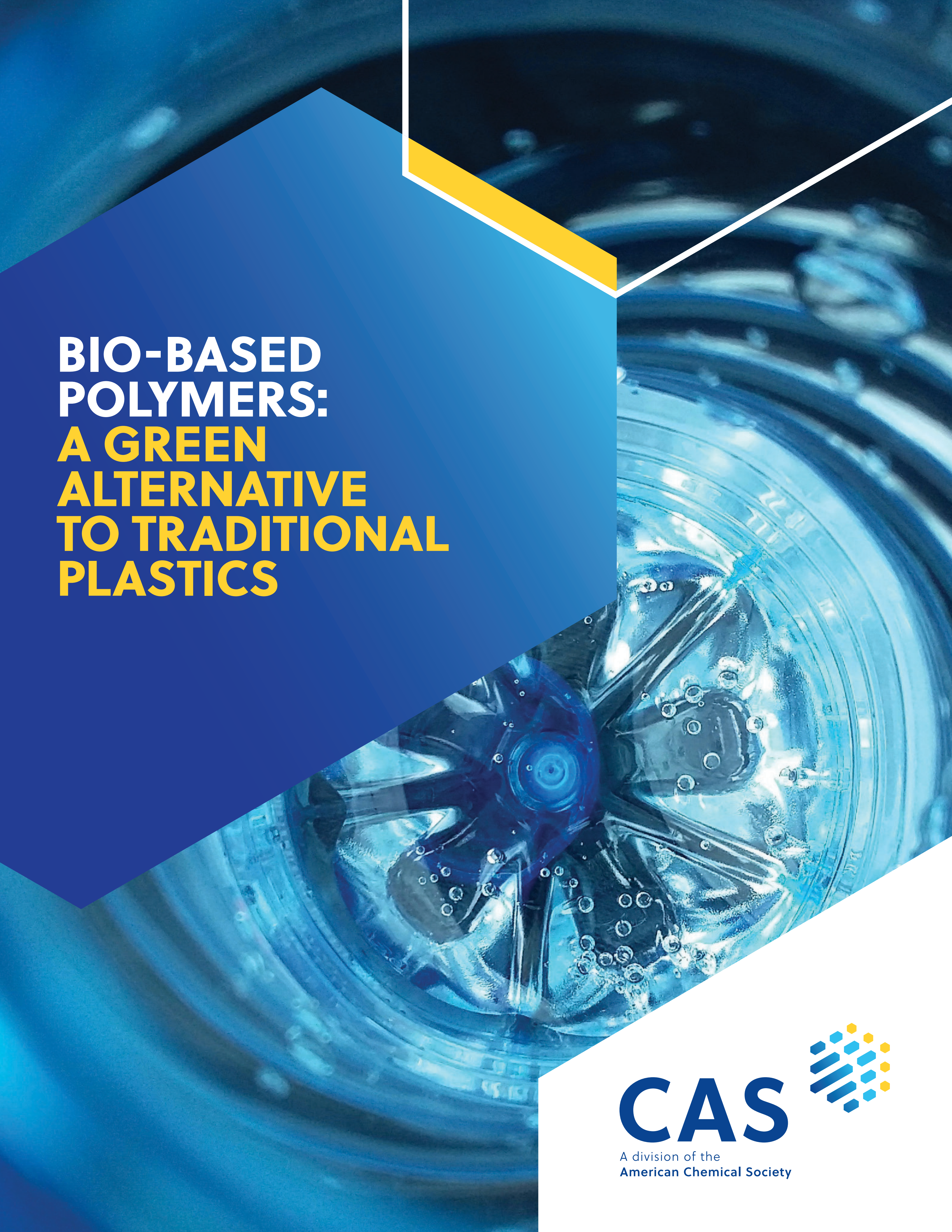
BIO-BASED POLYMERS: A GREEN ALTERNATIVE TO TRADITIONAL PLASTICS



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Introduction

Plastics are found in a wide variety of products, ranging from grocery bags to car bumpers and are composed predominantly of synthetic polymers derived from **petroleum.**

It is estimated that the plastic-manufacturing processes consume 8-10% of the global oil supply, and the number is forecast to double by 2040.[1] Petroleum is non-renewable, and the oil resources are rapidly being depleted from planet earth. Unless alternative sources are well established, the oil shortage will negatively impact plastic production. The answer is bio-based polymers, sometimes called biopolymers, which refer to polymers that are prepared from biomass.

