

Synthetic Route And Application of Photodegradable Polymers

Haotian Yan ^{1,*}

¹College of Letters, Arts, and Science, University of California, Berkeley, California, United States

*Corresponding author: hyan2024@berkeley.edu

Abstract: With the accumulating mass of land wastes, designing end-of-life principles for plastic wastes is becoming one of the most debated topics for polymer scientists. A developing family of materials called photodegradable polymers carries great environmental and commercial values. Photodegradable polymers will engage in photolysis under specific wavelengths, resulting in cleavages on the polymer backbone and smaller molecular weights. This research will discuss standard methods of photodegradation, such as Norris I&II, along with common photodegradable polymers and their functionalities. Examples of photodegradable polymers illustrated are polybutadiene, isotactic poly(propylene oxide) (iPPO), polylactide (PLA), and polystyrene. In Particular, this research used polystyrene as an example to explain the common degradation steps of photodegradable polymers. Nevertheless, the synthetic route and plans utilized for those polymers are discussed, shedding light on future possibilities in this field. Promising directions, such as metal-organic polymers with metal-to-metal bonds that can be synthesized through ring-opening metathesis polymerization (ROMP) are touched upon by the end of the research, introducing possible future implications in polymer science.

Keywords: Polymer Design, Photodegradable Polymer, Ring-Opening Mechanism.

1. Introduction

As the growing concerns of environmental and biodiversity protection, degradable polymers have been put into the light of chemical research in recent years. The growing demand for plastic polymer products has enormously increased in the past few decades, resulting in huge volumes of municipal solid waste way surpassing the landfill capacity. Plastic wastes of different sizes have been collected in the most significant concentrations, near metropolitan areas, in enclosed seas, and at water convergences. Lesser concentrations on distant island coastlines, the continental shelf seafloor, and the deep sea and the Southern Ocean, where there is nevertheless a recorded presence, are observed. Plastic has a projected lifespan of hundreds to thousands of years, although it is likely to be much longer in deep marine and non-surface polar settings. Plastic waste could injure birds, animals, and marine creatures, causing great harm to countless species across the globe. Unfortunately, many of the polymers the general public utilizes are non-degraded, as they contain additives that prevent their natural degradation process, which will have long-lasting negative impacts on the environment. As a result, the research of degradable polymers as possible substituents has been brought to public attention [1-6].

Currently, there are two effective methods aiming to address the issue of plastic waste accumulation: One of them targets recycling the current plastic waste into benign products. Recycling is one of the most vital actions currently available to reduce the impacts and represents one of the most dynamic areas with inside the plastics employer today. Recycling offers opportunities to reduce oil usage, carbon dioxide emissions, and the quantities of waste requiring disposal. While plastics have been recycled due to the fact the 1970s, the quantities which is probably recycled vary geographically, in step with plastic-type and application. Recycling packaging materials has seen rapid expansion over the past long term in a few countries. Advances in the era and systems for the collection, sorting, and reprocessing of recyclable plastics are developing new opportunities for recycling. With the combined actions of the public, employers and governments, it can be viable to divert the majority of plastic waste from landfills to recycling over the subsequent long term. At the same time, the other focuses on redesigning the plastic structure, making them self-degradable. In

this paper, it will emphasize and elaborate more on the second approach, namely the current innovations and challenges around degradable polymers.

The common degradable polymers utilize either photodegradation, biodegrading, or thermal degradation methods. In this paper, it will focus on explaining the synthetic route and application of photodegradable polymers. To achieve photo degradability, researchers rely heavily on the mechanism of photolysis, which means molecules have been broken down into smaller pieces with the presence of light. There are two major ways of photolysis, direct and indirect photolysis. Molecules will absorb UV lights, which will eventually result in the breakage of the weaker bonds resulting in optical dispersion in direct photolysis. Meanwhile, photosensitizers (oxygen, hydroxyl, etc.) could engage in the disintegration of light, resulting in indirect photolysis. One of the main goals when designing photodegradable polymers is that researchers can carefully tune the polymers to photolysis (either direct or indirect) at specific wavelengths and intensities. The previous work and review on polymers focused mainly on researching the exposure to light radiation of polymers that were not designed to be photodegradable. PMMA, as an example, has been researched extensively in the 80s for its photolysis properties under different testing conditions. However, these polymers failed to achieve either material or chemical properties other than photolysis, and photoresponsive polymers were designed to address such issues [1-3]. On the other hand, tensile and temperature are known to be the two major contributing factors when deciding the degradability of certain materials, yet there has not been any research studying the performance of photo-degradable polymers under such conditions. This lack of research prevents these plastics from being utilized in commercial industries.

