REVIEW

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Polybutene, polyisobutylene, and beyond: a comprehensive review of synthesis to sustainability

J. I. Mnyango, [ID] *[ab] B. Nyoni,[ab] N. Mama,[b] B. G. Fouda-Mbanga, [ID] [b] Z. Tywabi-Ngeva[b] and S. P. Hlangothi*[ab]

Polymers derived from butene and isobutylene are highly versatile and exhibit unique properties. These include polybutene, polyisobutylene, butyl rubber, polybutylene terephthalate, polybutylene succinate, and poly(styrene-*b*-isobutylene-*b*-styrene), each of which has a specific use in sectors such as packaging, automotive, and healthcare. However, despite their potential, the body of research on butene- and isobutylene-based polymers is less extensive than that of more significantly researched and used polymers like polyethylene or polystyrene. This disparity underscores the need for further comparative research to evaluate their performance, sustainability, and commercial viability relative to these traditional polymers. By highlighting new trends and finding knowledge gaps, this study presents a thorough analysis of progress in the synthesis, properties, processability, and applications of butene- and isobutylene-based polymers. The development of eco-friendly synthesis processes and the growing interest in high-performance applications—especially in the packaging, automotive, biomedical, and electronics industries—are some of the key findings. Particularly, polybutylene succinate and poly(butylene adipate-*co*-terephthalate) demonstrate how combining eco-conscious polymerization processes with biodegradability can result in the manufacture of more sustainable materials, with definite benefits when evaluated *via* life cycle assessments. Furthermore, concerns about the degradation capacities of biodegradable butene- and isobutylene-based polymers were noted in the review. Combining all the findings provides insights into future research directions, highlighting the necessity of more investigation into the economical manufacturing, green chemistry solutions, and innovative applications of these polymers. The inferences of this work suggest that these polymers have considerable potential for utilization not just in domestic and high-performance industrial applications but also as sustainable materials.

1. Introduction

Butene- and isobutylene-based polymers have emerged as a key component of contemporary polymer science and engineering due to their versatility, potential for sustainability, and various applications across several industries. These butene- or isobutylene-derived polymers comprise a wide range of materials, each with unique properties that make them valuable in different domains. A broad spectrum of polymer families, including polybutene (PB), polyisobutylene (PIB), butyl rubber (IIR), polybutylene terephthalate (PBT), polybutylene succinate (PBS), and poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS rubber),

has drawn a lot of interest from academic, domestic, and industrial circles because of their performance-based properties, biodegradability, and potential economic benefits in various sectors, which include packaging, automotive, healthcare, and electronics.

One of the earliest innovations in the history of isobutylene-based polymers was the development of IIR in the early 20th century.[1] When this polyolefin-like material was initially introduced in the 1940s, its remarkable gas impermeability and excellent resilience made it indispensable for applications like tyre production.[1,2] Thenceforth, polyolefins (PB and PIB) have established themselves in specific markets, especially those requiring high flexibility and resistance to chemicals.[3] Such homopolymers, because of their completely saturated backbones and low glass transition temperature (T_g) values, present superior flexibility and long-term chemical stability, which underpin their widespread utilization in various applications, such as seals, adhesives, and flexible materials.[3] Research into

[a] *Centre for Rubber Science and Technology, Department of Chemistry, Nelson Mandela University, P.O. BOX 77000, Gqeberha, 6031, South Africa. E-mail: mnyangojabulani@gmail.com*

[b] *Department of Chemistry, Nelson Mandela University, Gqeberha, 6031, South Africa. E-mail: percy.hlangothi@mandela.ac.za*

the synthesis, processability, and applications of materials with enhanced mechanical properties and biodegradability was further fueled by the development of polyesters (PBT and PBS) in subsequent decades.[4,5] Moreover, due to its superior elastomeric properties, processability, and thermal stability, as well as the evolving need for high-performance block copolymers, SIBS, which emerged in the late 20th century, has commercially matured into a versatile block copolymer that finds usage in adhesives, coatings, and medical devices.[6,7]

The synthesis of butene- and isobutylene-based polymers has undergone significant changes over the years, with improvements in polymerization pathways enabling precise control over characteristics such as molecular weight (M_w) and branching as well as processes like copolymerization. For example, Ziegler–Natta or metallocene catalyst systems, which offer a high M_w and a controlled polymer structure, are employed to synthesize PB, with the former being used commercially for isotactic PB-1 synthesis.[8–10] Similarly, cationic polymerization, which can also be precisely controlled to obtain the required molecular characteristics, is primarily used to synthesize PIB.[11,12] The ability to tailor these polymers for specific end-use applications, from flexible packaging items to high-strength fibers utilized in engineering plastics, has improved with the advent of innovative catalysts and reaction conditions. Nevertheless, despite these developments, much remains unknown about the long-term stability and degradation mechanisms of these materials in practical environments.

Generally, butene- and isobutylene-based polymers are not as widely studied as traditional polymers like polyethylene (PE) and polystyrene (PS). The main differences between representative butene- and isobutylene-based polymers (PB, PIB, PBT, and PBS) and PE/PS in a few selected properties are outlined in

J. I. Mnyango

Dr Jabulani Mnyango is a materials science and green chemistry researcher with a passion for designing sustainable polymers. His expertise spans the synthesis, characterization, and application of both conventional and functional polymer systems, with a strong emphasis on waste valorization, circular material flows, and end-of-life strategies for plastics and elastomers. Driven by a commitment to real-world impact, his work bridges laboratory innovation and practical application, addressing urgent global challenges in sustainable manufacturing, resource efficiency, and environmental stewardship. He also brings experience in teaching and mentorship, helping shape the next generation of scientists and engineers.
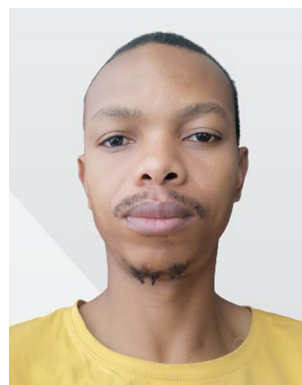
B. Nyoni

Dr Bothwell Nyoni is an active researcher specializing in sustainable materials for applications in energy generation and water treatment technologies. His research focuses on developing and optimizing advanced materials, including bio-based adsorbents and fuels that address critical global challenges related to environmental sustainability and resource efficiency. He has lectured extensively on reactor technology, chemical process engineering, and other related subjects, nurturing the next generation of engineers and scientists. His work is guided by a passion for science-driven solutions that promote sustainability, resilience, and technological advancement in both developed and resource-limited contexts.

N. Mama

Dr Neliswa Mama is a Senior Lecturer in the Department of Chemistry at Nelson Mandela University, with a notable career in organic chemistry for over two decades. She holds a PhD in Organic Chemistry from Nelson Mandela University, a master's degree from the University of Port Elizabeth, and an Honours degree (cum laude) in Polymer Chemistry from Stellenbosch University. Her research focuses on the synthesis and application of fluorescent chemosensors for detecting ionic species during water purification. She has published many papers in scientific journals, especially on materials made from coumarin-based polymers.

B. G. Fouda-Mbanga

Dr Bienvenu Gael Fouda Mbanga obtained his MSc and PhD degrees in Chemistry from the University of Johannesburg, South Africa, in 2017 and 2021, respectively. His research centers on the design and fabrication of nanocomposites for environmental remediation, with a focus on the removal of major contaminants from wastewater. He has also explored the innovative reuse of these materials in diverse applications, including forensic science (e.g., latent fingerprint detection) and photocatalysis. His interdisciplinary work integrates materials chemistry, environmental sustainability, and applied analytical science.