Bio-based polymers have multiple advantages over fossil resource-derived plastics.[2,3] They are generated from renewable sources, which also fix CO_2 from the atmosphere. If bio-based polymers are prepared using similar amounts of energy to plastics from non-renewable sources, their fixation of CO_2 will decrease greenhouse gas emissions at the same output.[4] In addition, many bio-based polymers are biodegradable,[5] providing more flexibility in disposing products made with them.

Bio-based polymer research has been trending in recent years and was chosen as one of the top ten emerging technologies for the year 2019.[6] Here, we explore the various types of bio-based polymers, highlight recent progress in research into these alternatives to traditional plastics and review the interest in them over the last two decades.

> **Bio-based polymers are biologically sourced and thus help to tackle environmental issues by decreasing reliance on fossil fuels, while biodegradability refers to the capacity for these materials to be broken down by living organisms - not all bio-based polymers are biodegradable.[7]**

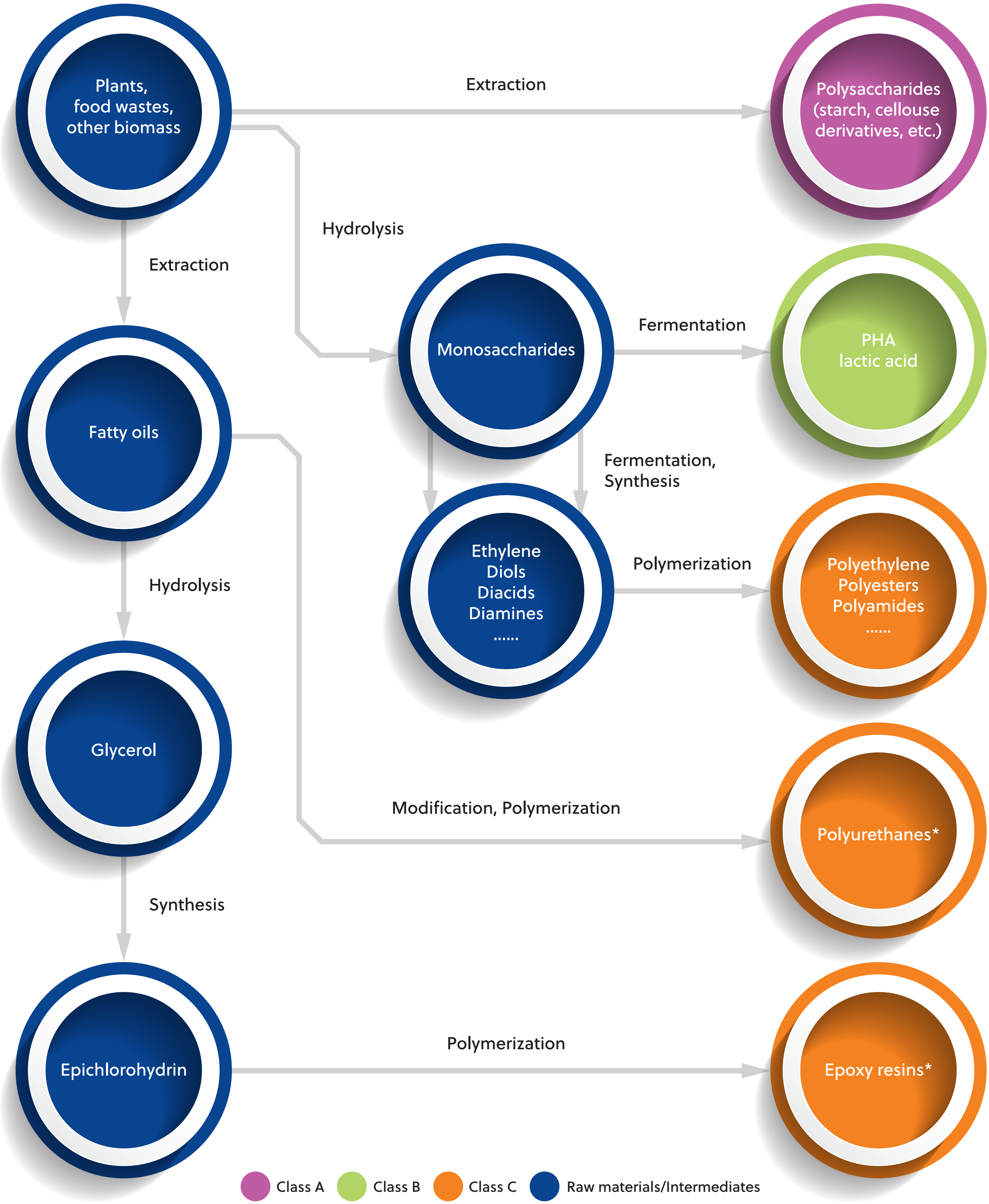

Figure 1. Illustration of production routes to bio-based polymers. *Less popular routes leading to only partially bio-based polymers
PHA, polyhydroxyalkanoate