2. Designing goals for photodegradable polymers

When sunlight reaches the earth's surface, the wide range of wavelengths (from ultraviolet to visible light to infrared light) provides a wide spectrum. Infrared light, visible light, and ultra-violet light have wavelengths of >700 nm, 700-400 nm, and <400 nm, accordingly. Nevertheless, photons with wavelengths of 700, 400, and 300 nm contain 170, 300, and 390 kJ/mol of energies, respectively. As mentioned earlier in the previous section, molecules can engage in direct photolysis by absorbing energies from light. The strength of C-C and C-H bonds are approximately 420 and 340 kJ/mol, which falls in the range of UV light and some of the stronger visible light photons, providing researchers with possibilities to design photodegradable polymers. However, the complicated mega structure of polymers creates difficulties in measuring the energy needed to degrade certain polymers. The presence of aromatic and unsaturated groups will affect the bond-breaking process during photolysis, making the molecule more subjective to the presence of light. These groups are abundantly used in polymer designs.

3. Photodegradation of polystyrene

Polystyrene (PS) is one of the most well-studied photodegradable polymers in the market now. The aromatic ring in its backbone provides feasible photodegradation applications to the polymer. Under a light in correct wavelengths, polystyrene undergoes photooxidative degradation, resulting in the breakage of monomer links and polymer chains. The reaction is relatively radical, and it lowers the molecule weight of compounds and alternates their mechanical and chemical properties. Polystyrene usually uses photodegradation in the range of 250-400 nm, and the reaction can occur under normal sunlight [7]. Different mechanisms for the degradation process for PS have been proposed over the decade and are yet to be agreed upon. The complex kinetics system and the wide variety of photodegradation side products have made the mechanism even more unpredictable. A classic mechanism of PS degradation is composed of four major parts: radicalization, photolysis, chain scission, and polyene radical intermediation, and here it will touch upon each of them in the following part of this research.