Table 1 Comparison of the typical properties of traditional polymers (PE and PS) and butene- and isobutylene-based polymers

Property	Polymer					
	PB[8]	PIB[12]	PBT[4]	PBS[13]	PE[3]	PS[2]
Ultimate tensile strength, MPa	20–30	0.5–1.0	50–60	30–40	10–30	30–50
Elongation at break, %	300–600	≥ 800	50–200	100–300	100–500	1–2
Thermal behavior, °C	*ca.* 120–150	*ca.* 100–120	220–250	*ca.* 90–100	120–135	*ca.* 80–100
T_g, °C	−25 to −40	−65 to −70	*ca.* 50	*ca.* −30	−100 to −125	*ca.* 100
Processing ease	Moderate	Complex	Complex	Moderate	Easy	Easy

Table 1, with an emphasis on mechanical and thermal behavior, as well as processability. Several factors contribute to this limited scope of research. The commercial adoption of some butene- and isobutylene-based polymers (*e.g.*, PIB and PBS) is restricted by their comparatively complex and expensive synthesis pathways.[5,12] In comparison, because of their wide range of applications, inexpensive cost of production, and well-established processing infrastructure, the market continues to demand well-known polymers like PE and PS.[2,3] Also, the specialized uses of some butene- and isobutylene-based materials, like PBS in biodegradable packaging[13,14] and PIB in sealants,[11,12] have not yet reached the volume or consistency required to support in-depth scholarly or commercial research.

As a biodegradable substitute for traditional plastics, PBS has gained significant attention from the perspective of environmental sustainability. This polyester material shares mechanical properties with polymers that are based on petrochemicals (*e.g.*, PE and polypropylene (PP)) and is made from plant-based feedstocks and renewable resources like succinic acid.[13–15] Durmaz *et al.*[16] have shown that solvent casting and melt mixing methods can be used to synthesize PBS-based films reinforced with alkaline-treated halloysite nanotubes. According to the literature, these films can greatly increase the shelf life of fruits by scavenging ethylene gas and controlling gas transport. This special feature demonstrates the potential of PBS as an active food packaging material. Notwithstanding these promising applications, comprehensive studies on maximizing the properties of this polymer for widespread commercial use—particularly concerning its mechanical strength and long-term durability—are still lacking.

Furthermore, PBT has earned prominence for its superior mechanical properties, high thermal stability, and chemical resistance, which make it an ideal material for use in fibers, electronics, as well as automotive exterior and interior components.[17,18] The main advantages of PBT lie in its high-performance qualities and durability, as opposed to PBS's emphasis on biodegradability, similar to poly(butylene adipate-*co*-terephthalate) (PBAT, also commonly known as Ecoflex). In engineering plastics, where strength and resistance to heat are of utmost importance, PBT is typically utilized.[17,19,20] However, even though it has been extensively studied for various applications, concerns with processing methods and cost-effectiveness still prevent it from being widely adopted in some sectors.[21,22] Therefore, the applications of PBT in a range of high-performance industries may grow as a result of further studies into developing more efficient processing methods and further enhancement of its properties.

PIB is another isobutylene-based polymer that is essential to various applications, including adhesives, sealants, and coatings.[11,12,23,24] Excellent flexibility, low-temperature performance, and exceptional chemical resistance are all made possible by the distinct chemical structure of PIB, even though the extent of these properties can depend on factors such as M_w, crosslinking, and the presence of additives.[23–26] The potential of blending this polymer with more biodegradable polymers to get hybrid materials with enhanced mechanical and environmental performance is one field that has not been thoroughly

Dr Zikhona Tywabi-Ngeva is an Academic Scientist at the Nelson Mandela University in the Department of Chemistry, where she has published research articles in peer-reviewed scientific journals and successfully supervised postgraduate students. She is a guest editor for the scientific journals: Journal of Hydrology & Water Resources and Nanoscale Advances.

Z. Tywabi-Ngeva

Percy Hlangothi (research group leader) is an Associate Professor of Physical & Polymer Chemistry and the Director of the Centre for Rubber Science & Technology at Nelson Mandela University. He is an established researcher and a Fellow of the Institute of Materials, Minerals & Mining (IOM3), FIMMM. His technical expertise is in polymer processing and characterization, and his research interests and activities are rooted in finding sustainable solutions for day-to-day materials such as rubbers, plastics, and biomass.

S. P. Hlangothi

investigated. Exploring the compatibility and interactions of PIB with polymers like PBS or PBAT may result in new materials that combine high performance with biodegradability.

Ultimately, even though each of the butene- and isobutylene-based polymers investigated in this review has achieved notable commercial success in a variety of applications, there is still a lack of studies into their long-term effects on the environment and their recyclability, as well as the development of more sustainable raw materials and alternative butene- and isobutylene-based polymers. For example, whilst IIR is widely recognized for its effectiveness in tyre applications, details are scarce on its capacity to be recycled and its potential for integration into models of the circular economy. Similarly, the challenges in enhancing the mechanical properties and degradation rates of biodegradable butene- and isobutylene-based polymers remain important ongoing research topics.

This review aims to present a comprehensive exploration of PB, PIB, IIR, PBT, PBS, and SIBS polymers, emphasizing their synthesis, processability, properties, and applications. Special attention is given to these saturated polymers. Unsaturated polymers, such as polybutadiene and polyisoprene, along with their derivatives, are excluded from the present discussion due to their distinct chemical behavior, synthesis methods, and application profiles, which warrant a separate and focused review. In addition to surveying established knowledge, this review highlights areas that are still under-explored, including scalability, environmental impact, and recyclability of the butene- and isobutylene-based

materials, while offering some suggestions for future research directions to address these gaps. Accordingly, this review promotes a better understanding of these polymers and their potential for domestic and industrial applications by consolidating the existing body of knowledge and identifying opportunities that necessitate more research.

2. Synthesis of butene- and isobutylene-based polymers: key steps, conditions, and challenges

This section covers the different types of butene- and isobutylene-based polymers, focusing on their classification and synthesis processes. These polymers can be generally divided into four primary groups, polyolefins, polyolefin-like materials, polyesters, and block copolymers, based on their backbone structure, the monomers involved, polymerization methods employed, as well as resultant material properties and applications (Fig. 1).[3,14,27,28] A variety of industrial applications can benefit from the unique characteristics of each group, which each represents a different category of materials. An extensive understanding of synthesis processes is essential for the design and development of innovative materials with desired functionalities and applications.

