

Biodegradable Polymers, History Tells Polymer Science's Fortune

Origin and Overview

Biodegradable polymer, according to the International Union of Pure and Applied Chemistry (IUPAC), is defined as “polymer susceptible to degradation by biological activity, with the degradation accompanied by a lowering of its molar mass”. More specifically, biodegradable polymer should ultimately degrade into CO₂ and water. The importance of biodegradable polymer is aroused due to the increasing concern on the rapidly growing volume of polymer waste after utilization, which is hard to recycle and exists “endless” in the earth since its birth. As microorganism is ubiquitous on earth, biodegradable polymer is usually chosen above other degradation modes for environmentally digestible polymers. Naturally, biodegradable polymers start from natural polymers like starch, cellulose, protein, etc., utilization of which dates back to the history of human civilization. Due to the length limits, this Editorial will focus on the development of synthetic biodegradable polymers pioneered in the early 1980s and mainly in China.

The basic research on biodegradable polymers started relatively late in China, but increased very rapidly. As shown in Fig. 1, China accounts for only ~0.5% of the world's publications in this field in 1981–1990, being much less than those from United States (15.6%). The output of biodegradable polymer research displays exponential growth since 1990, over 40,000 papers, or 25.0% of the world's publications are from China in 2011–2021. Meanwhile, the progress in basic scientific research greatly promotes industry involvement. Nowadays, China possesses mass production capacity for almost all kinds of commercial biodegradable polymers. Notably, the annual demand for biodegradable polymers is expected to grow 9% in the coming decade, and the new fortune is now welcoming great progresses in polymer science.

Milestones in the Past Four Decades

Synthetic biodegradable polymers are mainly prepared by (co)polymerization of corresponding monomers, though a few is from biorefinery in bacteria. They have common characteristics in molecular structures, with aliphatic ester or carbonate, or both linkages in the polymer backbone. Therefore, they are easy to be attacked or “eaten” by bacteria, leading to degradation and molecular weight loss. It is noteworthy that new fortune comes from fundamental polymer science in biodegradable polymers, especially the biggest three brands, poly(lactic acid) (PLA), poly(butyleneadipate-co-terephthalate) (PBAT), and poly(propylene carbonate) (PPC).

PLA is the landmark biodegradable polymer from renewable sources, and has been the subject of abundant

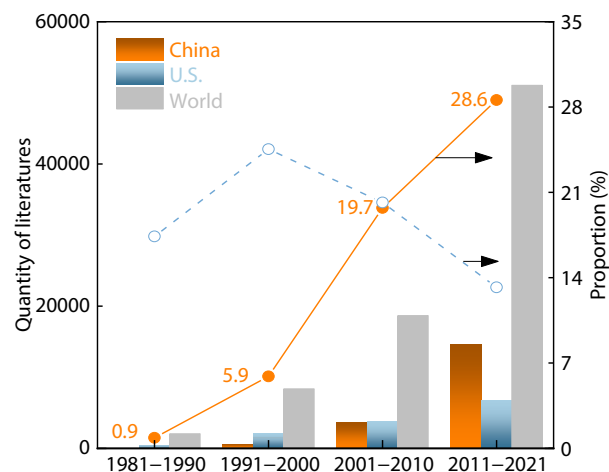


Fig. 1 Trends of the publications in synthetic biodegradable polymers from China, United States (U. S.) and the world total (data from Science Citation Index Expanded from Web of Science).

literatures over the past decades. It is usually synthesized from the ring-opening polymerization (ROP) of lactide. In 1999, the research group of Prof. Xuesi Chen (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CIAC, CAS)) initiated PLA synthesis in China. In 2004, Chen's group invented Schiff base aluminum complex catalysts for the stereoselective polymerization of *rac*-lactide, affording high-molecular-weight poly(D,L-lactic acid) (PDLLA). A 5,000 ton/a PLA production line was built in 2008 in Hisun Plastics (Zhejiang, China), being the second production line after Natureworks' 1.4×10^5 tons line in Nebraska since 2002.

