Depolymerization for polymers with heteroatom-containing main chain: mechanism and applications

Di Song1au†, Yuqi Wang2b†, Ching-Fai Yip3c†, Quan Zuo4d†

1Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z4, Canada
2College of Material Science and Engineering, Tongji University, Shanghai 201800, China
3School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China
4College of Material Science and Engineering, Shenyang Aerospace University, Shenyang 110136, China

*Corresponding author email: a*songdi18@student.ubc.ca, b1752128@tongji.edu.cn, c191850228@smail.nju.edu.cn, d17621777097@163.com
†These authors contributed equally.

Abstract—With the flourishment of the polymer industry, many polymers have been produced and used. However, it has been acerbically criticized that most of the polymers, such as polyolefins, polyesters, cannot be naturally degraded or depolymerized, leading to polymer waste, which has exacerbated the growing global contamination. Therefore, it is essential to research and ameliorate depolymerization methods to diminish the polymer waste and recycle them. This article reviews a series of novel depolymerization methods in recent years, including pyrolysis, ionic liquids, hydrolysis, and biological methods, aiming to depolymerize the waste polymer with heteroatom-containing main chain, such as poly (ethylene terephthalate), polyamides, polyesters. The mechanisms and applications of these depolymerization methods are highlighted. Although traditional pyrolysis methods have relatively low yield, selectivity, and harsh conditions, some catalytical pyrolysis methods have better selectivity, energy consumption, etc. Besides, due to the good recyclability of ionic liquids, an excellent yield of monomers, and relatively moderate conditions, ionic liquids have been widely used in depolymerizing the polymers with heteroatom-containing main chain, which are processing a stepwise ionic depolymerization mechanism. Moreover, because water is economical and environmentally friendly, depolymerization via hydrolysis is also worthy of research. Finally, some biological methods are prevailing because of their high selectivity, high efficiency, and mild conditions, although the mechanisms are still obscure that there have been only a few uniform theories, such as oxidizing-degrading mechanism, hydrolysis mechanism.

1. Introduction
Polymeric materials, such as polyolefins, polyesters, have been widely utilized for civil and even military industries due to their excellent performance of density, mechanical properties, insulativity, corrosion resistance, etc. However, the polymer problem has a deep influence on human beings and flora
and fauna on our planet because of overproduction, and plastic is one of the most productions. According to the data of global plastic production in 2020 on Statista [1], the global yield of plastic products has reached approximately 367 million tons per year and about 6.3 billion tons of plastic waste has been accumulated since the 1950s but only 9% of them are recycled [2], while most of them are filled underground, incinerated or dumped into the sea, which can harm the ecosystem. Although several pieces of research on recyclable and degradable products, such as polylactic acid (PLA) and polycaprolactone (PCL), have achieved quite a little success, traditional polymeric materials, such as polyethylene terephthalate (PET), are still predominantly occupying the global market because of the lower cost. However, most of the polymers are not able to be naturally degraded or depolymerized. Therefore, it is urgent to research economical and effective methods of depolymerization of polymeric plastic materials. This article focuses on polymers with heteroatom-containing main chains, such as polyethylene terephthalate and polyamides, which are distinguished from polyolefins and can be depolymerized by the methods as follows.

There are various methods to depolymerize the polymers, such as pyrolysis, ionic liquids, hydrolysis, and biological methods. Pyrolysis is a traditional method for the depolymerization of polymers involving heating and separating processes, which can be used for the separation of oil, water, and hydrocarbons [3]. Pyrolysis is suitable for most of the types of polymers, and it is economical and flexible, except for the ones that produce toxic substances.

However, there is a novel method utilizing ionic liquids as depolymerization reagents. Some polymers are hard to dissolve and recycle, such as Nylon 6. Kamimura and Yamamoto developed a new method called ionic liquids to depolymerize this type of polymers [4]. This method is milder and safer because the process is rarely evaporated.

Hydrolysis refers to the process of depolymerizing and producing small molecules in an alkaline, acidic or neutral medium with water as a degradation agent at low pressure and low temperature [5]. The advantage of hydrolysis is that it can use simple acid or alkali medium as a depolymerization catalyst to reduce temperature and pressure so that mild conditions are enough to initiate the reaction [5]. Hydrolysis is a reaction in which the ions ionized by salt combine with the ions ionized by water to form a weak electrolyte. It is widely used in the depolymerization of polyurethane or polyester plastics [5].