Types of bio-based polymers

Separated by their sources and production methods, there are three major types of bio-based polymers:

A. Polymers obtained directly from biomass, such as starch, cellulose, and derivatives

B. Polymers bio-synthesized using microorganisms and plants, or prepared directly from monomers that are predominantly bio-synthesized, such as polyhydroxyalkanoates (PHAs) and polylactic acid (PLA)

C. Conventionally oil-based polymers prepared from alternative bio-sourced monomers, such as polyethylene and PET

Some general paths to the production of bio-based polymers are schematically shown in **Figure 1**, and a summary of the advantages and limitations of the classes can be found in **Table 1**.

Table 1. Advantages and limitations of the three classes of bio-based polymer
PBAT, polybutylene adipate terephthalate; PBS, polybutylene succinate; PE, polyethylene; PET, polyethylene terephthalate; PHA, polyhydroxyalkanoate; PLA, polylactic acid

Class of bio-based polymer	Advantages	Limitations	Ongoing research
Class A Polysaccharides including starch,[8] cellulose,[9] chitosan,[10] alginates[11]	– Low cost – Wide availability – Biodegradable	– Inadequate mechanical strength compared with fossil-based plastics, so often need to be used in combination with other polymers or reinforced	– Blending with other polymers or additives[12–14]
Class B Polylactic acid (PLA)[15] and polyhydroxyalkanoates (PHAs)[16]	– Can be produced through microbial fermentation – Biodegradable – PLA: good mechanical strength, low melting point – PHAs: high biocompatibility	– High manufacturing costs; economical production of PLA/ PHAs is challenging – PHAs: nonoptimal thermal and mechanical properties mean applications without combining with other polymers are limited	– PLA: Improving the yield and purity of lactic acid and utilization of biomass[17,18] – PHA: Improving utilization of biowaste substrates[19]
Class C Including polyethylene (PE),[20] polyethylene terephthalate (PET),[20] polybutylene adipate terephthalate (PBAT),[21] and polybutylene succinate (PBS)[22]	– Structurally similar to fossil fuel-derived polymers – Can fit seamlessly into existing production lines of traditional plastics manufacturing facilities	– Nontrivial conversion of renewable feedstocks to the required synthetic monomers – Mostly non-biodegradable	– Catalysts for improved conversion and selectivity[23,24] – Better purification to obtain polymerization-grade monomers[25,26]

The production and market status of key bio-based polymers

Commercial bioplastics have been mainly used in packaging: starch and PLA are the most manufactured bioplastics, most likely due to their lower costs; PHAs, on the other hand, have high production costs and thus have been made in much lower quantities. The production volumes, leading suppliers, and main applications for some of the most important commercial bio-based polymers are summarized in **Table 2**.

Table 2. Production and applications of top commercial bio-based polymers
PBAT, polybutylene adipate terephthalate; PBS, polybutylene succinate; PE, polyethylene; PET, polyethylene terephthalate; PHA, polyhydroxyalkanoate; PLA, polylactic acid

Bio-based polymer	2020 Global capacity (tons)[27]	Major producers	Main applications	Biodegradable?
Starch and blends	435K	Futerro, Novamont, Biome	Flexible packaging, consumer goods, agriculture	Yes
Polylactic acid (PLA)	435K	NatureWorks, Evonik, Total Corbion PLA	Flexible packaging, Rigid packaging, consumer goods	Yes
Polyhydroxyalkanoates (PHA)	40K	Yield10 Bioscience, Tianjin GreenBio Materials, Bio-on	Flexible packaging, Rigid packaging	Yes
Polyethylene (PE)	244K	Neste, LyondellBasell	Flexible packaging, Rigid packaging	No
Polyethylene terephthalate (PET)	181K	Toray Industries, The Coca-Cola Company, M&G Chemicals	Rigid packaging	No
Polybutylene adipate terephthalate (PBAT)	314K	Algix, BASF	Flexible packaging, Rigid packaging, agriculture	Yes
Polybutylene succinate (PBS)	95K	Roquette, Mitsubishi Chem., Succinity	Flexible packaging, agriculture	Yes

Publication trends in bio-based polymers

Using publication volume data from the CAS Content Collection™, the trends of journal and patent publications pertinent to each of the three classes of bio-based polymers in the past two decades were studied.