Since the polyolefins are synthesized from butene and isobutylene (commonly known as isobutene in industrial contexts) through homopolymerization, respectively, PB and PIB
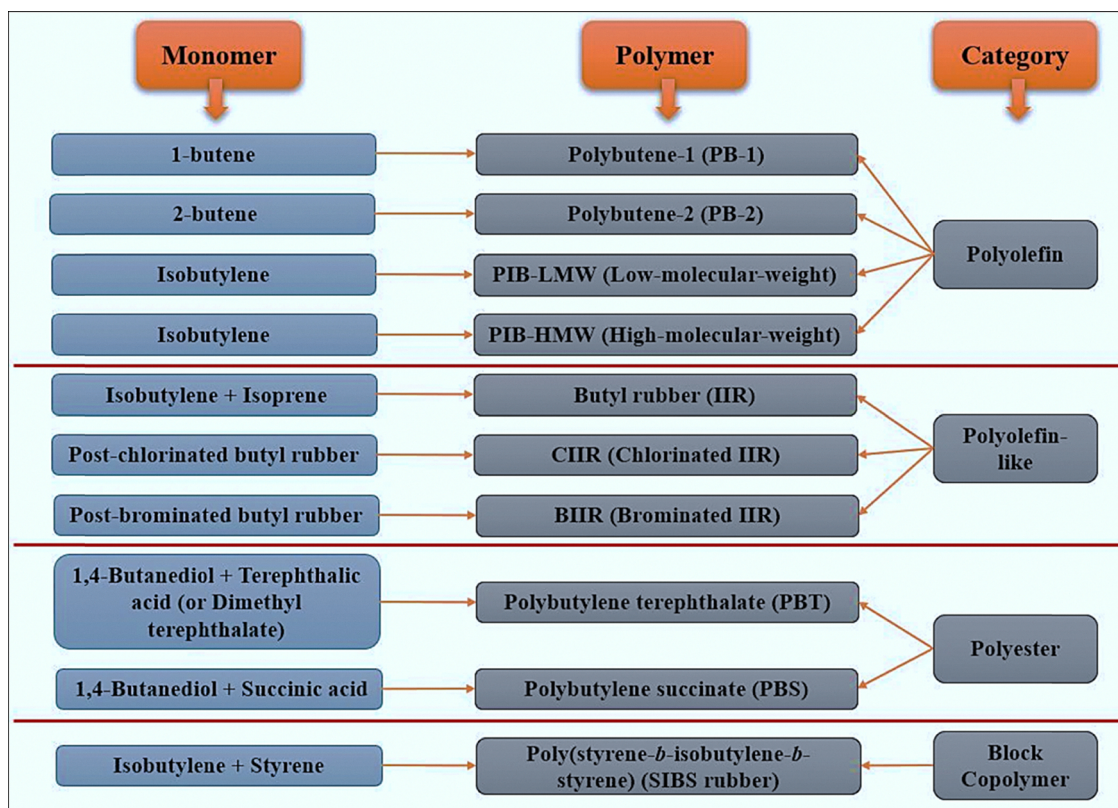

Fig. 1 Classification of butene- and isobutylene-based polymers by monomer composition, polymer type, and category.[3,14,27,28]

are included in the polyolefin group. Catalytic methods such as Ziegler–Natta or metallocene-based systems (for PB)[8–10,29] and cationic polymerization (for PIB)[11,12,30–33] are used to synthesize these materials. Although polyolefin-like materials (IIRs), which are typically synthesized *via* solution and cationic polymerization, exhibit a structure that is relatively similar to polyolefins as a result of isobutylene monomer copolymerized with 1 to 4 wt% of isoprene,[34] their synthesis methods and the resultant properties differ, making them a separate category. Furthermore, PBT and PBS, two isobutylene-based polymers that are polyesters, are synthesized *via* polycondensation reactions between diols and dicarboxylic acids.[35–41] PBS is made from succinic acid and butylene glycol, whereas PBT is made by reacting butylene glycol with terephthalic acid. Despite being a block copolymer (another category), SIBS is considered an isobutylene-based polymer due to the significant presence of an isobutylene-originating central block polymer, PIB, which generally makes up 40–70 wt% of SIBS, where the styrene blocks occupy the remaining portion.[6,42,43] Even though fewer studies are devoted to the core synthesis of SIBS itself, cationic polymerization has been used to synthesize this SIBS.

2.1. Synthesis of polyolefins

2.1.1. Radical polymerization. Syntheses of PB and PIB can be easily accomplished through the radical polymerization method. Radical polymerization of a monomer (1-butene or 2-butene for PB and isobutylene for PIB) begins with the breakdown of an initiator, azobisisobutyronitrile (AIBN, an azo compound) or benzoyl peroxide (BPO, an organic peroxide), where the latter is the most utilized chemical.[25,44–46] BPO breaks down between 50 and 90 °C to generate benzyl radicals that initiate polymerization, whereas AIBN decomposes at *ca.* 70 to 80 °C, producing cyanopropyl radicals.[44,45,47,48] Higher temperatures accelerate the reaction by increasing the rate at which radicals are generated.[45,46] The temperature is typically controlled by dissolving the reactants (monomer and initiator) in solvents like toluene or dimethylformamide (though bulk polymerization is possible), which also improves their mixing, where the viscosity of the reaction mixture is better monitored.[44,46] The concentration of the reactant, particularly a monomer, affects the polymerization rate; a higher concentration often leads to a faster reaction rate. This can also lead to the generation of highly branched or crosslinked structures.[25,45,47] Moreover, although organic peroxides are more often thermally broken down to generate free radicals, they can also be photodecomposed under ultraviolet (UV) radiation, which produces free radicals in a manner that is similar to that of heat. However, compared to azo compounds, which are more sensitive to UV radiation, the photochemical activation of an organic peroxide by UV light may not be as widespread in industrial applications due to its lower quantum efficiency, higher activation energy (hence, less responsive to typical UV source), and the potential for uncontrolled decomposition under certain conditions. AIBN is activated at ambient (or slightly elevated) temperatures by UV light typically in the 300 to 365 nm range.[49,50] While atmospheric pressure is usually used, pressures ranging from 1 to 1×10^3 atmospheres can be applied

to promote specific monomer conversions or to increase the rate of reaction.[50] Therefore, the choice between heat, light, and other reaction conditions influences the duration of the polymerization process, which can range from a few hours to a full day when synthesizing a polyolefin *via* the radical polymerization method.[51] Furthermore, after an initiator has reacted with the monomer, the polymer chain can be initiated by the radical that has developed at the reactive site of the monomer, which subsequently reacts with the growing chain radical. The radical attack at the unsaturated, active site of a monomer is repeated until the polymer chain reaches the desired length or its growth is terminated when two radicals combine, effectively neutralizing each other. Apart from the radical combination (or disproportionation), termination can also occur through chain transfer, where a growing polymer chain transfers its reactive site to another molecule, which can be the monomer, solvent, or another polymer. However, in contrast to the radical combination, chain transfer tends to affect the polymerization kinetics and can influence the characteristics of the PB or PIB, including their molecular weight (*i.e.*, number-average molecular weight and weight-average molecular weight), molecular weight distribution (MWD), and architecture.[32,52,53]

Among the primary advantages of the radical polymerization process are its versatility as well as simplicity as it does not require highly specialized equipment and can be initiated with easily accessible initiators (therefore, it is economical).[54,55] It can also polymerize a wide variety of monomers.[54] This makes it well-suited for use in bulk, solution, or suspension conditions as well as for the large-scale industrial manufacture of polyolefins with different M_ws.[54–56] However, radical polymerization can also produce homopolymers with a rather broad distribution of molecular chain lengths due to the random nature of the process, especially the initiation and termination stages.[57,58] The resultant broad MWD is detrimental as it causes processing challenges, *e.g.*, issues in controlling melt flow during injection molding or extrusion, as well as complex polymer blending.[58] It also lacks precise control over the polymer stereochemistry or block structure, *i.e.*, results in irregular arrangement of the side groups along the polymer backbone.[58,59] Accordingly, the radical polymerization method, especially if the reaction conditions are not carefully controlled, leads to the polymer's inconsistent behavior, which can be a result of the formation of increased branched structures, crosslinking, and gelation (a network that prohibits polymerization from occurring), all of which decrease performance consistency in numerous applications.[60]