Biodegradation of plastics refers to the process in which plastics are gradually decomposed into environmentally friendly substances under the action of organisms (such as bacteria, fungi, and algae) within a certain time range [6]. At present, the common most polymers can be biodegraded are those with heteroatom-containing main chains. In the past two years, the types of biodegradable plastics with rapid capacity growth in the market are PBAT, PLA, and other plastics. Among them, PLA is a widely used material with excellent barrier properties. High-performance PLA is an excellent substitute for most plastics at present, and the demand will grow rapidly in the future [7]. Therefore, biodegradation has broad development prospects. In the past two years, the types of biodegradable plastics with rapid capacity growth in the market are PBAT, PLA, and other plastics. Among them, PLA is a widely used material with excellent barrier properties. High-performance PLA is an excellent substitute for most plastics at present, and the demand will grow rapidly in the future [8]. Therefore, biodegradation has broad development prospects.

In this review, we summarized four different depolymerization methods of plastic materials: pyrolysis, ionic depolymerization, hydrolysis, and biological depolymerization. We analyzed the mechanism and contributing factors of these depolymerization methods and listed the practical application of various depolymerization methods.

2. Pyrolysis for depolymerization

Polymers with heteroatom-containing main chains, such as PET, have been widely used in the world, such as bottles, disposable bags and packaging [9]. Pyrolysis is one of the ways to turn polymers into something useful, and it is suitable for most of these polymers. However, this method could produce harmful gases during the heating process [10].
2.1. Pyrolysis mechanism

Pyrolysis is a chemical thermal process that uses heat to decompose the polymers to liquid crude oil without oxygen at a high temperature range of 300-500 °C [3]. In detail, taking as an example of a reasonable pyrolysis mechanism for PET, shown in Fig.1 [9]. The C-O bond in the polymer chain, which is the one next to the C=O bond, is most likely to be thermally cleaved and then depolymerized into benzoic acid, possibly releasing CO2 to form benzene.

Catalyst can make the chemical reaction faster and decrease the activation barrier. Pyrolysis requires a high temperature but adding catalysts can lower the required temperature for pyrolysis, reducing the heat energy required for pyrolysis, and achieving better yield [11]. Heterogeneous catalysts involve two phases, which are commonly used in the industrial process, and some typical examples are nitrogen(II) oxide, zeolite, and so on [12,13]. Fig.2 shows the mechanism for the conversion of plastics into aromatic oil by adding zeolite catalyst [14]. Adding catalysts can make the aromatic-rich oil product, producing a high yield.

Zeolite catalyst for pyrolysis

Zeolite is a microporous aluminosilicate mineral with a high surface area and acid site, which plays an important role in the industrial process as a heterogeneous catalyst, such as the conversion of hydrocarbons and oil refining [15]. Lee et al. reported the influence of different types of zeolite catalysts on the yield of oil by pyrolysis of plastics waste, such as HZSM-5, Y zeolite [16]. Compared to homogeneous catalysts, H-ZSM-5 is more common in industry because of its non-corrosive, stable, relatively selective, and recyclable properties [17]. Miskolczi et al. have studied the product yields of the pyrolysis of PET with ZSM-5 catalyst [11]. In their experiment, PET was pyrolyzed at 520 °C and distilled to produce gases, gasoline, light oil, and heavy oil. They find that with adding the ZSM-5
catalyst, the product yields for gases, gasoline, and light oil are 7.1%, 16.3%, and 11.9% higher than without catalyst. Therefore, the addition of catalysts produces more products, especially gasoline.

2.1.2 Metal oxides for pyrolysis

Metal oxide is widely used in the industry for the refining process, and it takes charge of producing more products with less pollution. In the mid-1950s, it was found that metal oxide catalysts have high effectiveness for catalyzing various oxidation, hydrogenation, and acid-base reactions, especially in the refining process [18]. For example, Anwar et al found that calcium oxide increases the pyrolysis yield from 23% to 77%, and it is the cheapest and the most effective compared with other metal oxides and metal carbonates [19]. This is a great success because of the high stability.

3. Ionic Liquids for depolymerization

Ionic The ionic liquid is a kind of organic salt in the liquid state, in which each molecule (more exactly each ion pair) can be separated from two ions: the cation and the anion, and at least one of the two opposite ions should be organic, which helps the melting point be in a reasonable temperature to make it liquidus under certain experimental temperature [20], while inorganic salts usually have such high melting points that it is difficult to keep them liquidous in most of the depolymerization conditions. Most of the ordinary liquids are made of electrically neutral molecules, while ionic liquids are predominantly composed of ions [21]. Therefore, some certain ionic liquids have an outstanding reactivity in the procedure of depolymerization without solvent disturbance[21]. Additionally, it is environmentally friendly and economical because the ionic liquids can be recollected after depolymerization[27]. Arguably, the ionic liquid is a kind of cutting-edge reagent of depolymerization.