To illustrate R&D interest in bio-based polymers in general, the annual journal and patent publication numbers for the years 2001-2021 were examined (**Figure 2**). The volumes of both journal publications and patents grew slowly in the first few years, then both started accelerating. However, beginning around 2014, the growth in patent publication volume slowed down considerably, while the strong increase in journal publication numbers continued up to 2021.

Since bio-based polymers are mainly developed as renewable alternatives to fossil-based plastics, substantial rises in the latter's prices would increase bio-based polymers' competitiveness and significantly boost enthusiasm and confidence among researchers and inventors. Plastic prices are known to be tightly linked to oil prices, which experienced substantial growth since the mid-2000s and an unprecedented sharp peak in 2008,[28] which may potentially explain the inflection point, particularly visible in the patent publication number curve at around 2008. Oil prices plummeted after 2014, making bio-based polymers relatively more costly again, thus presumably discouraging inventors and causing the patent publication volume to level off at the exact same year.

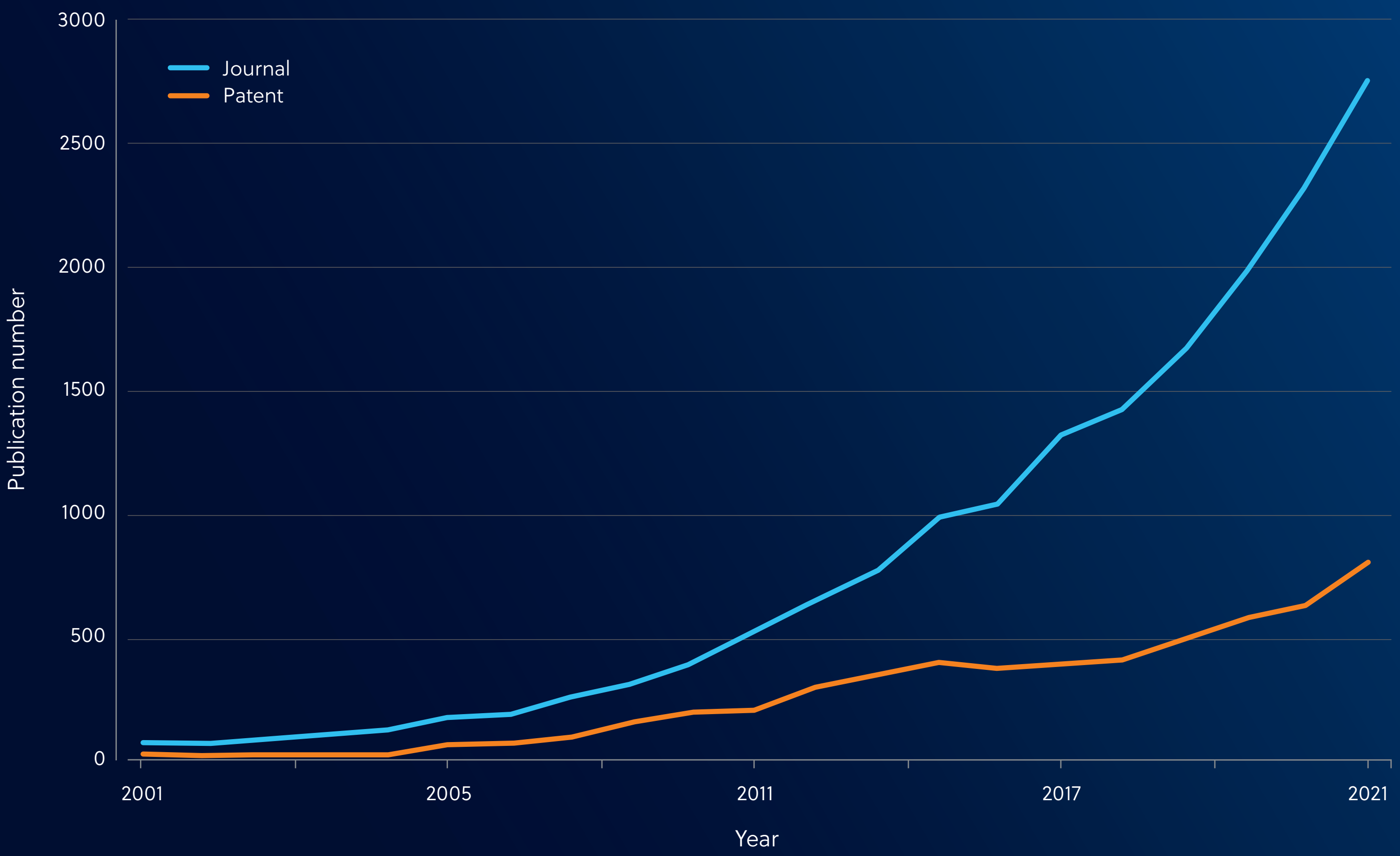

Figure 2. Numbers of publications related to bio-based polymers in general from 2001 to 2021