2.1.2. Cationic polymerization. Cationic polymerization is another fundamental method for synthesizing polyolefins, commonly the PIB.[11,30,32,33,61–64] For this process, the cationic species (initiator) can be a Lewis acid (*e.g.*, boron trifluoride (BF$_3$), aluminum chloride (AlCl$_3$), or an onium salt like tetraethylboronium ion (Et$_4$B$^+$)) or Brønsted acids (*e.g.*, protonic acids like hydrochloric acid). Moderately polar solvents like methanol, acetone, dioxane, and tetrahydrofuran are typically used to aid in stabilizing these species and preventing adverse pathways. In essence, Lewis acids produce a carbocation (C$^+$) by accepting a lone pair of electrons from a monomer, whereas

Brønsted acids donate protons (H^+) to generate the C^+. Additionally, the choice of solvent is essential, as its polarity plays a key role in controlling the cationic polymerization rate, alongside the concentration of the initiator. For example, PIB synthesis employs moderately polar solvents to achieve high reaction rates and desired M_w control since highly polar solvents may slow down the rate due to over-stabilization of the cationic species and the formation of ion pairs.[32,64–67] Similarly, increased monomer concentration often results in a faster rate of polymerization due to a higher availability of monomer molecules for chain propagation. Furthermore, since the cationic species are more stable and reactive at low temperatures, cationic polymerization is usually conducted between 0 and 30 °C.[65,67] This low-temperature requirement, while advantageous for controlling reactivity, also promotes energy demand and could limit process scalability, especially under standard industrial conditions. Following the generation of the cationic species, the C^+ electrophilically attacks the monomer, breaking its double bond open. By adding monomer units one after the other, the resulting positively charged species lengthen the polymer chain. Cationic polymerization of polyolefin can also be terminated in two ways: recombination or chain transfer, where a stable polymer is typically synthesized through the former, which occurs when two growing polymer chains with positively charged ends interact.[61,65]

The advantage of using cationic polymerization to synthesize polyolefins is that it offers more control over the resultant polymer's molecular structure, weight, and stereochemistry.[62,67] This level of control, however, is typically accompanied by elevated operational costs, especially as a result of the need for stringent purity, dry conditions, and the employment of moisture-sensitive and often expensive catalysts. In contrast to the radical-based process, cationic polymerization produces a polymer with (i) a narrower MWD (i.e., lower Đ), indicating greater uniformity of chain lengths, and (ii) chains that have constant tacticity—the arrangement of side groups along the backbone chain.[61–66] In addition, the cationic polymerization method is selective, i.e., not every butene isomer may be suitable for it, and is more effective when 1-butene and isobutylene monomers are used, which generally counts as its limitation.[67] Oxygen, moisture, or other contaminants can also deactivate the cationic initiators and impede the polymerization process, making cationic polymerization susceptible to these effects.[63,66] However, to overcome some of the challenges, the cationic polymerization of PIB has been advanced to produce a highly reactive version of PIB (viz.: HR PIB), which has been thoroughly discussed by Karthikeyan et al.[31] Because of its reactive nature, HR PIB is the most vital industrial polymeric material used as an additive for lubricants, fuels, and various polymers.[31,52,65,68] The authors[31] described a variety of synthetic methods for HR PIB, such as the living carbocationic approach, organometallic catalyst systems, and the extensively studied carbocationic polymerization that involves the chain transfer promoting catalysts based on Lewis acids. An actual example of this is a study by Li et al.,[30] who used the cationic polymerization method to synthesize HR PIB. They used a water/titanium tetrachloride ($H_2O/TiCl_4$) initiating system in the 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) ionic liquid (IL) at −10 °C to make the HR PIB (Fig. 2), which had a high exo-olefin end group content ($>80\%$) and a relatively narrow MWD ($M_w/M_n \leq 2.7$). According to the authors, the main characteristic of isobutylene polymerization in ionic liquids (ILs) is that it occurs heterogeneously at the interface of the isobutylene droplets and the IL particles. The [PF_6]$^-$ anion served as both a deactivator, similar to a nucleophile or electron donor for the carbenium ion, and an activating initiator in conjunction with a Lewis acid.[30] The narrow MWD and functionality selectivity of PIB were enhanced by the conditions of a mixture.[30] ILs thus exhibit significant benefits and promise for HR PIB synthesis.[30]

Additionally, Yang et al.[69] sought to develop novel PIB telechelic prepolymers with a range of epoxide functionalities, such as cycloaliphatic epoxide, exo-olefin epoxide, aliphatic glycidyl ether, and phenyl glycidyl ether. A complete process

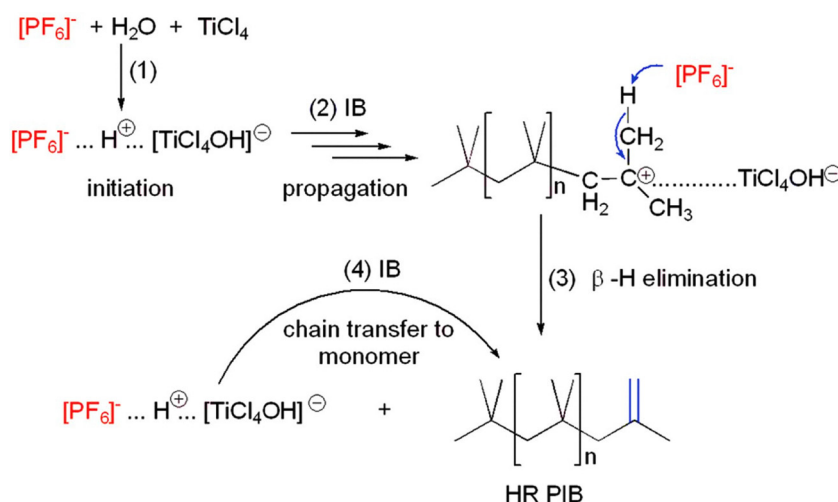

Fig. 2 Feasible mechanism of $H_2O/TiCl_4$-initiated cationic polymerization of isobutylene in [Bmim][PF_6] ionic liquid at −10 °C. Reproduced from ref. 30 with permission from Royal Society of Chemistry, copyright 2019.

is schematized in Fig. 3, where the method employed involved combining living carbocationic polymerization with post-polymerization modifications, including reaction with epichlorohydrin, epoxidation with *meta*-chloroperoxybenzoic acid, and nucleophilic substitution to introduce the desired end-group functionalities. The findings revealed that all PIB prepolymers exhibited a functionality of 2.0 and achieved the targeted M_w with narrow distributions. The study also showed how versatile the synthesis approach employed is, enabling the production of prepolymers with a variety of additional functional groups. The authors suggested that the synthesized PIB prepolymers have the potential to be applied in coatings, adhesives, sealants, and other industrial products through thermal curing or photoinitiated cationic ring-opening polymerization.