3.1 Mechanism

Since the ionic liquids mostly consist of ions, the polymer to be depolymerized must have a reactive main chain for bimolecular Nucleophilic Substitution (S\textsubscript{N}2) [22], specifically, heteroatom-including main chain, like polyamide and polyester, which can be attacked by the ions so that an ionic stepwise depolymerization proceeds. In addition, some natural polymers, for instance, lignin and cellulose, which have heteroatoms on the main chain, can also be depolymerized. However, ionic liquids are hardly available for the depolymerization of polyolefins, in which the main chain is all composed of carbon atoms so that has scarcely S\textsubscript{N}2 reactivity [22]. For example, poly (ethylene terephthalate) (PET) was depolymerized under supercritical ethanol (scEtOH), catalyzed by 1-butyl-3-methylimidazolium tetrafluoroborate([Bmim][BF\textsubscript{4}]), which is an ionic liquid [23]. The mechanism is shown in Fig.3. For example, poly (ethylene terephthalate) (PET) was depolymerized under supercritical ethanol (scEtOH), catalyzed by 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF\textsubscript{4}]), which is an ionic liquid [23]. The mechanism is shown in Fig.3.
Fig. 3 Proposed mechanism for PET depolymerization under scEtOH in the presence of the ionic liquid [Bmim][BF4] [23].

3.2 Types of ionic liquids used in depolymerization

According to the Brønsted-Lowry acid-base theory, acids are defined as substances that dissociate in aqueous solution to give H⁺ (hydrogen ions), while bases are defined as substances that dissociate in aqueous solution to give OH⁻ (hydroxide ions) [24,25]. Therefore, ionic liquids can also be roughly classified by this standard into neutral ionic liquids and acidic ionic liquids.

3.2.1 Neutral ionic liquids

Many of the neutral ionic liquids are nitrenium salts, such as substituted imidazolium [23,26,27], quaternary ammonium [28] as shown in Table 1. Because these ionic liquids cannot ionize H⁺ or OH⁻ and show acidity or alkalinity, so these can be classified as neutral ionic liquids based on Brønsted-Lowry acid-base theory [24,25]. These neutral ionic liquids can be universally used in depolymerization [23,26,27].

| Types                     | Examples                                      | Structure                      |
|---------------------------|-----------------------------------------------|--------------------------------|
| Substituted Imidazolium Ionic Liquids | [Bmim][X] X=Ac, Cl [26], BF₄[23], etc. 1-butyl-3-methylimidazolium | ![Structure](image1.png)       |
|                           | [emim][X] X= BF₄[27], etc. ethyl-3-methylimidazolium | ![Structure](image2.png)       |
| Quaternary Ammonium Ionic Liquids | [PP13][NTf₂] N-Methyl-N-propylpiperidinium bis(trifluoromethylsulfonylimide [28] | ![Structure](image3.png)       |
3.2.2 Acidic ionic liquids
There is usually an acidic group, such as hydrosulfate as shown in Table 2, in each acidic ionic liquid molecule, which can provide hydrogen ions, leading to acidity. These ionic liquids can be used for polyether, especially for lignin [29], which is a natural polymer with a polyether structure. All of these ionic liquids can depolymerize lignin and have different reactivity respectively. In addition, some Lewis-acidic ionic liquids are also available for the depolymerization of certain polymers (although these Lewis acids can’t ionize protons under anhydrous conditions) [30].

Table.2 Acidic ionic liquids

| Types                              | Examples                     | Structure |
|-----------------------------------|------------------------------|-----------|
| Quaternary Ammonium Hydrosulfate  | [Nmnxxy][HSO₄]              | ![structure](image1) |
|                                   | m, n, x, y≥0, which means the number of carbon atoms connected to the nitrogen atom mnxy=4111, 4110, 2221, etc [29] |           |
| Substituted Pyridinium Hydrosulfate | [N-MePyr][HSO₄]           | ![structure](image2) |
|                                   | N-Methylpyridinium hydrosulfate |           |
|                                   | [HPyr][HSO₄]               | ![structure](image3) |
|                                   | Pyridinium hydrosulfate     |           |
| Substituted Imidazolium Hydrosulfate | [CxCyim][HSO₄]          | ![structure](image4) |
|                                   | x, y≥0, which means the number of carbon atoms connected to the nitrogen atom xy=41, 04 (x or y=0, Cx or Cy=H) [29] |           |
| Lewis acidic Ionic Liquid         | [Hmim][MX₃]               | ![structure](image5) |
|                                   | MX₃=ZnCl₃, CoCl₃, FeCl₄, CuCl₃ [30] | 1-hexyl-3-methylimidazolium |