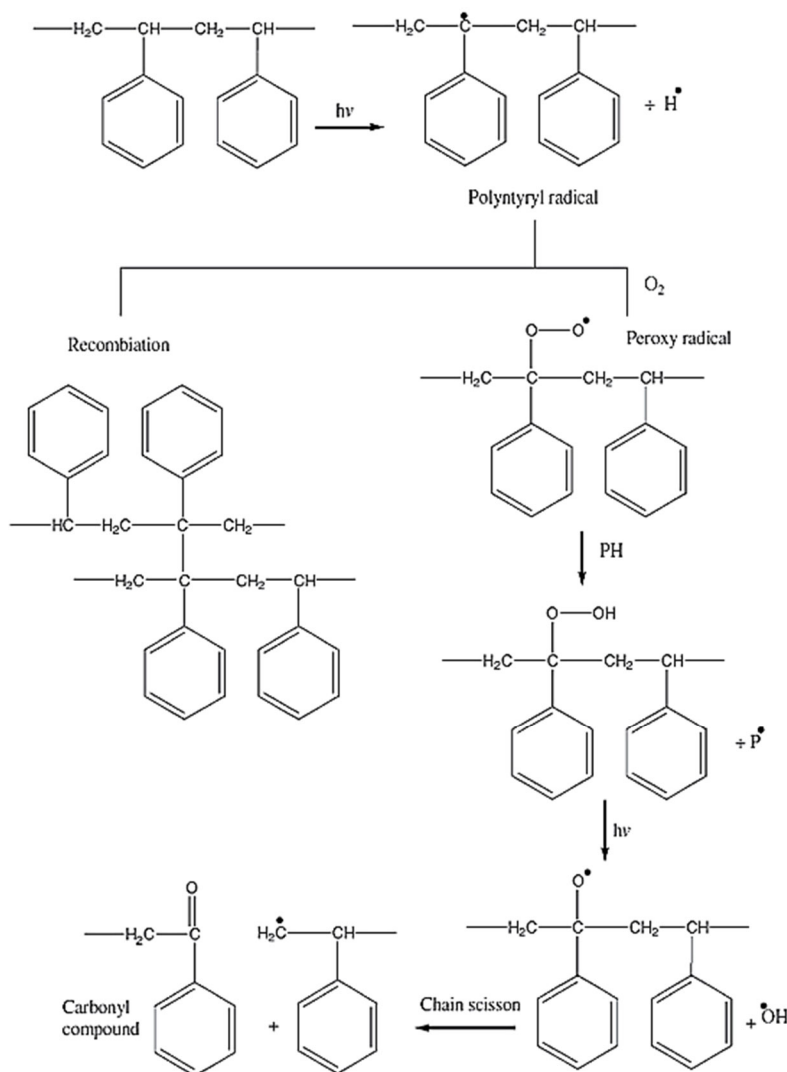


Figure 1. The photodegradation mechanism of polystyrene [7]

Figure 1 shows the photodegradation mechanism of polystyrene [7]. For radicalization, the radicalization process emphasizes the carbon connected to the ring. The carbon is being radicalized, releasing H, and giving the carbon a free electron. The positive charge is later connected to O_2 from the atmosphere, leading to a peroxy radical. The peroxy radical later reacts with another PS, forming a PS hydroperoxide, similar to the initiation reaction. For photolysis, in the presence of light, the PS hydroperoxide turns into an alkoxy radical, releasing HO into the environment. For chain scission, the carbonyl group and the PS radical are being separated, resulting in a shorter chain and a lower molecular weight. For polyene radical intermediation, after the scission, conjugate alkenes are formed throughout the aliphatic portion of the chain through polyene radical intermediation, which allows the polymer to be more easily radicalized. In general, the four major mechanism steps reflect how the photodegradation process of PS is initiated under atmospheric oxygen [7].

4. Photodegradation of aliphatic polyesters

Aliphatic polyester attracts research attention for its photodegradable functionalities as it can be prepared from renewable biomass (Unlike the majority of other polymers relies heavily on fossil fuels), and it can be recycled and decomposed easily with low environmental effects. As shown in Figure 2, aliphatic polyesters also possess great commercial and industrial values: taking polylactide (PLA) as an example, as one of the aliphatic polyester family, industries producing more than 10

million kilograms per year, and they utilize numerous fields, such as food packaging and clothing industries [1].

However, polylactide has its limitations. Polyesters such as polylactide rely heavily on homopolymers, which are single monomers, to define their functionalities. The limiting functionality of homopolymers restrains the possibilities for polyesters like PLA, and researchers throughout the years have been focusing on using creative methods to enable PLA for broader, more diverse applications. And two methods were mentioned. The first strategy focuses on preparing PLA-rich polymer blends and integrating them into aliphatic polyester block polymers. The method is appealing since the mechanical property (strength, tacticity, etc.) can be improved depending on the blends. With the synthetic strategy mentioned above, photodegradable polylactide polymer species were made possible. Take poly(L-lactic acid) (PLLA) as an example: as a plant-derived polymer that is widely used in numerous applications, it can expose under the exposure of UV light. Under UV light, PLLA will break into smaller molecular weight segments and form C=C double bonds under the Norrish mechanism explained earlier in this research [6]. However, PLLA fragments are too fragile to support more diverse mechanical applications as the photodegradation process proceeds via the bulk erosion mechanism, leading to overregulation. To improve their properties and to be hydrolysis-resistant, the method of stereocomplexation with PLLA and poly(D-lactic acid (PDLA), enantiomer of PLLA is frequently utilized. Using solution casting and spinning methods, the blends of PLLA and PDLA can combine and crystallize, forming PLLA/PDLA blends. The combined PLLA/PDLA blends contain different amorphous regions than neat PLLA and PDLA, which significantly affect their photodegradation behaviors. Studies have shown that PLLA/PDLA blend films are, in general, more photodegradation-resistant than pure PLLA or PDLA. The blend films also show higher tensile strength and elongation, allowing them to perform in more industrial or commercial applications [1].