On the other hand, Hulnik *et al.*[12] demonstrated the advantage of inducing the cationic polymerization of isobutylene (and β-pinene) using visible light. Their study aimed to investigate a visible-light-induced cationic polymerization system for synthesizing PIB-LMW (and poly(β-pinene)) (Fig. 4). The method involved using a photo-initiating system comprising dimanganese decacarbonyl ($Mn_2(CO)_{10}$) and diphenyl iodonium hexafluorophosphate ($[Ph_2I]^+[PF_6]^-$) in a dichloromethane (CH_2Cl_2)/

n-hexane mixture at $-30\ °C$. The polymerization reaction was initiated by the formation of chloromethylisobutyl carbocations, generated by oxidizing the chloromethylisobutyl radicals using $[Ph_2I]^+[PF_6]^-$. These radicals were generated through chlorine abstraction from the CH_2Cl_2 by $MnCO_5^•$ radicals, which were formed upon photo-induced decomposition of $Mn_2(CO)_{10}$. The findings revealed that the studied photo-initiating system allowed the controlled synthesis of PIB with relatively low M_w (2000 to 3000 g mol^{-1}) and a Đ of less than 1.7. Notably, the synthesized PIB exhibited a high content of *exo*-olefin end groups (up to 90%), and the M_w of the polymer could be easily tuned in the range of 2000 to 12 000 g mol^{-1} by adjusting the diphenyl iodonium salt concentration. This study highlighted the significant advantage of using visible light as an initiation method for cationic polymerization, offering greater control over polymerization conditions and properties compared to traditional methods that do not employ light.

2.1.3. Coordination polymerization. Although specific cationic and radical polymerization variants, such as living cationic systems and certain radical processes, can achieve relatively narrow MWDs, coordination polymerization is widely regarded as a highly controlled method, especially for synthesizing PB-1.[9,70–75] This is due to the use of transition metal
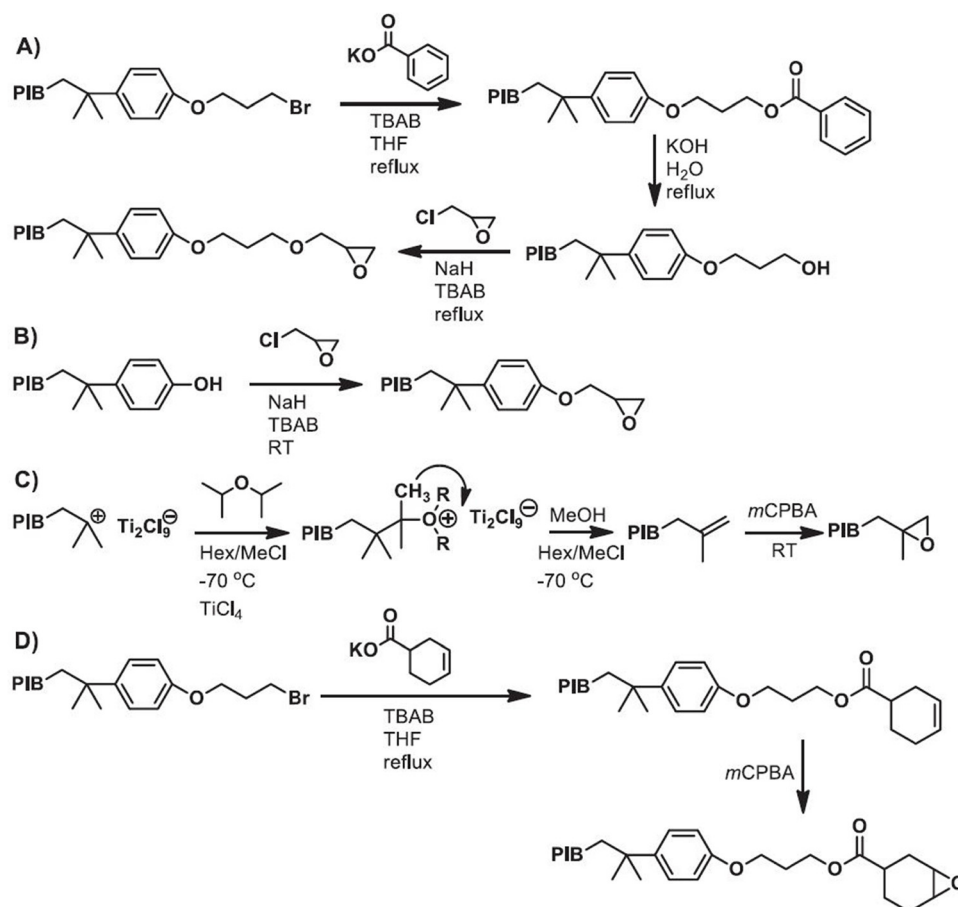

Fig. 3 Synthesis of PIB telechelic prepolymers with different epoxide functionalities: (A) PIB with aliphatic glycidyl ether, (B) PIB with phenyl glycidyl ether, (C) PIB with *exo*-olefin epoxide, and (D) PIB with cyclohexene epoxide. Reproduced from ref. 69 with permission from Elsevier, copyright 2020.
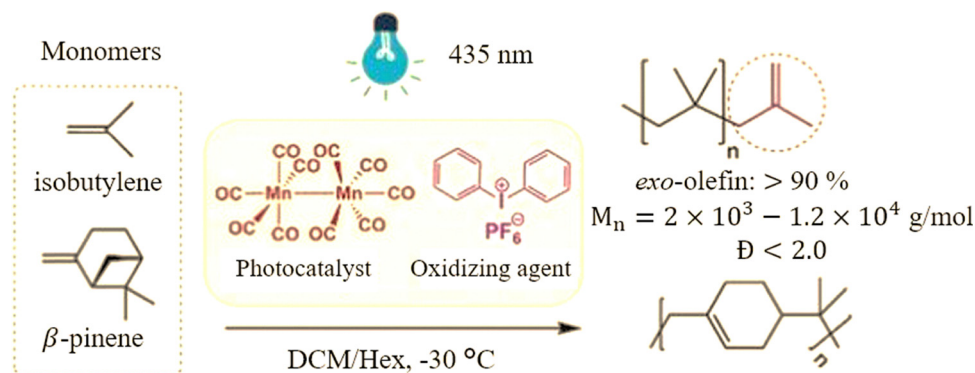
Fig. 4 Cationic polymerization of isobutylene and β-pinene *via* a photo-initiating system. Reproduced from ref. 12 with permission from American Chemical Society (ACS), copyright 2023.

catalysts and ligands, both typically requiring precise heat conditions to perform optimally, that effectively form a complex with 1-butene monomer, allowing it to polymerize through a mechanism that combines coordination and insertion.[72,75] The overall coordination polymerization process, therefore, begins with the generation of a metal–ligand complex (the catalyst), where its medium is commonly provided by a non-polar solvent, such as heptane, toluene, or hexane, that also influences the polymerization's stereospecificity (*i.e.*, MWD and tacticity of PB-1).[71,73,75] This catalyst then reacts with the monomer to activate it and generate a metal chelate monomer or monomer-metal complex at moderate temperatures and pressures, ranging from 50 to 90 °C and 1 to 50 atm, depending on the system like gas-phase, solution-phase, slurry, and autoclave (batch) polymerization reactors.[73–75] However, this can also be achieved under high pressures (up to 100 atm) to increase the monomer concentration and improve the polymerization rate, which is further influenced by the metal catalyst and co-catalyst concentrations.[74,75] Moreover, the process employs two types of catalysts: Ziegler–Natta catalysts, which are typically $TiCl_4$ coupled with an alkyl aluminum co-catalyst such as triethylaluminum (TEA), and metallocene catalysts, which are transition metal complexes (*e.g.*, Ti or zirconium (Zr)) paired with cyclopentadienyl-based ligands.[70–73] Once the monomer is coordinated with the catalyst, polymerization proceeds through an insertion process, where the monomer is inserted into the growing polymer chain.[9,72] This causes the chain to grow longer by forming a new metal–carbon connection. The monomer insertion process can be interrupted through a variety of means, including transfer pathways and catalyst deactivation.[71,74] The former occurs similarly to already discussed polymerization methods, while the latter materializes when the catalyst becomes inactive (deactivated), producing the final polymer product.

