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Polymer Degradation Mechanisms and Emerging Strategies for Sustainable Plastics

Sihao Chen

The University of California, Berkeley, USA
cshmmua@gmail.com

Abstract: Plastic waste is becoming an increasing environmental problem owing to the durability, chemical inertness, and poor recyclability of most traditional plastics. New developments in polymer chemistry are offering various types of degradability mechanisms which can address physical, catalytic, thermal, photochemical, and hydrolytic routes toward catalyzed depolymerization to enable closed-loop material cycles. Mechanochemical routes employ force-responsive mechanophores to accomplish gated or cascade degradation, and metal catalyzed systems—including MOFs, redox catalysts, and organometallic complexes—to selectively cleave bonds and recover monomers under mild conditions. Thermal and photochemical degradation routes are improved with catalytic additives, porous organic photocatalysts, and photo responsive backbone designs, providing clean and energy-saving ways. Hydrolytic approaches including those involving the hydrolysis of polyesters and polycarbonates exploit structural features as well as catalytic scaffolds to enhance ecologically significant rates of hydrolytic decomposition. Together, these new approaches demonstrate how combining smart degradability, closed loop depolymerization, and environmentally triggered breakdown into future polymer design, contributing to a more sustainable and circular plastic economy.

Keywords: Polymer degradation, Mechanochemistry, Metal-catalyzed depolymerization, Thermal degradation, Photodegradation

1. Introduction

Plastic pollution is a global problem caused by the persistence and inertness of traditional polymeric materials; their chemical stability leads them to decompose very slowly, leading to microplastic build-up and future environmental effects. To overcome these obstacles, researchers proposed various methods which induce degradation by mechanochemical stimulation, catalytic degradation, thermal degradation, photodegradation, and hydrolytic degradation which could be used to selectively degrade polymers in an energy efficient manner for a sustainable economy.

2. Mechanochemical degradation

Mechanochemical degradation is defined as utilizing a mechanical force to activate certain chemical moieties present within polymer backbones. The moieties, which are called mechanophores, break (bond scission) or change their structure (structural rearrangements) under the influence of tension , grinding, or sonication .

Mechanically gated acid-labile systems were first reported by Lin and Craig, who found that incorporation of acetal-based mechanophore in the polymer backbone inhibits premature acid hydrolysis. Once mechanically triggered, however, the exposed ketal is acid-labile and rapidly cleaved to allow for a force-triggered degradation [1]. This concept ensures stability during use while enabling controlled depolymerization.

To balance this between stability and degradability, Hsu and coworkers developed a cyclobutene-fused lactone system wherein the fused ring stabilizes the polymer against hydrolysis at ambient conditions. Mechanical activation opens the fused ring, transforming the backbone of the polymer into a linear polyester, which is then degraded by hydrolysis [2].This force-driven transition enables durable polymers to be depolymerized at end-of-life.

Craig's group also extended mechanophore chemistry with the development of bicyclic systems undergoing multiple step mechanochemical cascades. These systems underwent forced coupled rearrangement and lactonization reactions after initial ring opening, allowing for more than a single chain scission to occur per acti- vation [3]. This can lead to faster degradation rates compared with only allowing one chain scission at a time.

Another major advance is mechanochemical conversion to deploymerizable polymer. Hsu et al. demonstrated that the application of mechanical activation converts stable cyclobutene-fused monomers to a low ceiling-temperature repeat unit that readily depolymerizes back to monomer [4]. This enables full chemical recycling via force-mediated backbone modification.

In addition, Diesendruck showed that also halogen containing polymers are subject to a mechanochemically induced heterolytic unzipping, to generate reactive intermediates which propagate depolymerization along the chain [5]. This process offers a way to efficiently degrade low-ceiling-temperature polymers.

A mechanochemical route to make acid degradable polyenolethers has been presented by Yang and Xia. They synthesized cyclobutene fused ethers, which are hydrolytically stable, but become enol ether after milling. These enol ether bonds readily cleave in aqueous solution at low pH values [6]. In combination, these mechanochemical systems demonstrate that the lifetime of a polymer may be controlled using applied forces.

3. Metal-catalyzed degradation

The transition metal catalyst enables the catalytic, selective breaking of bonds allowing for depolymerisation to take place at milder, more controlled conditions.

The Zr-based MOFs such as UiO-66 have also proven able to catalyze the depolymerization of PET into terephthalic acid in good yield. During the reaction, the transformation of UiO-66 to MIL-140A reveals additional Zr Lewis-acid sites for enhanced catalytic ester cleavage [7]. This transition is not only solventless but also energy efficient.

Vinyl polymer degradation is not limited to organic catalysts. Kimura et al. introduced carbon–halogen bonds along vinyl backbones, which are normally inert, but can be selectively scissed by Fe(II) and tertiary amines [8]. This allows for switchable, degradation on demand.