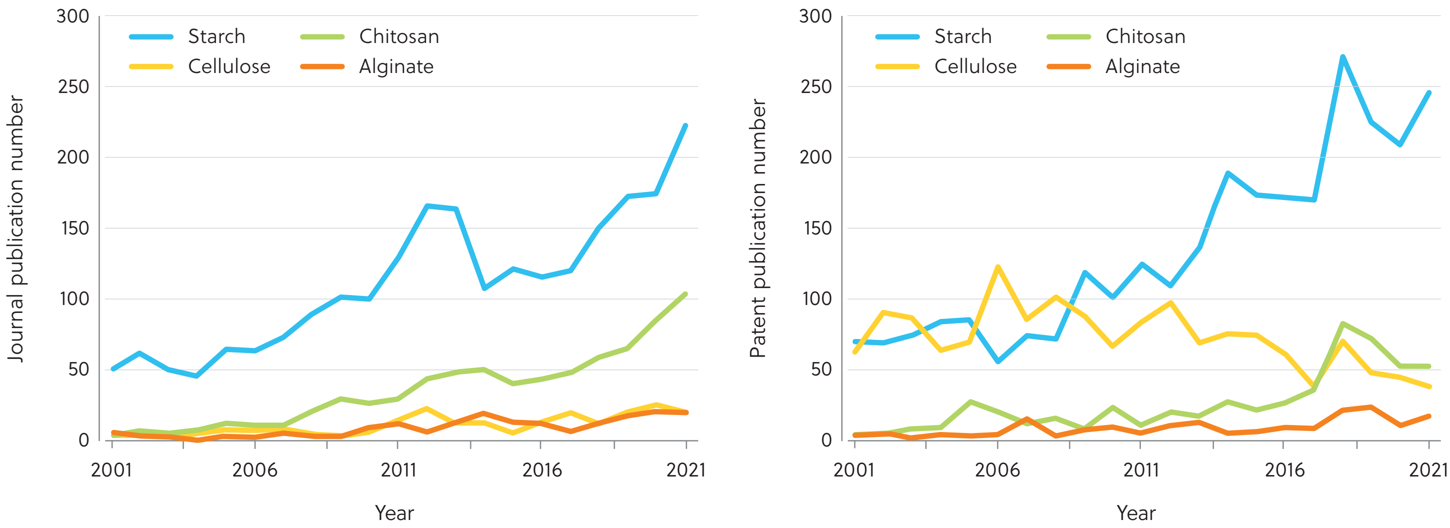

Figure 3. Numbers of journal (left) and patent (right) publications on Class A bio-based polymers for the years 2001–2021

The publication trends for the different classes of bio-based polymers were then analyzed individually. **Figure 3** shows the publication trends of the most important Class A polymers; both journal and patent publications for starch dominated the other polymers in the class. Despite fluctuating numbers, a patent publication trend consistent with that observed in **Figure 2** can still be identified for starch, with accelerated growth after 2008 and stabilization after 2014, although greater fluctuations occurred afterwards. No clear trends, however, are seen in patent publications for cellulose, chitosan, and alginates.

It is worth mentioning that Class A polymers offer much inferior overall performance than the other two classes and thus have long been developed for undemanding applications specific to them than for the replacement of oil-based plastics. Furthermore, they have always been widely used as reinforcing fillers for other plastics, and it is impossible to completely exclude the related "false positive" publications from the search results. These may well explain the lack of identifiable patterns in patents for most Class A polymers, as well as the high starting publication numbers for starch and cellulose. The journal publications, on the other hand, do show a continuous increase for starch and cellulose, albeit the bumps around 2011–2014. Chitosan and alginates had much fewer journal publications, but the increases since around 2009 are still evident.

Publication volumes for PHA and PLA, the most representative Class B bio-based polymers, are shown in **Figure 4**. Here, both polymers display clear trends of increasing publication numbers up to 2013–2014, leveling off or going down afterward (except patent publications for PLA which peaked in 2008). Particularly, journal publication volumes for both polymers follow almost the same pattern. Again, the decreases after 2013–2014 can likely be attributed to dropping prices of oil-based plastics and the resulting fading interest in bio-based polymer development.