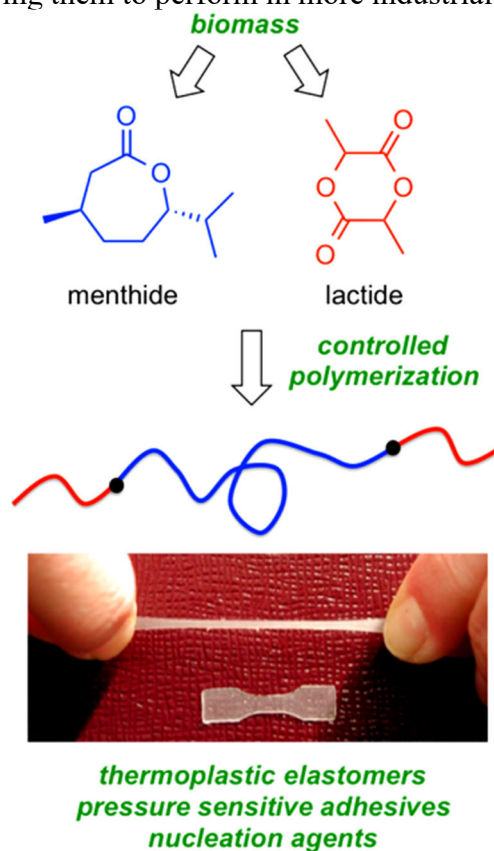


Figure 2. Synthesis and application of aliphatic polyester block polymers [1]

However, the method mentioned above required in-depth research to establish fundamental structure-property correlations, and its resulting products are still not wholly renewable and degradable. An alternative method suggested utilizes ABA triblock copolymer synthetic methods, which is polymers being synthesized with distinct polymer segments in A-B-A fashions. This method

not only made the properties of the polymer tunable but also more cost-efficient than aliphatic polyester block copolymers. With A (glassy) and B (rubbery) chosen to be thermodynamically incompatible subunits, the polymer can be self-organized, with designated properties designed by researchers.

5. Designing desirable photodegradable polymers

According to the previous paragraphs, researchers could use certain design mechanisms to create polymers with designated properties. Research carried out by Prof. Bryce Lipinski and his colleagues in 2020 focused on synthesizing highly isotactic poly(propylene oxide) (iPPO) that has addressed the issue of previous photodegradable polymers [3]. The previous polymers, such as isotactic polypropylene (iPP), high-density polyethylene (HDPE), and polyamides (PA), have been well-researched and were widely utilized in industries. Although they possess photodegradabilities, the hydrocarbon backbone of iPP and HDPE hinders the rate of their degradation process, making the process less efficient. Nevertheless, the material properties of these polymers are not ideal as well. They are too facile to be practiced in certain settings, adding to their uncontrolled and incomplete degradation, making them less ideal for commercial practices. Therefore, iPPO was brought to the attention of the researchers; higher degrees of tacticity in iPPO will increase the crystallinity of the polymer, resulting in increased mechanical strength, which is critical for a variety of applications. The higher tacticity of PPO may allow for mechanical capabilities similar to iPP while containing ether linkages vulnerable to photochemical breakdown.

Although seeming ideal at first glance, the end-of-life design of polymers remained unclear. The breakage of polymers will result in the creation of microplastics, whose toxicology and environmental impacts remain unclear. The iPPO, on the other hand, becomes more ideal since its amorphous analog atactic poly(propylene oxide) (aPPO) has been reported to have low environmental persistence. Utilizing enantioselective catalysts, researchers can successfully synthesize iPPO. The iPPO has shown potential as a high-strength photodegradable polymer for use in ambient environments. The maximum strength of this substance is generated through strain hardening, similar to that of nylon-6,6. Under prolonged UVA exposure, iPPO also photodegraded within 30 days by 75%. This research has shed light on enabling iPPO to be used as a nylon-6,6 substitute with limited toxicology and environmental impacts.