Ma et al., showed SaBOX/copper catalysts can selectively cleave PMMA based copolymer with α-chloroacrylate units at 65–100°C, these copolymers are efficiently depolymerized, and their degraded products can be repolymerized, which allows for a true upcycling [9]. Hydrosilylation routes have also been used to achieve depolymerization of oxygenated polymers. Monsigny et al. demonstrated that Ir(III)catalysts drive hydrosilylation-assisted cleavage of PET, PLA, and PC, to form silylated intermediates at much lower temperature than pyrolysis [10]. This approach leads to well-defined molecular fragments amenable to reuse. The zinc has also been used in effective PLA depolymerisation. Payne and Jones showed that Zn(II) complexes transform PLA to methyl lactate under milder conditions, enabling closed loop chemical recycling [11]. Such advances illustrate that metal catalysts are versatile tools for polymer sustainability.

4. Thermal degradation

The thermal process usually includes the production of radicals and random chain scission that occurs at high temperature. Recent developments aim to enhance the selectivity and decrease the number of toxic by-products.

NiPIm based nanocomposites accelerate thermo-oxidative degradation of PE, PVC, and PS through the catalyzed generation of reactive oxygen species [12]. Catalyst lowers the activation energy for overall degradation. Catalytic nano-additive could change the mode of degradation of PMMA. Bahadur et al demonstrated that nanoparticles of AlI3 alter the PMMA decomposition behavior, minimizing formation of toxic by-products [13]. This demonstrates how the chemistry of thermal degradation can be tailored using additives.

For complex polymeric mixtures like PET/PLA specific modelling is needed. Researchers used the random chain-scission kinetics to better describe their pyrolytic behavior, promoting better prediction of the mixed plastics recycle [14]. Hydrothermal Fenton chemistry has shown great potential on microplastics remediation. Hu et al. showed PE microplastics could be degraded faster by combining hydrothermal treatment and hydroxyl radical production from Fenton system [15]. The combined approach provides enhanced oxidative cleavage and polymer accessibility.

5. Photodegradation

The photodegradation requires the use of UV or visible light for generating radicals which oxidizes polymer chain. Porous organic polymers (POPs) have been considered as a photocatalyst. Benzotriazole based POPs activate O_2 and degrade tetracycline efficiently under visible light with high efficiency [16]. Porphyrin based POPs are used as photo-Fenton catalyst under neutral pH, allowing for environmentally compatible pollutant degradation. Another important direction is the photo responsive backbone design, such as [17]. Photo responsive backbone designs represent another major direction. Kubota and Ouchi developed alternating copolymers with o-nitrobenzyl ether pendants that undergo rapid photolysis and subsequent backbone cleavage upon UV exposure [18]. This enables precisely timed polymer degradation. Environmental photodegradation is more complex than single-polymer systems. Liu et al. found that polystyrene microplastics accelerate the photodegradation of polypropylene through photosensitization and release of reactive organic compounds [19]. This demonstrates synergistic degradation pathways in mixed microplastics. ROMP-derived acylsilane-containing polymers offer clean photodegradation pathways. Huang et al. showed that acylsilane units undergo Norrish-type cleavage under 390 nm light, producing defined small-molecule fragments suitable for biomedical applications [20].

6. Hydrolytic degradation

Hydrolysis plays a central role in the degradation of polyesters, polycarbonates, and other heteroatom-containing polymers. De Hoe and Hillmyer introduced alkenes into polyacrylate backbones, which can be cleaved by ozonolysis to initiate controlled degradation without compromising properties during use [21]. Kim et al. enhanced polyester degradability by incorporating salicylate units. These motifs accelerate hydrolysis in seawater and alkaline environments due to intramolecular catalysis while maintaining mechanical performance [22]. Graphene oxide has been shown to accelerate PLA degradation by promoting water diffusion and assisting ester bond cleavage [23]. This is particularly valuable for biodegradable scaffolds requiring controlled resorption. Hydrophilicity tuning also improves hydrolysis rates. Pesenti et al. demonstrated that MDO-based copolymers with hydrophilic vinyl ether or glycosylated units degrade more rapidly due to increased water uptake [24].New hydrolysis-resistant yet recyclable polycarbonates have also been developed. Xu and co-workers synthesized long-chain aliphatic polycarbonates that are durable in use but chemically recyclable under specific conditions [25].