3.3 Applications of ionic liquids for depolymerization

3.3.1 Poly (ethylene terephthalate) (PET)
Poly (ethylene terephthalate) is a kind of polyester, which has ester groups on the main chain. Therefore, it can be depolymerized to diethylterephthalate (DET) by certain ionic liquids [23,30]. Chen’s group researched that PET can be glycolysis under the condition of mixed Lewis acidic ionic liquids, including [Hmim]ZnCl₃, [Hmim]CoCl₃, [Hmim]FeCl₄, and [Hmim]CuCl₃, which was proceeded by cation synergistic mechanism [30], and concluded that these distinguished Lewis-acidic ionic liquids have different reactivity and selectivity respectively. Cátia’s team also studied that PET can be depolymerized by 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) and supercritical ethanol, in which there were a good yield of DET and a lower required reaction time [23].

3.3.2 Polyamide (PA/Nylon)
Polyamide, which is also called Nylon, is also a kind of ionic liquid reactive polymer, in that there are amide bonds on the main chain available for depolymerization. Akio Kamimura’s group researched that Polyamide 6 (polycaprolactam) can be depolymerized by [emim][BF₄] under microwave and at a certain
temperature [27]. They found that they could circulate the reaction and caprolactam was greatly produced, the ionic liquids can be recovered as well, which is both environmentally friendly and economical.

3.3.3 Fiber-reinforced plastics (FRPs)
Akio’s team also studied other polymers. Waste fiber-reinforced plastics (FRP) and unsaturated polyesters were depolymerized by subjecting them to treatment with ionic liquids, such as [PP13][NTf₂], under heating conditions [28]. Eventually, they successfully recollected the glass fiber in FRP and the recycled unsaturated polyesters.

4. Hydrolysis of polymers
In moist conditions, the long chains of large molecules which make up polymers are broken down by water molecules, causing the polymers to slowly degrade, which is known as “hydrolysis” [31-33]. Hydrocarbon polymers are generally stable to water, and the water content is very low when they reach equilibrium in the aqueous solution. However, polymers such as polyethylene terephthalate (PET) and polylactic acid (PLA), which are generated through polycondensation reactions, contain many highly polar groups. When they are at high temperature and high humidity, the water molecules react with the polar groups of the polymer molecular chain and cause degradation [34-36].

4.1 Mechanism of hydrolysis
Hydrolysis resulted in the break of the main chain of the polymers, and the formation of carboxyl-terminated, hydroxy-terminated, and amine-terminated products. The carboxyl-terminated products ionize H⁺, catalyzing the fracture of the polymer chain, which is a self-catalytic reaction. Once hydrolysis occurs, the degradation proceeds rapidly. The surface smoothness, strength, elasticity, and hardness of the hydrolyzed plastics are much lower than those before hydrolysis [37-40].

4.2 Factors influencing hydrolysis
Hydrolysis is an economical and simple way of degradation, which has great application potential [34-36, 41-44]. Understanding the process of hydrolytic degradation and analyzing the influencing factors will further clarify the mechanism of hydrolytic degradation and make it better applied in production. Solution concentration, temperature, and pH all affect the hydrolysis degradation rate [35, 41, 42].

4.2.1 Solution concentration
Proper solution concentration is very important for the hydrolysis and degradation process. Although higher concentrations produce higher hydrolysates, which greatly reduce the time and economic cost of concentration, higher concentrations also lead to longer hydrolysis and degradation process times, which also leads to increased costs [35]. Therefore, in the actual production, we should choose the appropriate solution concentration according to the production conditions to obtain higher economic benefits. Bi et al. studied the effect of PLA/water ratio on the hydrothermal degradation process of PLA materials [35]. A higher PLA/water ratio results in a higher concentration of the product lactic acid solution for further concentration and utilization. However, it also leads to a longer time for the hydrothermal degradation process, resulting in an increase in cost [35].