PB synthesized *via* the coordination polymerization method often has a narrower MWD, ensuring consistent properties and performance.[9,70–75] This is especially the case if metallocene catalysts are used, whereas the Ziegler–Natta catalysts generally make the method stereoselective, meaning that it often produces a polymer with specific tacticity such as isotactic, syndiotactic, or atactic configuration.[70–73] As a result, while both systems use transition metals to facilitate coordination polymerization, they differ in terms of control over stereochemistry and final polymer characteristics. They are also susceptible to moisture and impurities, which typically deactivate their ability to perform optimally and reduce polymerization efficiency, all of which disadvantage the coordination synthesis method.[70,72] Additionally, the Ziegler–Natta and metallocene catalysts are expensive due to the necessity for their precise manufacturing and activation as well as the need to be handled cautiously, which increases the overall cost of the synthesis process and commercialization.[9,70–76] The complexity and challenges associated with scaling up, due to the need for precise control over reaction conditions, are additional disadvantages of the coordination polymerization method compared to other options.[77,78] Even so, Huang *et al.*[10] used a catalyst precursor, *viz.*: η^5-pentamethyl cyclopentadienyl titanium trinzyloxide $(Cp^*Ti(OBz)_3)$, which was novel when reported in 2001, in combination with methylaluminoxane (MAO) to synthesize a stereoregular PB-1. The primary focus of the study was to find out how the conditions of polymerization affected the catalyst's activity as well as the M_w and stereoregularity of the final polymer. Variables like the polymerization temperature, Al/Ti ratio, and concentration of Ti were investigated. According to the results, the catalyst reached its maximum activity of 91.2 kgPB mol Ti^{-1} h^{-1} at 30 °C and an Al/Ti ratio of 200. Furthermore, changes in the polymerization conditions, specifically the temperature and the Al/Ti ratio, had an impact on both M_w and catalytic activity. As the temperature decreased, the M_w of the PB-1 samples increased, and the microstructure of the polymer varied: the ether-soluble portion was atactic, whereas the heptane-extracted fraction was stereoregular. It was found that the PB-1 had a narrow MWD (M_w/M_n = 1.1 to 1.2) and a M_w greater than 1×10^6 g mol^{-1}. These results provided important insights into the synthesis of highly stereoregular PB-1, although further recent research may build on this work using more refined catalysts or different polymerization conditions.

Similarly, Huang *et al.*[62] explored the synthesis and application of a catalyst precursor, *viz.*: the monotitanocene (η^5-pentamethylcyclopentadienyl) titanium tricinnamyloxide $[Cp^*Ti(OCH_2–CH=CHC_6H_5)_3]$, for the polymerization of 1-butene in the presence of MAO. The study aimed to investigate

how various coordination polymerization conditions impacted the catalytic activity, M_w, stereoregularity, and regioregularity of the resultant PB-1. The findings demonstrated that the mono-titanocene catalyst was effective in producing atactic PB-1 with good yields under typical polymerization conditions. The polymer exhibited high M_w (5.3 to 9.6 × 10^5 g mol^{-1}), stereoirregularity, and a Bernoullian factor (B) of 0.95, which suggested that chain-end control was a predominant mechanism in the polymerization process. This study also provided important insights into the synthesis of PB-1 with specific properties, further advancing the understanding of catalyst behavior in coordination polymerization pathways. In contrast, Resconi et al.[79] explored the performance of C_2- and C_1-symmetric zirconocenes in the polymerization of 1-butene, focusing on the synthesis of isotactic PB-1 with variable isotacticity and melting points. Their results revealed that the C_1-symmetric zirconocenes, especially those with heterocyclic ligands, created PB-1 with high M_w (up to 4.0 × 10^5) and fully regioregular structure. The degree of isotacticity could be tuned by altering the substitution pattern of the indenyl ligand, achieving isotactic triad contents ranging from 86 to ca. 100%. Some C_2-symmetric zirconocenes exhibited even higher isoselectivity, though they were less regioselective, with a small % of 4,1 units from secondary 1-butene insertion. The study also illustrated that the melting point and mechanical properties of the PBs correlated with their stereoregularity, with higher isotacticity resulting in higher melting points and stiffness. Notably, catalysts revealed high productivity and activity even at lower Al_{MAO}/Zr ratios, suggesting their potential for industrial application. These findings highlighted the versatility of zirconocene catalysts in producing a broad range of PBs and copolymers, with Fig. 5 illustrating the proposed elementary steps following a secondary 1-butene insertion for the synthesis of isotactic PB.

Recently, Zheng et al.[80] studied the impacts of alkylaluminium compounds, including TEA, triisobutylaluminium (TIBA), and diethylaluminium chloride (DEAC), as co-catalysts in

1-butene polymerization with MgCl$_2$-supported TiCl$_4$ Ziegler–Natta catalysts. The study aimed to evaluate the influences of these co-catalysts on catalyst activity, isotacticity, and the M_w of PB-1. The results demonstrated that TEA exhibited the highest catalytic activity, but produced PB with the lowest M_w compared to TIBA and DEAC. TIBA led to more high-isotactic PB-1 fractions with higher M_w. The solvent sequential extraction fractionation process successfully separated PB into atactic PB-1, medium-high isotactic PB-1, and high-isotactic PB-1. The incorporation of TIBA or DEAC with TEA enhanced the content of high-isotactic PB-1 fractions, with the results supporting the hypothesis that multiple active species resulted during polymerization, influencing the properties of the final polymer. Similar work has been undertaken and reported by Hakim et al.,[70] who synthesized the isotactic PB-1 in n-hexane by employing excess 1-butene monomer and an industrial Ziegler–Natta catalyst with TEA as a co-catalyst. Different properties of PB-1 were observed by varying the 1-butene pressure and the amount of hydrogen. The study demonstrated that PB-1 may be produced with a narrow MWD and enhanced mechanical properties, allowing a range of products to be commercialized under expanded operational conditions.[70] On the other hand, D'Anania et al.[81] conducted a comprehensive mechanistic study of 1-butene polymerization promoted by a C_2-symmetric ansa-metallocene prototype complex using density functional theory (DFT) calculations. The results showed that chain termination from a secondary growing chain is favored over propagation, contributing to the lower M_w observed in PB synthesized by ansa-metallocene systems. The study also identified a stepwise mechanism for the isomerization of 2,1 units into 4,1 units, with DFT findings supporting this mechanism as more feasible than a concerted one. These insights can be applied to other analogous systems, and the results lay the foundation for future work aimed at enhancing the M_w of PB. This research helps address the key limitations of PB and provides a pathway for expanding polymer molecular
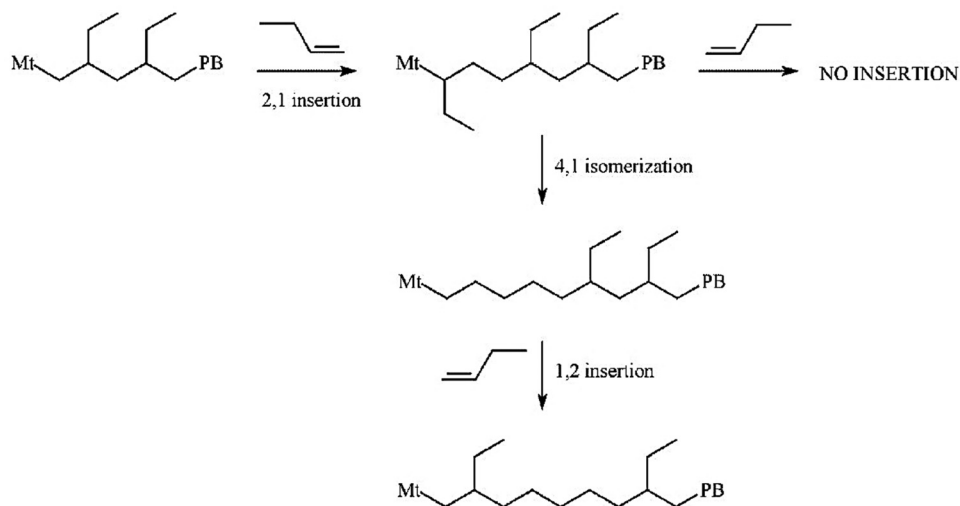