References

[1] Lin, Y.; Kouznetsova, T. B.; Craig, S. L. Mechanically Gated Degradable Polymers. J. Am. Chem. Soc. 2020, 142, 2105–2109.
[2] Hsu, T. G.; Zhou, J.; Su, H. W.; et al. A Polymer with "Locked" Degradability: Superior Backbone Stability and Accessible Degradability Enabled by Mechanophore Installation. Nat. Commun. 2020, 11, 4987.
[3] Lin, Y.; Kouznetsova, T. B.; Chang, C.-C.; Craig, S. L. Enhanced Polymer Mechanical Degradation through Mechanochemically Unveiled Lactonization. Nat. Commun. 2020, 11, 4987.
[4] Hsu, T. G.; Liu, S.; Guan, X.; et al. Mechanochemically Accessing a Challenging-to-Synthesize Depolymerizable Polymer. Nat. Commun. 2023, 14, 225.
[5] Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; et al. Mechanically Triggered Heterolytic Unzipping of a Low-Ceiling-Temperature Polymer. Nat. Chem. 2014, 6, 623–628.
[6] Yang, J.; Xia, Y. Mechanochemical Generation of Acid-Degradable Poly(Enol Ether)s. Chem. Sci. 2021, 12, 4389–4394.
[7] Wu, Y.; Wang, X.; Kirlikovali, K. O.; et al. Catalytic Degradation of Polyethylene Terephthalate Using a Phase-Transitional Zirconium-Based Metal–Organic Framework. Angew. Chem. Int. Ed. 2022, 61, e202117528.
[8] Kimura, T.; Kuroda, K.; Kubota, H.; Ouchi, M. Metal-Catalyzed Switching Degradation of Vinyl Polymers via Introduction of an "In-Chain" Carbon–Halogen Bond as the Trigger. ACS Macro Lett. 2021, 10, 1535–1539.
[9] Ma, Y.; Zhao, Y.-N.; Yang, X.-M.; et al. SaBOX/Copper-Catalyzed Synthesis, Degradation, and Upcycling of a PMMA-Based Copolymer. Macromolecules 2023, 56, 7032–7042.
[10] Monsigny, L.; Berthet, J.-C.; Cantat, T. Depolymerization of Waste Plastics to Monomers and Chemicals Using a Hydrosilylation Strategy Facilitated by Brookhart's Iridium(III) Catalyst. ACS Sustain. Chem. Eng. 2018, 6, 10481–10488.
[11] Payne, J.; McKeown, P.; Mahon, M. F.; Emanuelsson, E. A. C.; Jones, M. D. Mono- and Dimeric Zinc(II) Complexes for PLA Production and Degradation into Methyl Lactate – A Chemical Recycling Method. Polym. Chem.2020, 11, 2381–2389.
[12] Aravind, R.; Sahu, A. K.; Brahma, G. S.; Swain, T. Investigation on the Thermo-Oxidative Degradation of PE, PVC, and PS Using NiPIm Nanocomposites. ACS Omega 2021, 6, 29869–29881.
[13] Bahadur, A.; Iqbal, S.; Alsaab, H. O.; et al. Thermal Degradation Study of PMMA with AlI_3 Nanoadditive. Microsc. Res. Tech. 2022, 85, 1494–1501.
[14] Xu, Y.; Li, Z.; Zhu, K.; et al. Thermal Degradation Behavior of PET/PLA Blends. Polym. Degrad. Stab. 2022, 204, 110103.
[15] Hu, K.; Zhou, P.; Yang, Y.; et al. Degradation of Microplastics by a Thermal Fenton Reaction. ACS ES&T Eng. 2022, 2, 110–120.
[16] Qin, Y.; Jiang, Z.; Guo, Y.; et al. Benzotriazole-Based POP Enhancing O_2 Activation for Degradation under Visible Light. Chem. Eng. J. 2023, 460, 141810.
[17] Gao, W.; Tian, J.; Fang, Y.; et al. Visible-Light-Driven Photo-Fenton Degradation by a Porphyrin-Based POP at Neutral pH. Chemosphere 2020, 243, 125334.
[18] Kubota, H.; Ouchi, M. Rapid and Selective Photodegradation of Polymers via o-Nitrobenzyl Ether Pendants. Angew. Chem. 2023, 135, e202217365.
[19] Liu, P.; Li, H.; Wu, J.; et al. PS Microplastics Accelerate PP Photodegradation. Water Res. 2022, 214, 118209.
[20] Huang, B.; Wei, M.; Vargo, E.; et al. Backbone-Photodegradable Polymers Incorporating Acylsilane Units via ROMP. J. Am. Chem. Soc. 2021, 143, 17920–17925.

[21] De Hoe, G. X.; Zumstein, M. T.; Tiegs, B. J.; et al. Sustainable Polyester Elastomers from Lactones: Synthesis, Properties, and Hydrolyzability. J. Am. Chem. Soc. 2018, 140, 963–973.
[22] Kim, H. J.; Hillmyer, M. A.; Ellison, C. J. Enhanced Polyester Degradation via Transesterification with Salicylates. J. Am. Chem. Soc. 2021, 143, 15784–15790.
[23] Shuai, C.; Li, Y.; Yang, W.; et al. Graphene Oxide Accelerates Ester Bond Hydrolysis in PLLA Scaffolds. Int. J. Bioprint. 2020, 6, 249.
[24] Pesenti, T.; Gillon, E.; Ishii, S.; et al. Hydrophilicity-Enhanced Hydrolysis of MDO-Based Copolymers. Biomacromolecules 2023, 24, 991–1002.
[25] Xu, Z.-W.; Pan, J.-L.; Xu, J.; et al. Reprocessable, Hydrolysis-Resistant Long-Chain Polycarbonates. ACS Appl. Polym. Mater. 2024, 6, 1551–1562.