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A Review of Research on Recyclable Polymer Materials

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Abstract. Polymer materials have been widely used in applications ranging from aerospace, automobile transportation, medical and health care due to their excellent properties. The current linear production and disposal model of polymeric materials has raised concerns about the continuous consumption of limited fossil fuels and the severe environmental crises. To address the dual challenges of the environment and resources, it is necessary to develop sustainable polymers and more promising recycling strategies. This contribution summarizes the recent research on the preparation of sustainable polymers and their chemical recycling, including polyesters, polycarbonates, polythioesters and polyurethanes.

1. Introduction

Polymer materials play an important role in people's lives. With the development of the economy and the improvement of living standards, people have put forward higher requirements for polymer materials. Polymer materials have been widely used in the fields of clothing, packaging, agriculture, electronics, biotechnology and aerospace due to their low cost, light weight, high strength, and facile processing. The production and varieties of polymer materials are increasing year by year, which have occupied a very important position in the material industry. The vast majority of polymer materials come from petrochemical products, such as rubber, plastics and synthetic fibers, which are difficult to degrade in nature, and will cause serious social, economic and environmental problems after they are discarded.[1] In order to meet the dual challenges of environment and resources, it is necessary to develop sustainable polymers and implement more promising recycling strategies, and many researchers have focused their attention on bio-based polymer materials.[2] Another advantage of these materials is that their raw materials are all derived from biomass, completely getting rid of the current situation that polymer materials are completely dependent on petrochemical resources, realizing carbon cycle, greatly reducing white pollution, improving the earth's atmospheric environment, and having an alternative to traditional the potential of polymer materials.[3, 4] However, most bio-based polymer materials have good durability and are difficult to decompose in the natural environment, causing white pollution. In order to solve the problem of environmental pollution, recyclable bio-based polymer materials have become a research hotspot.[5]

2. Recyclable polyester, polycarbonate, polythioester

With the wide application of bio-based polymer materials, the bio-based polymer material industry has been listed as one of the seven strategic emerging industries in China. In recent years, bio-based polymer material industry is growing at a rate of more than 20% per year, with a total output of more than 6 million tons per year in China. At the same time, it is also facing serious energy and environmental crises. There are two solutions: one is to develop new polymers that avoid the use of plasticizers; the other is to find a polymer monomer that can be chemically recycled.[6, 7] The ideal sustainable polymers should include but not limited to the following criteria: (1) they are completely biologically derived and make maximum use of industrial waste. (2) They improve the properties of existing bio-derived plastics, especially reducing the use of plasticizers. (3) Allowing selective use of catalytic chemistry for recovery. At present, great achievements have been made in recyclable polymer materials. For example, there have been outstanding achievements in the research of polyesters, polycarbonates, polythioesters, polyacetals and so on.

Polyester is a large class of biodegradable polymer materials, which are widely used in aerospace, biomedicine, and textiles.[8] Aliphatic polyesters can be prepared by ring-opening polymerization of cyclic lactones or polycondensation of diols and diacids. Currently the most studied are poly(ε-caprolactone) (PCL), poly(glycolide) (PGA) and poly(L-lactide) (PLLA) due to their good biocompatibility and degradable, which can be degraded into carbon dioxide and water in nature. It is a kind of environmental friendly polymer material with great market potential. Its general structural formula is shown in Figure 1.

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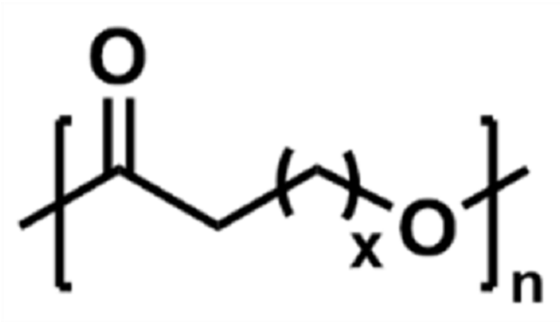

Figure 1. The structure of aliphatic polyester

Alpha-methylene-gamma-butyrolactone (MBL) occurs naturally in tulips and can be obtained from biological sources. MBL has been intensively investigated as a sustainable alternative to petroleum-based methyl methacrylate (MMA) monomers due to the higher glass transition temperature of MBL-derived polymers compared to polymethyl methacrylate (PMMA) and better solvent durability, so MBL is a functionalizable monomer with potential chemical recyclability. In 2020, our group achieved the selectively ring-opening polymerization of MBL by using an organophosphazene base/urea binary catalyst. The prepared polymer P(MBL)ROP can be completely depolymerized to recover MBL monomer.[9]

Aliphatic polycarbonate (APC) and polythioester (PTE) have also made great breakthroughs due to their potential degradability and biocompatibility. In 2022, Zhu and coworkers prepared a class of seven-membered ring carbonates containing trans-cyclohexyl fused rings. This kind of monomer has high activity for ring-opening polymerization, and the molecular weight of the prepared polycarbonate is as high as 673 kg·mol-1. Depolymerization studies were carried out on the prepared polycarbonate, and it was found that it can be completely depolymerized into its corresponding cyclic dimer, which can be repolymerized to obtain the same polymer as the original monomer polymerization, indicating that the chemical cycle is realized potential pathways (Figure 2).[10]

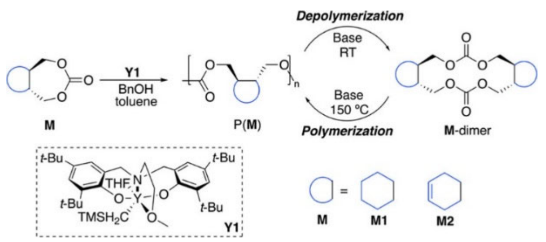

Figure 2. Accessing Chemically Recyclable Polycarbonates through Ring-Opening Polymerization of M1 and M2.[10] Reprinted with permission from ref. 10. Copyright (2022) American Chemical Society.