Fig. 5 Key steps involved in secondary 1-butene insertion for the synthesis of isotactic PB-1. Reproduced from ref. 79 with permission from Wiley, copyright 2006.
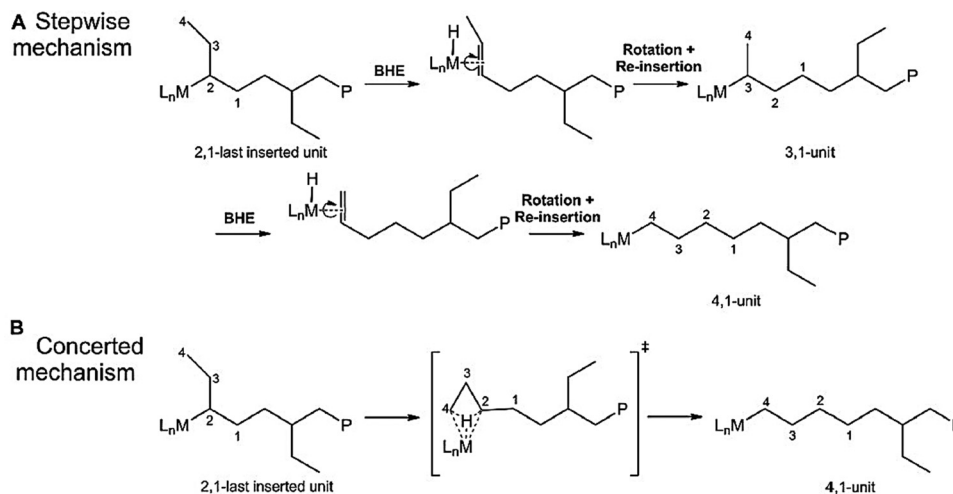
Fig. 6 Two different mechanisms for the isomerization of 2,1-last inserted butene units to 4,1 units. Reproduced from ref. 81 with permission from Frontiers Media S.A., copyright 2024.

structures, as shown in Fig. 6, which schematizes the mechanisms for the isomerization of 2,1-last inserted butene units leading to 4,1 units.

2.2. Synthesis of polyolefin-like polymer

IIR is mostly synthesized by copolymerizing isobutylene (98%) with isoprene (2%), making the process more complex compared to that of PIB synthesis. Cationic polymerization is a preferred method for IIR synthesis because it properly addresses the unique challenges presented by the monomers and ensures the generation of a high-performance material with tailored characteristics and properties for a range of applications.[1,82] The reaction during IIR synthesis typically takes place in a low-temperature environment, between -105 °C and -90 °C, to control the highly reactive carbocation intermediates.[82] A strong Lewis acid—$AlCl_3$, BF_3, tin(IV) chloride ($SnCl_4$), or $TiCl_4$—is utilized as the catalyst in the presence of a co-catalyst, commonly H_2O or alcohol, which creates the initiating proton source.[1,83,84] To ensure the solubility as well as adequate dispersion of the monomers and catalysts, the polymerization is conducted in an inert solvent such as hexane or chloromethane.[1,82,84] Controlled unsaturation sites are introduced by adding isoprene (ca. 1 to 3%), which has a more reactive conjugated diene architecture, to the predominantly isobutylene backbone, enhancing the vulcanization characteristics of the polymer.[1,82–84] This special structural characteristic

makes IIR different from other cationically polymerized polymers. The end product is a rubbery material with final properties that are dependent on the isobutylene-to-isoprene ratio, which is generally versatile in that it can be adjusted thereby enabling these properties to be tuned and making the IIR suitable for a variety of industrial applications. Furthermore, because of its lower polarity and minimal reactivity, in contrast to isoprene, which reacts more readily with the growing molecular chain, isobutylene requires precise reaction conditions in order to achieve controlled M_w, tacticity, composition, and topology.[1,82–85] This emphasizes how important the interplay between reaction kinetics and thermodynamics is in the manufacture of high-performance IIR.

A detailed overview of developments in IIR synthesis through cationic polymerization, with a highlight on enhancing the process's efficiency and sustainability, has recently been presented by Sharma et al.[1] The objective of the exploration was to provide a description of the advancements in the cationic copolymerization of isobutylene and isoprene, emphasizing how different initiating systems affect the microstructure and M_w of the polymer as well as the unsaturation content. The authors presented details regarding the chemistry and performance of initiating systems based on rare earth metals, metallocenes, boron, aluminum, aluminoxane, and zinc. They also discussed the drawbacks of commercial polymerization practices, such as the requirement for cryogenic settings and the effects of chlorinated solvents on the environment, as well as a

Table 2 Production of IIR via slurry process[1]

| Step	Description of a process
1	Mixing of chloromethane-dissolved isobutylene and isoprene with chloromethane-dissolved $AlCl_3$
2	Polymerization in a reactor kept between -105 to -85 °C
3	Formation of IIR slurry in chloromethane
4	Removal of chloromethane and volatiles in a flash tank, followed by mixing with hot H_2O
5	Incorporation of anti-agglomerates and stabilizers, followed by drying to remove H_2O and other impurities
6	Attainment of the final product, the IIR bales
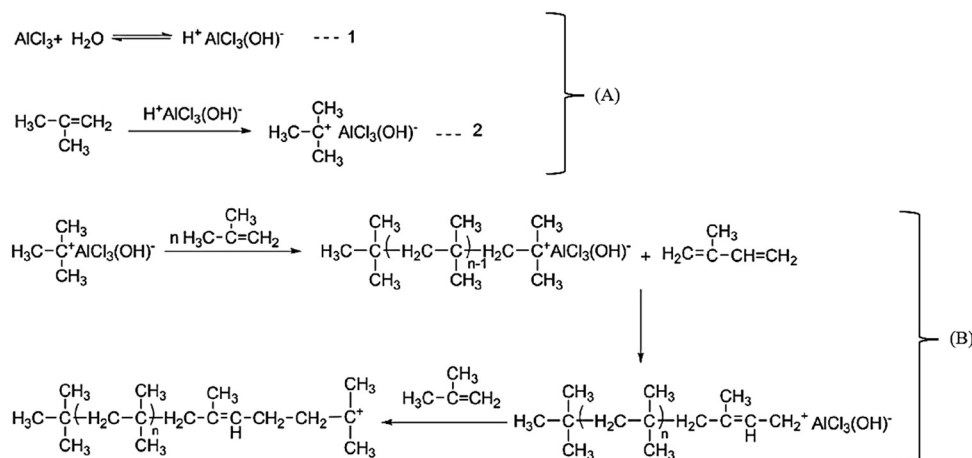
Fig. 7 Initiation (A) and propagation (B) for the synthesis of IIR *via* cationic polymerization. Reproduced from ref. 1 with permission from John Wiley & Sons, Ltd., copyright 2021.

slurry procedure (Table 2) and the solution process. Methodologically, the study looked at the cationic polymerization reaction mechanisms; Fig. 7 partly schematizes the synthesis process. Here, Lewis acid-based or organometallic initiating systems were used to first generate the highly reactive carbocation. The polymer chain is propagated by the sequential addition of monomers, whereas it is terminated by chain transfer processes, chain terminating agents, or ion pair collapse. The results demonstrated important developments in the field, especially the creation of catalysts based on metallocene and containing weakly coordinating anions, which allow for high-molecular-weight IIR synthesis at elevated temperatures. The environmental issues and energy consumption of traditional processes are addressed by these advances.

