accessed by adding the corresponding hydroxylamine or hydroxylamine hydrochloride salt. Treatment of the poly(oxime) with 20 wt % *p*-toluene sulfonic acid (PTSA) in wet tert-amyl alcohol cleaved the oximes to form the starting polymer in quantitative yield. Lastly, they examined the mechanical and adhesive properties of the various modified polyethylenes. The benzyloxy polymer possessed similar tensile strength but higher toughness and elongation at break than unmodified LDPE (roughly 4- and 5.5-fold, respectively). By comparison with a butyryloxy polymer, they determined that the enhanced mechanical properties stem from the interchain interactions of the esters. Tensile testing on catechol polymers revealed higher values than LDPE, with the tensile strength (33.6 ± 1.9 MPa) being comparable to commercial ionomers, attributed to the formation of cross-links of pendant catechol units. Through lap shear testing, the hydroxy (6.16 ± 0.59 MPa) and keto (4.67 ± 0.50 MPa) polymers were found to be more adhesive to aluminum compared with LDPE, owing to the hydrogen bonding capabilities. Interestingly, the oxime (6.03 ± 1.01 MPa) and carboxylic acid substituted oxime (6.68 ± 1.10 MPa) were comparable to the hydroxy, while the catechol (2.60 ± 0.53 MPa) polymers were not as adhesive. Overall, these adhesive strengths are comparable to commercial adhesives. Additionally, they reported lower contact angles of water droplets on the surface of the oxime and carboxylic acid substituted oxime polymer films (84.2° ± 4.3° and 86.1° ± 3.7°) compared with LDPE (97.0° ± 2.1°), demonstrating the increased hydrophilicity. Finally, they demonstrated that the solubility of these materials can be leveraged for their separation from a composite material.

CONCLUSIONS AND OUTLOOK

Although polyketones are a longstanding class of materials, new interest in these polymers as a degradable alternative to existing commercial polymers has witnessed the development of new polymerization strategies and catalyst development. Exquisite catalyst design has enabled the synthesis of HDPE with low percentages of in-chain ketones to provide degradability while maintaining desired properties. Similarly, free-radical polymerization provides LDPE polyketones, or controlled radical polymerization provides terpolymers with unique properties. Additionally, identifying other comonomers like isocyanides or ketone-containing monomers allows the synthesis of new polymer microstructures. Future work in catalyst development or polymerization strategy should target more defined control over polymer sequence and the extension to more polar or activated monomers. Leveraging the ketone functionality for further post-polymerization modifications is an exciting, underexplored opportunity.

Studies into the degradation of these polymers are still in their infancy. Although photooxidative degradation, the naturally occurring degradation pathway for most polyolefins, is well-known for the eventual degradation of these polymers, including in-chain ketones, their effect on the rate and product distribution is still under investigation. What remains to be elucidated is the desired degree of incorporation for a specific rate of environmental degradation. Will these polymers degrade quickly into microplastics, or will the inclusion of in-chain ketones cause an autocatalytic effect to enhance degradation further? Can these microplastics or oligomers be feedstocks for microorganisms to finish the degradation process? These revelations hold profound significance in designing future materials and determining the fate of plastic waste, echoing the interconnectedness of our science with the world around us.

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AUTHOR CONTRIBUTIONS

L.C., C.A.H., and E.E.S. prepared the outline of topics for this perspective. L.C., C.A.H., and E.E.S. wrote and edited the paper and approved the final version of the manuscript.

DECLARATION OF INTERESTS

E.E.S. is a member of the *Chem* Advisory Board.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES IN THE WRITING PROCESS

During the preparation of this work, the author(s) used Grammarly to edit prose. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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