PBAT is the first certified biodegradable polymer on a fossil basis, which was pioneered by BASF and a 7.4×10^4 ton/a production line was built since 1998 in Ludwighafen, Germany. Due to its compatible processing with all the other biodegradable polymers, PBAT has grown into the most popular biodegradable polymer. The research group of Prof. Baohua Guo (Tsinghua University) developed new Ti-Si-rare earth metal complex catalysts, and synthesized high-molecular-weight PBAT with low acid value. With this technology, assuring the first 6.0×10^4 ton/a production line was built in 2016 in Lanshan Tunhe Chem. Co., Ltd. (Xinjiang, China).

PPC, an alternating copolymer of propylene oxide and CO₂, was invented by Prof. Inoue's group in 1969. High-molecular-weight PPC not only exhibits unique gas barrier property, but also is low cost owing to high CO₂ fixation. Therefore, PPC may be the solution to compensate PLA and PBAT in performance as well as cost. In 1991, the research group of Prof. Zhiqian Shen (Zhejiang University)

developed a new type of rare earth metal catalyst to prepare high-molecular-weight PPC. Initiated by the catalyst design mode, our group developed a series of heterogeneous rare earth ternary catalysts that can generate high-molecular-weight PPC. A ton-scale pilot test was completed in 2004 in Inner Mongolia, China, being a breakthrough for PPC industrialization in the world. A 1.0×10^4 ton/a production line was built in 2013 in Taizhou Bangfeng Plastics (Zhejiang, China). Afterwards, several scale-up PPC production lines, like mushrooms after rain, have been completed in China. In addition to heterogeneous metal catalysts, the research group of Prof. Xiaobin Lu (Dalian University of Technology) invented bifunctional Salen Co complex in 2006, enabling high efficient synthesis of high-molecular-weight PPC with high selectivity, creating a new era for the high-performance homogeneous metal catalyst.

Meanwhile, important progress has been achieved in China on other biodegradable polymers like poly(butylene succinate) (PBS), polycaprolactone (PCL), poly(*p*-dioxanone) (PPDO), poly(glycolic acid) (PGA), and polyhydroxyalkanoates (PHA). Notably, PHA, developed by the research group of Prof. Guoqiang Chen (Tsinghua University), is the solely commercialized biodegradable polymer from bacterium synthesis. Most of these biodegradable polymers have been industrialized in China, or at least in a pilot plant scale, providing versatile choices for future specific applications.

Perspectives

Biodegradable polymer is certainly the origin of a new and huge polymeric industry, a waiting-for gold mine in addition to polyolefin, and intensive scientific polymer research is impending. One of the key issues is the unfavorable cost as compared with polyolefin, and others include fewer candidates for versatile applications, an issue that is never a question for the well-developed polyolefin industry. Development of new catalyst systems that enable regio-/stereo-selective polymerization for high-molecular-weight polymers with low cost, easy separation is urgent. Central metal environment-friendly catalysts or metal-free organocatalysts are possible solutions to meet these demands. Functional biodegradable polymers are highly

demanding, examples like heat-resisting polymers serviced above 100 °C, or marine environment degradable polymers. High-molecular-weight poly(amino acid)s and PHAs may be the choices, if their mass productions can be solved. New concept biodegradable polymers like PPDO deserve more concerns, as disclosed by the research group of Prof. Yuzhong Wang (Sichuan University). PPDO has the benefit of a closed-loop biodegradable polymer whose monomer can be recycled by degradation of PPDO. Finally, an old story but still being urgently needed, collaboration of researchers in polymer chemistry, physics, and processing is very important to determine where the biodegradable polymers go in the future, an issue that being less concerned in the past decades. It is noteworthy that many biodegradable polymers, typically PGA, PHA and PBS, are hard to be processed or even not suitable for practical applications, mainly due to their easy thermal degradation or fast deterioration of mechanical performance prior to use. These inferior properties are the main barriers to their cost-effective applications. In addition to processing, polymer physics is extremely important in finding worldwide acceptable biodegradation mechanism, though multidisciplinary cooperation with biology and others are necessary.



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The views expressed in this editorial are those of the author.