4.2.2 Temperature
The higher the temperature, the faster the hydrolysis reaction rate. Xu et al. found that the polymer for oil displacement without improved thermal stability had a slow hydrolysis rate in an environment below 95 °C, but the hydrolysis rate increased significantly at 95~120 °C [41]. After 30 days of storage, the degree of hydrolysis was about 100%, and the oil displacement performance decreased significantly, which could not meet the requirements of polymer flooding in such reservoirs [41].
4.2.3 pH
Different polymers require different pH when hydrolysis. Too high or too low pH will affect the hydrolysis effect. Sun et al. studied the effect of pH value of hydrothermal pretreatment on hydrolysis characteristics of corn straw [42]. In the process of hydrothermal pretreatment, the change of pH value had a great influence on the degradation of the main chemical components of corn straw, and the chemical components of hydrolysate also changed. Adding acids could increase the production of carbohydrates in hydrolysate while adding alkali could help to remove the acetyl groups in lignin and hemicellulose [42].

4.3 Applications of hydrolysis
Hydrolysis is a simple way to degrade polymer, which has many applications in daily life. Hydrolysis can be used to degrade some polymers found in natural plants and animals. Gao explored the hydrolysis optimization of lignocellulosic raw materials with high solid concentrations [43]. Six raw materials such as corn straw were treated with dilute sulfuric acid, and it was found that hemicellulose content decreased significantly, while cellulose and lignin content had a slight loss [43]. The production process can also be controlled by the conditions associated with hydrolysis. Wang explored the preparation of microfibrillated cellulose by high-temperature self-hydrolysis combined with oxidation pretreatment [44]. With the increase of temperature, the hydrolysis reaction rate of lignocellulosic fiber gradually accelerated, and long-chain cellulose was continuously broken into short-chain cellulose [44].

5. Biological method of depolymerization
Compared with other traditional depolymerization methods, biological depolymerization products are pollution-free and environment-friendly and can be more widely used in life [45]. As is known to all biodegradable plastics can be divided into partial degradation and complete degradation according to the degree of degradation [45]. Among them, starch-based plastics can only be partially degraded, while representative biodegradable plastics PLA (polylactic acid) and PBAT (Poly (butyleneadipate-co-terephthalate)) can be completely degraded. At present, these two materials have industrialized production capacity, and manufacturers have also increased their layout about the two materials.

5.1. Mechanism of biological depolymerization
Biological depolymerization recovery is to use microorganisms or enzymes to depolymerize plastics into oligomers or monomers [45]. It has mild reaction conditions, and there will be no secondary pollution. They hydrolyze, ionize or protonate polymer components, mechanically destroy them, and split them into oligomer fragments. After being discarded, these materials can be degraded into small molecules with low molecular weight by microorganisms in soil or water, and finally decomposed into carbon dioxide without environmental pollution by microbial activities [45].

5.2. Factors affecting biological depolymerization
Biological depolymerization uses enzymes, microorganisms, and other bioactive organisms to depolymerize [48]. Therefore, temperature, pH, and other factors will change the depolymerization efficiency by affecting the depolymerization activity [49]. In addition, soil nitrogen content, moisture, and oxygen will affect depolymerization by affecting the diversity of microbial species in soil [49].

5.2.1 Temperature
The temperature will directly affect the activity of microorganisms. Microorganisms need to grow in a suitable temperature range. For example, Ammonia oxidizing bacteria (AOB) can grow at low temperatures [46], Ammonia oxidizing archaea (AOA) slowly at 4-25 °C [47]. Both are degraded by converting ammonia in nitrogenous materials into nitrite or nitrate. Therefore, materials at different temperatures can be biodegraded by selecting enzymes with activities at different temperatures.
5.2.2 PH
PH can affect the physiological activity of microorganisms and the solubility of chemicals to affect degradation. At the same time, too large or too small pH will inhibit microbial growth and affect the proportion of fungi and bacteria in the system. Hu et al [48] mentioned the effect of microorganisms at different temperatures on the depolymerization of PBS, and the pH corresponding to the depolymerization performance of different microorganisms is also different. For example, when pH = 4, the final depolymerization efficiency of some fungi can reach 97.6%, while when pH = 5, the depolymerization effect of other fungi is the best [48]. Therefore, depolymerization can be prevented in use by setting the specific pH of materials in different use environments.