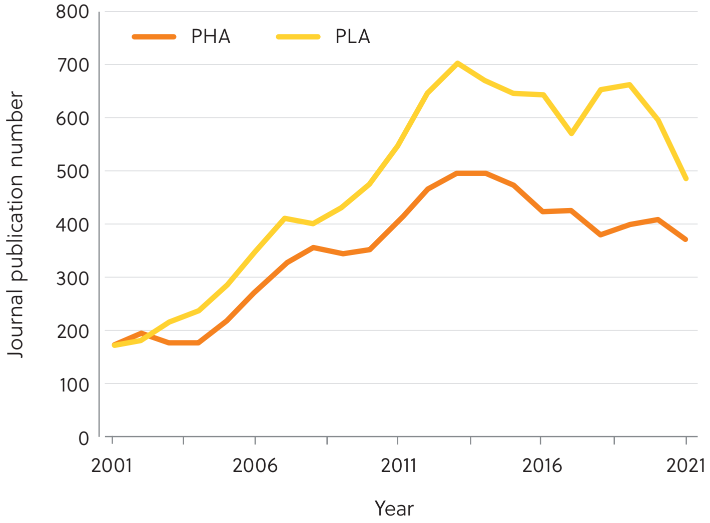

Figure 4. Numbers of journal (left) and patent (right) publications on Class B bio-based polymers for the years 2001-2021
PHA, polyhydroxyalkanoate; PLA, polylactic acid

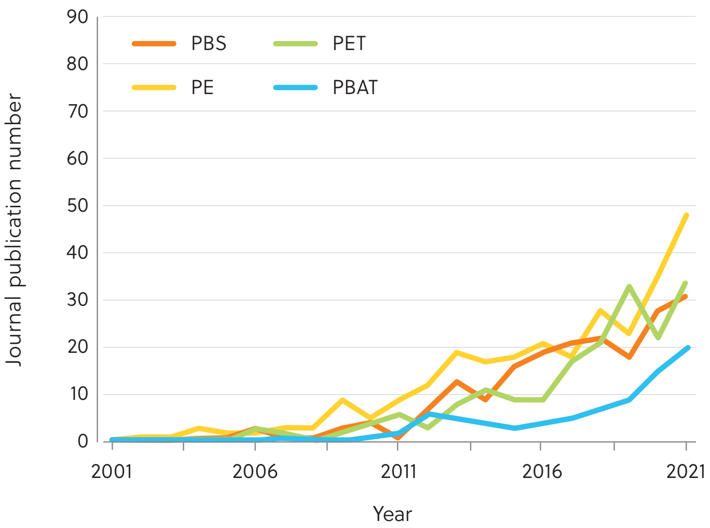

Figure 5. Numbers of journal (left) and patent (right) publications on Class C bio-based polymers for the years 2001-2021
PBAT, polybutylene adipate terephthalate; PBS, polybutylene succinate; PE, polyethylene; PET, polyethylene terephthalate

It's important to note that since Class C polymers have structures identical to their oil-based counterparts, and are simply instead manufactured from bio-based monomers, most of the research and inventions are expected to focus on the monomers, rather than the polymers. Data from **Figure 5**, obtained using the polymers as search terms, should therefore be considered merely as a general indication of research interest and not necessarily as accurate reflections of research trends in the area.

To gain better insights into the development status of Classes B and C bio-based polymers, publication trends in the production of some representative bio-based monomers have been studied.

Figure 6 shows the publication numbers for some of the most developed monomers: ethylene, succinic acid (SA), and lactic acid (LA). Data for PHAs are also shown since their preparation via fermentation is the bottleneck in their development, and related publication volumes would be a major indicator of their popularity with researchers and inventors. Here, unmistakable trends of patent volumes growing first then decreasing since 2013–2014 are observed for all four substances. The similarity in shapes among all the curves is striking, considering that different search queues were used and tailored to fit each material. The trends are, again, less pronounced for journal publications, where a significant reduction in publication volume in the late 2010s is only observed for PHA.