Lu et al from Peking University is committed to using renewable amino acids as raw materials to construct recyclable functional polymer materials. They synthesized three proline derivatives with different substituents, NBoc- PTL, NCbz-PTL and Nene-PTL. Polythioesters with high molecular weights and narrow molecular weight distributions were then prepared using bases such as triethylamine, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as catalysts and benzyl mercaptan as initiator. The polythioester PNBoc-PTL can be depolymerized and recycled back to monomers under mild conditions. When the more basic DBU was used, complete depolymerization of obtained polythioesters was achieved within 2 min at 50 °C (Figures 3).[11]

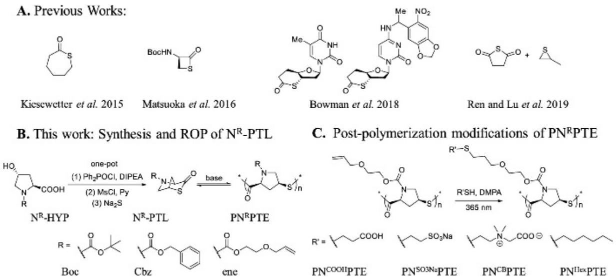

Figure 3. Preparation of Recyclable Polythioesters from Proline Derivatives.[11] Reprinted with permission from ref. 11. Copyright (2019) American Chemical Society.

3. Recyclable Polyurethane

As one of the important members of the polymer material family, polyurethane is the only organic synthetic material that has application value in the fields of plastics, rubber, fibers, coatings, adhesives and functional polymers because of its superior properties. However, the recyclability of polyurethane has not been fully studied. To date, a common strategy to achieve chemical recovery of polyurethanes is to recover polyols by alcoholysis or hydrolysis. For example, in 2017, Chen and coworkers explored an optimal process condition for recycling and reusing polyurethane flexible foam waste by alcoholysis. The optimum alcoholysis agent, reaction temperature, reaction time and material ratio were studied to achieve the maximum utilization of resources.[12]

The use of alcoholysis or hydrolysis has disadvantages such as large use of solvent, complicated purification involved in the recovery process, high recovery cost, and low yield. In order to overcome these deficiencies, it is attractive to develop biodegradable, recyclable and recyclable bio-based polymer materials that can be completely depolymerized into monomers under mild and energy-saving conditions. In 2016, Hillmyer and colleagues used bio-degradable poly(β-methyl-delta-valerolactone) as polyol precursor to synthesize thermoplastic polyurethane and flexible foam. The chemical recycling of prepared polyurethanes to recover β-methyl-delta-valerolactone (MVL) was achieved by the tandem dissociation of carbamate groups and the pyrolysis of poly(β-methyl-delta-valerolactone) polyols. This strategy bypasses many technical challenges and realizes the recycling of building blocks with excellent purity under mild conditions for the first time.[13]

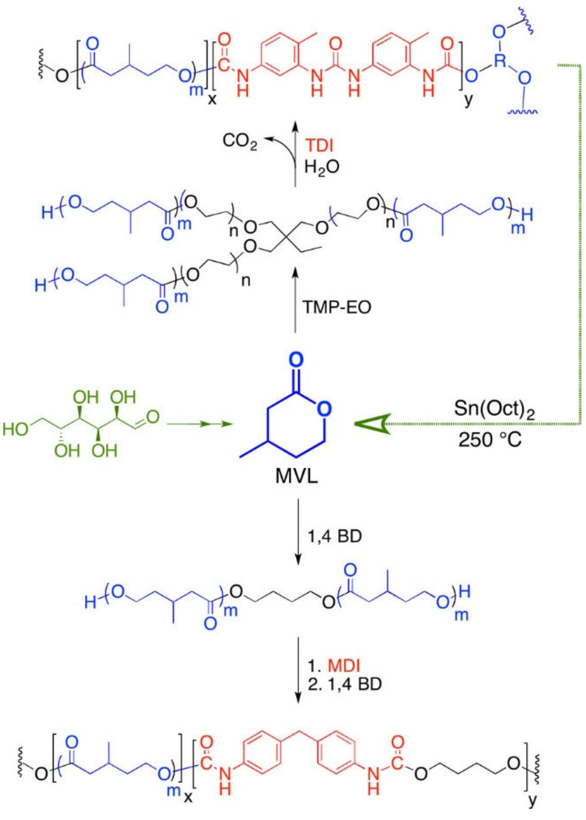

Figure 4. Synthesis mechanism and degradation of polyurethane and foam.[13] Reprinted with permission from ref. 13. Copyright (2016) American Chemical Society.

4. Conclusion

With the advent of the material age, countries around the world are looking for solutions to address the challenge of energy and the environment. It is attractive to develop more sustainable polymers with capability to chemical recycling back to pristine monomers from bio-derived resources, thus successfully establish a circular closed-loop life cycle. Despite the recent advancements, the polymers with closed-loop life cycle are still in their infancy. More efforts should be devoted to solve the current challenges including tedious monomer syntheses, harsh conditions for polymer preparation as well as poor thermal and mechanical properties of obtained polymer materials.

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