6. Synthesizing backbone-photodegradable polymer

Through years of effort trying to apply creative methods when synthesizing photodegradable polymers, recent researchers have discovered the method of ring-opening metathesis polymerization (ROMP). Unlike the previous efforts focusing on studying the photosensitive properties of the already existing polymers, ROMP allows scientists to introduce facile photodegradability into the backbone of polymers, endowing the previously non-photosensitive polymer photo degradability. The backbone-photodegradable polymer, in definition, is polymers containing a photodegradable backbone, which enables them to conduct photolysis under certain wavelengths. One of the most commonly used photolysis methods is Norrish photocleave, which creates a cleavage of a ketone, reducing free radicals to form nanoparticles [2].

With the development in monomer designs, certain monomers with degradable functionalities, such as enol ethers, acetals, animals, and silyl ethers, were brought to the attention. The ROMP methods can be used to combine ketone-containing polybutadiene with polylactide. The resulting polymer was able to degrade through a Norrish photocleavage under UVC light (280 nm). This has shrouded light on the possibilities for using ROMP to combine monomers with photodegradable functionalities into the backbone. In addition, copolymers can be also synthesized through ROMP with photodegradable functionalities. As shown in Figure 3, the copolymer reported can cleave its

backbone, under the irradiation of 52 W, 390 nm Kessil LED, in both liquid and solid state, generating low molecular weight heteroelechehc fragments.