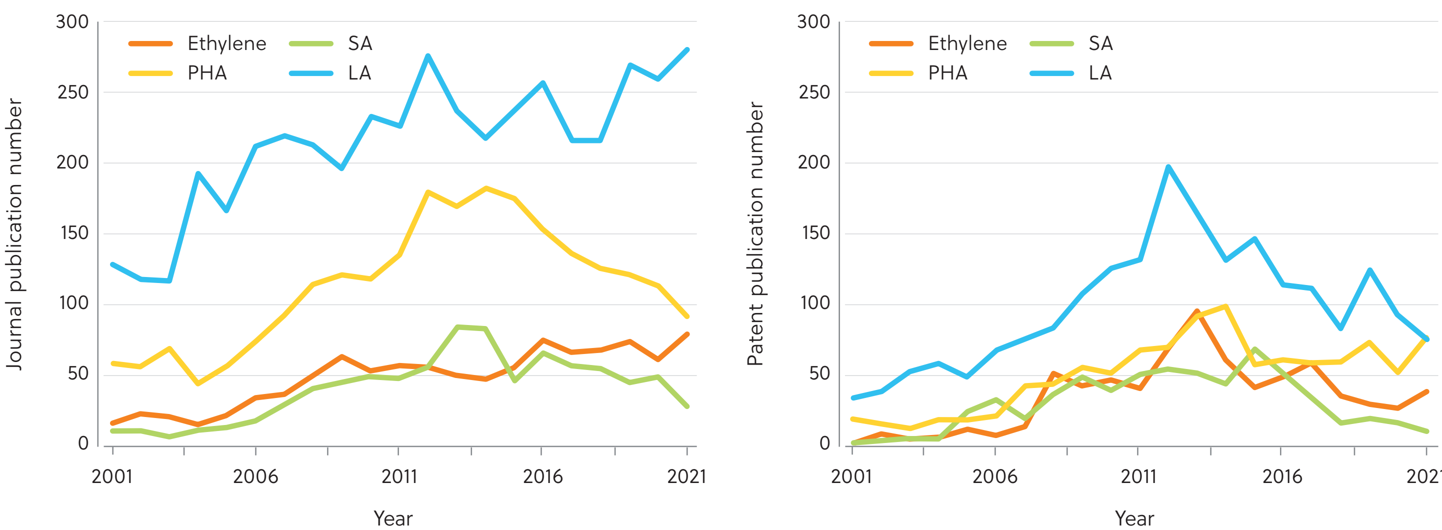

Figure 6. Numbers of journal (left) and patent (right) publications on the preparation of leading bio-based monomers and PHAs for the years 2001–2021
LA, lactic acid; PHA, polyhydroxyalkanoate; SA, succinic acid

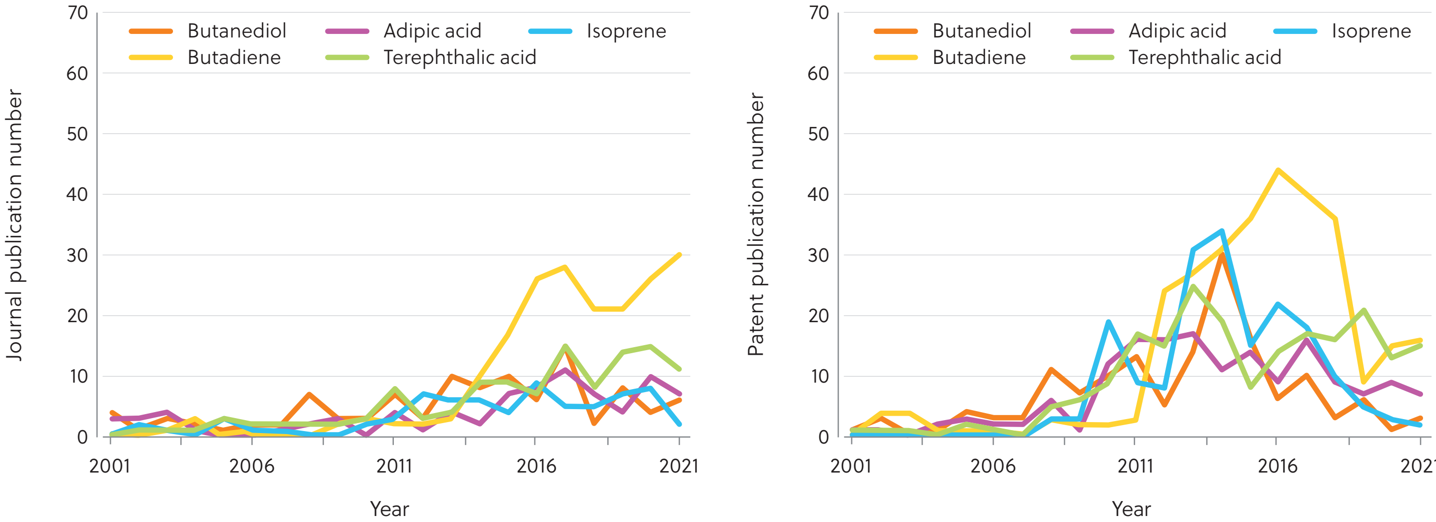

Figure 7. Numbers of journal (left) and patent (right) publications on the preparation of some less studied bio-based monomers for the years 2001–2021

The results for some newer, less-established bio-based building blocks are shown in **Figure 7**. It can be seen that these monomers received research and innovation interest later compared to those in **Figure 6**: there are very limited numbers of publications prior to around 2009 for both journal articles and patents. Patent and journal publications of these less-established bio-based monomers behave similarly to their more-established siblings otherwise, with publication volumes for most monomers peaking in the early 2010s and decreasing afterwards.