5.3. Application of biological depolymerization

5.3.1 Poly (butylene adipate-co-terephthalate) (PBAT)
PBAT (Poly (butylene adipate-co-terephthalate)) has been studied extensively since the early years of this century [49]. It has good mechanical and thermal properties and is currently used more and can be commercial one of the biodegradable polyesters. There are two main degradation pathways of PBAT. One is to decompose PBAT through the enzymes of bacteria and fungi in the environment, and the other is through the non-enzymatic action of thermal degradation and chemical hydrolysis [49]. In general, PBAT can self-depolymerize in fungi rich and humid soil. PBAT has excellent mechanical and thermodynamic properties and is widely used to improve the depolymerization properties of PBS and PLA.

5.3.2 Poly (butylene adipate-co-terephthalate)/Polybutylene succinate (PBAT/PBS)
Polybutylene succinate (PBS) has good biodegradability and can be depolymerized under natural conditions or by biological enzymes. (PBS) is easily decomposed by a variety of microorganisms or enzymes in nature to form CO₂ and H₂O to avoid polluting the environment [48]. PBS can be better depolymerized in moist soil which is rich in microorganisms, PBS degrading bacteria, and about 30 degrees. Although PBS has good biodegradability, the processing temperature of PBS, the viscosity, and the melt temperature are low. Due to poor strength, it is difficult to process by blow molding and tape casting, so it needs to be modified to expand the application range [50].

A study shows that the shear viscosity of PBS/PBAT blends with different ratios decreased gradually. The melt mass flow rate of PBS/PBAT blends was significantly reduced and the melt viscosity of the blends was increased. With the addition of PBAT, the tensile strength of PBS/PBAT blends decreased, and the elongation at break and tear strength increased continuously [51]. It means that PBAT/PBS materials are more widely used in depolymerization.

From the above data, we can conclude that the properties of PBAT/PBS are improved after modification. After PBS is modified by PBAT, the application range of the material can be expanded, and it can be used more widely and better in daily biological depolymerization.

5.3.3 Poly (butylene adipate-co-terephthalate)/polylactic acid (PBAT/PLA)
Like PBAT, PLA can also depolymerize in fungi fungi-rich and humid soil, and its depolymerization efficiency is faster than PBAT in a sludge environment. However its toughness and thermal stability are poor, so PBAT needs to be introduced for modification. At the same time, PBAT has good flexibility, but its strength and modulus are low. PBAT is an excellent biodegradable material, which can be used to improve the mechanical properties of PLA. Therefore, PBAT and PLA can be blended to improve the comprehensive properties of the two polymers [52].

Su et al. have tried to predict the possible miscibility of PBAT/PLA blends at the molecular level and the solubility parameters were calculated by different calculation methods [53]. According to the calculation, PBAT/PLA can be immiscible to immiscible, but it depends on their molecular weight and temperature. The higher the molecular weight, the worse the miscibility, and the higher the temperature, the better the miscibility. Therefore, it may be possible to compatibilize PBAT/PLA blends by
introducing chain extenders. By adding a compatibilizer, the interfacial tension of PBAT/PLA blend system was reduced, the interfacial bonding force was improved, and the mechanical properties of the blend system were improved. It may be more conducive to the degradation and application of plastic.

6. Conclusion
This paper summarizes the main mechanism and application of pyrolysis, ionic liquids, hydrolysis, and biological methods widely used for depolymerization of polymers with heteroatom-containing main chains, respectively. Also, the factors which can influence the efficiency of different methods for the depolymerization of polymers are introduced, such as the selection of catalysts, pH, temperature, acidic and basic conditions for the chemical reactions. The product yield of the pyrolysis method is low and may produce harmful substances due to the high temperature reaction, which is around 300-500°C. However, the yield can be increased by adding a catalyst, such as zeolites and metal oxides catalysts. It is used in most of the polymers with heteroatoms in main chains, except the ones which can produce harmful substances. Ionic liquids methods have high selectivity, and efficiency. It is used for almost all the polymers that can proceed with an SN2 stepwise ionic depolymerization, such as Nylon 6, PET, and so on. Hydrolysis methods are also important due to their economic value, simplicity, and self-catalytic properties. It can be used for the depolymerization of PLA, PET, and so on. In addition, the biological method is more complicated, and it is because there is less research on it compared to other methods, it is necessary to continue to investigate it. It can be used for the depolymerization of PLA, PBAT, and so on. This paper summarized the mechanism and application for the polymers with heteroatoms in the main chain, which there are few articles on this topic. Therefore, this paper can pave the way for future research on the specific polymer structure. The limitation of this paper is the summarized points are not comprehensive. There might be some other factors that can influence depolymerization. Future studies may conclude glycolysis, solvolysis, methanolysis and other depolymerization methods.

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