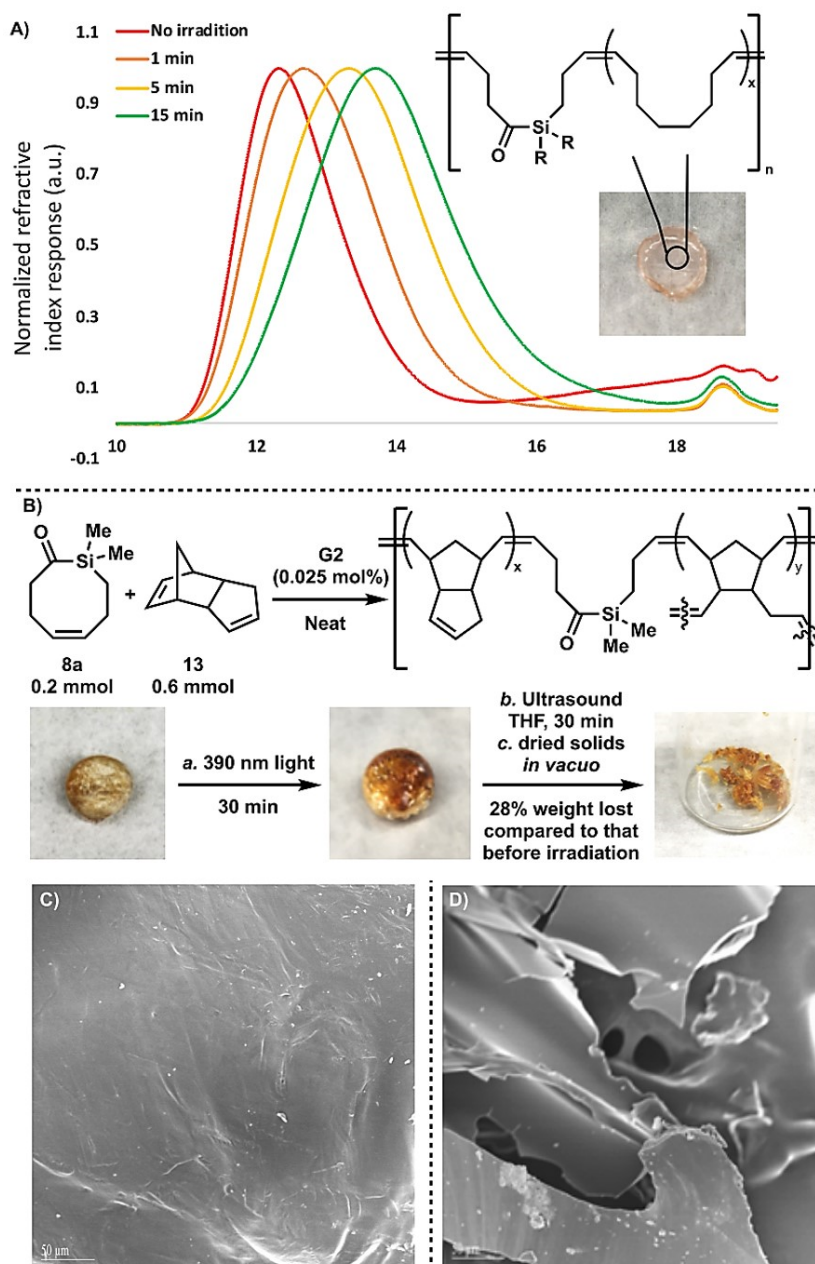


Figure 3. The photodegradation performance of acylsilane copolymers [2]

7. Metal containing photodegradable polymer

Utilizing the ROMP method mentioned in the previous chapter, researchers can combine different function groups and monomers within polymer design. One promising design is adding a metal element into polymer structures. Because they combine the processability with the redox, magnetic, and catalytic capabilities of metals, metal-containing polymers are intriguing materials. Despite their usefulness, there are few synthetic methods for metal-containing polymers and synthetic difficulties still exist. In particular, the metal-metal bond (M-M bond) within the backbone of the polymer enables the polymer to possess photochemical properties. The M-M bond can form cleavages until a certain wavelength, breaking up large polymer chains into microplastic segments [4].

The general synthetic method uses step polymerization techniques, which substitute the cyclopentadienyl rings with designated function groups, which in this are monomers containing metal

bonds. However, the limitation of this method is due to the relatively fragile M-M bonds, which may lead to bond failure under harsh synthetic processes. The ROMP methods, on the other hand, are potentially versatile to address such issues. An organometallic polymer with ferrocene units in its backbone can be synthesized using ROMP [5]. For example, an organometallic divinyl molecule can be synthesized, as shown in Figure 4. These polymers were created by converting ferrocenophane monomers into large molecular-weight polymers. These polymers were intended to make use of the thermal, redox, and optical characteristics that the ferrocene units impart.

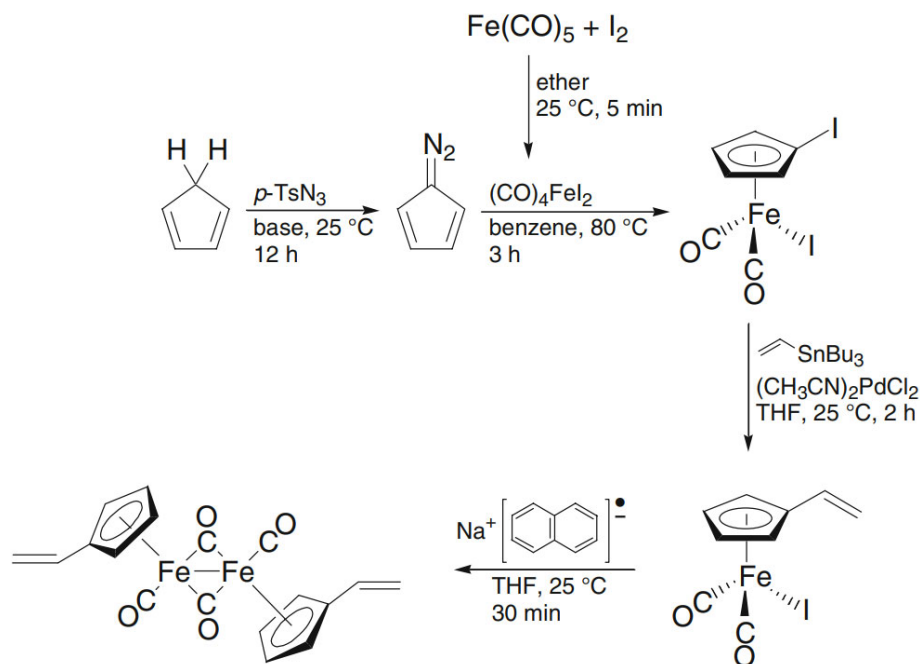


Figure 4. Synthesis of organometallic divinyl molecule [5]