Challenges of bio-based polymers

Despite the recent dwindling patent publication activities, industrial production volumes of bio-based polymers are increasing every year. However, conventional plastics production has been growing at a faster pace, and the global market of bio-based polymers has remained only about 1 percent of all plastics.[29] The obvious leading reason is cost.

The sinking oil prices since 2014, along with recent rapid developments in shale oil,[30] have apparently exacerbated bio-based polymers' cost disadvantage, forcing a number of producers out of business.[31–35]

Increasing oil prices, diversification of plastics supplies due to the COVID pandemic, and advancements in production may improve the commercial and financial prospects of bio-based polymers.

Public perception has been another challenge faced by bio-based polymer researchers and developers. While the great benefits of bio-based polymers are generally acknowledged, they have sometimes been subject to criticism, and even ridicule, on the basis that they will not solve the world's plastics waste problem; that their productions use farmland and compete for food sources; that they produce methane greenhouse gas while biodegrading; that they have very limited applications and would not replace the majority of conventional plastics; and so on.[36–39]

Myths versus Facts of bio-based polymers

With the belief that the benefits of bio-based polymers far outweigh their disadvantages, we take this opportunity to share our opinions on some of the most frequently raised concerns in the following myth/fact discussions (**Table 3**). We hope these discussions will help raise public awareness of the value of bio-based polymers, providing a fair assessment of these products to aid decisions around subsidies and regulations for the bio-based polymer market.

Table 3. Myths vs. facts about bio-based polymers
PBAT, polybutylene adipate terephthalate; PBS, polybutylene succinate

Myths	Facts
Bio-based polymers = biodegradable polymers	Not necessarily. Whether a polymer is biodegradable depends ultimately on its structure rather than how it is produced. While most Class A and Class B bio-based polymers happen to be biodegradable, only a few Class C polymers (e.g., PBS and PBAT) are
Bio-based polymers are actually not biodegradable, as they are claimed to be, and thus will not solve the plastics crisis	Bio-based polymers and bioplastics do not directly address the accumulation of plastic waste; biodegradable plastics and plastic recycling are the primary means to address waste. The primary advantage of bioplastics is the use of renewable biomass as raw material instead of non-renewable oil and gas
Bioplastics, even if biodegradable, do not degrade fast enough under normal conditions, and composting facilities must be used	Biodegradability is only a side benefit of some bio-based polymers and slow degradation is common to all biodegradable plastics, not just those that are bio-derived. Furthermore, too fast degradation would undermine a plastic product's usefulness
Bioplastics are only good for packaging applications and would not replace all conventional plastics	Applications for bio-based polymers have diversified significantly, especially with developments of Class C bio-based polymers. The proportion of bio-based polymers produced for packaging in 2020 was 47%,[27] only slightly higher than 40% for conventional plastics[40]
The production of bio-based polymers takes up much agricultural land and impacts human and animal food production	In 2019, 0.016% of the world's total agricultural land was used to produce feedstocks for bio-based polymers.[41] Therefore, even if all plastics produced today were bio-based, and even assuming the land area used increases proportionally with production volume, the proportion of farmland used would not exceed 2%

Conclusion

Bio-based polymers can be produced from biomass feedstocks via a variety of routes, and the past two decades have seen strong overall growth of research and development activities. Our analysis of publication data during this time showed that the volumes of patent publications involving most bio-based polymers, with the exception of some Class B polymers, share the common trend of an initial rapid increase that peaks at the mid-2010s and stabilizes or declines afterward. Journal publication volumes do not present distinct trends but somewhat share the patterns seen in the patent landscape.

Frequent and wide adoption of bioplastics, made from bio-based polymers, will reduce our dependency on fossil fuels, with the added benefits of lower carbon footprint and biodegradability. However, in the absence of key technical breakthroughs and government support, bio-based polymers' relatively high production costs have limited their ability to gain more market share from conventional plastics. Decreases in oil prices (and thus in the costs of oil-based polymers) after 2013 have likely had a negative impact on research around the development of bio-based polymers as viable alternatives. There are plenty of inaccurate perceptions and confusions about bioplastics among the public. Therefore, we encourage scientists and entrepreneurs to actively engage in knowledge sharing and public education, which would be vital to bioplastics gaining favorable public attention as well as government policies.

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