Creating polymers with metal-metal linkages in their backbones is a challenging and mostly untapped field [8-10]. Although great progress has been achieved in this field, it is still difficult to create reliable techniques for creating well-defined, high MW polymers with metal-metal connections. These difficulties can be potentially solved with the ROMP method, providing polymers with higher molecular weights. The main difficulty in creating these approaches is creating cyclic monomers with M-M bonds with enough ring strain to advance polymerization. Unfortunately, it is often difficult to synthesize such organisms.

8. Conclusion

A relatively recent field of study, the synthesis of photodegradable polymers has already produced novel photolabile structures aimed at particular applications with prospective applications in several commercial and industrial fields. This research has covered the main methods of polymerization and degradation process. Moreover, the main categories of photodegradable polymers, including polybutadiene, iPPO, PLA, etc, are introduced briefly, along with the modern polymerization technique ROMP. The current existing photodegradable polymers have limited applications due to their material behaviors. Luckily, with the design techniques mentioned above in the paper, polymers with designated properties can be synthesized, shedding great light on multiple applications. For future implications, metal photodegradable polymer possesses great possibilities for further research, yet the complex structures and bonds within metal-organic polymers cast great challenges for researchers.

References

- [1] Hillmyer, M. A., & Tolman, W. B. (2014). Aliphatic polyester block polymers: Renewable, degradable, and Sustainable [J]. *Accounts of Chemical Research*, 47(8), 2390-2396.
- [2] Huang, B., Wei, M., Vargo, E., et al. (2021). Backbone-photodegradable polymers by incorporating Acylsilane monomers via ring-opening metathesis polymerization [J]. *Journal of the American Chemical Society*, 143(43), 17920-17925.
- [3] Lipinski, B. M., Morris, L. S., Silberstein, M. N., et al. (2020). Isotactic poly(propylene oxide): A photodegradable polymer with strain hardening properties [J]. *Journal of the American Chemical Society*, 142(14), 6800-6806.
- [4] Radzinski, S. C., Foster, J. C., Chapleski, R. C., et al. (2016). Bottlebrush polymer synthesis by ring-opening metathesis polymerization: The significance of the Anchor Group [J]. *Journal of the American Chemical Society*, 138(22), 6998-7004.
- [5] Shultz, G. V., & Tyler, D. R. (2009). Preparation of functionalized organometallic metal–metal bonded dimers used in the synthesis of photodegradable polymers [J]. *Journal of Inorganic and Organometallic Polymers and Materials*, 19(4), 423-435.
- [6] Wu, H., Wen, B., Zhou, H., et al. (2015). Synthesis and degradability of Copolyesters of 2, 5-furandicarboxylic acid, lactic acid, and ethylene glycol [J]. *Polymer Degradation and Stability*, 121, 100-104.
- [7] Yousif, E., & Haddad, R., (2013). Photodegradation and photostabilization of polymers, especially polystyrene: Review [J]. *SpringerPlus*, 2, 398.
- [8] Lisiecki, J., & Szabelski, P. (2020). Surface-confined metal–organic precursors comprising naphthalene-like derivatives with differently distributed halogen substituents: A Monte Carlo model [J]. *The Journal of Physical Chemistry C*, 124(37), 20280-20293.
- [9] Lal, G., Derakhshandeh, M., Akhtar, F., et al. (2018). Mechanical properties of a metal–organic framework formed by covalent cross-linking of metal–organic polyhedral [J]. *Journal of the American Chemical Society*, 141(2), 1045-1053.
- [10] Papananou, H., Katsumata, R., Neary, Z., et al. (2021). Dopamine-mediated polymer coating facilitates area-selective atomic layer deposition. *ACS Applied Polymer Materials*, 3(10), 4924-4931.