2.3. Synthesis of polyester polymer

A polycondensation reaction, which is a type of step-growth polymerization process, is used to synthesize an engineering thermoplastic or polyester copolymer known as PBT.[22,35,86–93] As illustrated in Table 3 and Fig. 8, this synthesis usually commences with either dimethyl terephthalate (DMT) or terephthalic acid (TPA) as the acid material, which reacts with a butene derivative (*viz.*: 1,4-butanediol or butane-1,4-diol (BDO)) that provides the diol group (HO–CH_2–CH_2–CH_2–CH_2–OH) under carefully monitored conditions.[87,90,93] The usage of DMT results in the production of bis(hydroxybutyl) terephthalate or bis(4-hydroxybutyl) terephthalate ($C_{16}H_{22}O_6$) through

the process of transesterification, in which DMT reacts with BDO in the presence of a catalyst, *i.e.*, Ti-based compounds or zinc acetate ($Zn(OAc)_2$), of which its function is to improve the polymerization rate and control the polymer's M_w and yield.[35,86,88,93] A small molecule like methanol (CH_3OH) is produced as a by-product during this stage and is continually eliminated to drive the reaction forward (*i.e.*, towards high M_w polymer formation).[22,35,87,93] On the other hand, TPA provides the dicarboxylic acid group (–COOH) (Fig. 9) and produces H_2O rather than CH_3OH when it interacts directly with BDO to form the same intermediate.[88,93] Specifically, the hydroxyl group (–OH) of BDO reacts with the –COOH of TPA to initiate the esterification reaction. Economic and environmental considerations frequently influence a selection between DMT and TPA, with the latter being utilized on more occasions because it is less expensive and does not produce a relatively toxic by-product (CH_3OH).[86–93]

An intermediate material ($C_{16}H_{22}O_6$) is polycondensed in the second stage to generate long PBT chains with high M_w.[90,92,93] To avoid oxidation and make it easier to remove by-products and excess BDO, this stage is normally carried out at high temperatures (250 to 280 °C) while under vacuum or inert gas flow.[89,92,93] Antimony trioxide (Sb_2O_3) and germanium dioxide (GeO_2) are two examples of catalysts that are regularly used to increase the rate of polycondensation reaction.[22,91] To limit adverse reactions like crosslinking or heat degradation and to attain the required degree of polymerization, the process is meticulously regulated. Purity is another important factor,

Table 3 An overview of the key polybutylene terephthalate synthesis stages

| Stage	Process	Condition	Catalyst	By-product	Ref.
Transesterification	DMT + BDO → $C_{16}H_{22}O_6$ + CH_3OH	150 to 220 °C, atmospheric pressure	Ti-based compound or $Zn(OAc)_2$	CH_3OH	86
Esterification	TPA + BDO → $C_{16}H_{22}O_6$ + H_2O	200 to 280 °C, atmospheric pressure	Ti-based compound or $Zn(OAc)_2$	H_2O	88
Polycondensation	$C_{16}H_{22}O_6$ → PBT + excess BDO + CH_3OH/H_2O	250 to 300 °C, decreased pressure or inert gas	Sb_2O_3 or GeO_2	CH_3OH/H_2O	93
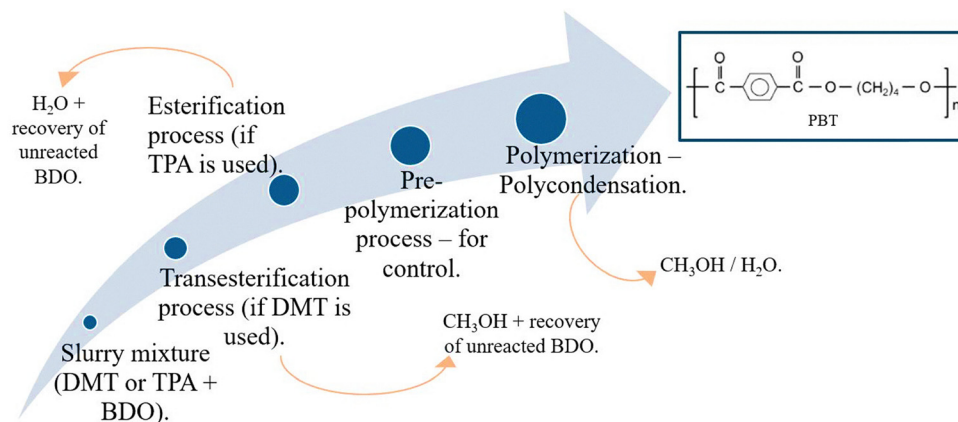
Fig. 8 Schematic representation of the synthesis of polybutylene terephthalate.

and the employment of an inert environment, vacuum, or low-pressure system typically ensures the effective elimination of volatile by-products. The resultant polymer melt is extruded, cooled, and pelletized for use or additional processing.[22,91,93] The step-growth polymerization process guarantees the effective synthesis of high-purity PBT suitable for use in various applications.[22,35,86–93]

Ittobane et al.[90] synthesized the partially renewable PBT copolyesters containing alditol units in the presence of titanium(IV) butoxide (Ti(OBu)$_4$) catalyst. The goal was to attach alditol-derived units—more precisely, 2,3-di-O-benzyl-L-threitol—to the PBT backbone in order to explore the impact on the resultant polymer structure and characteristics. The synthesis was carried out via solution-phase polycondensation, by means of mixtures of BDO and 2,3-di-O-benzyl-L-threitol with terephthaloyl chloride in 1,2-dichlorobenzene as the solvent. The chemical reaction yielded PBT copolyesters with weight-average M_ws ranging from 4.0×10^3 to 1.2×10^4 g mol^{-1} and Đ of ca. 1.5. The results revealed that the copolyesters had high M_ws, a random microstructure, and were thermally stable at temperatures >300 °C. Copolyesters containing up to 30% alditol units retained a semi-crystalline topology, with the same crystal form as parent homopolyester PBT. However, increasing the alditol content led to a significant decline in melting temperature (T_m) and crystallinity, but the T_g increased. On the other hand, Mao et al.[94] synthesized the poly(butylene terephthalate-co-tetramethylene ether glycol) (PBT-co-PTMEG) copolymers through melt polymerization, where polycondensation reactions were carried out between DMT, BDO, and PTMEG with contents of the latter ranging from 0 to 40 wt%. As schematized in Fig. 9, the synthesis route highlights the reaction scheme for incorporating PTMEG into the PBT backbone during melt polymerization. The findings demonstrated that all synthesized PBT-co-PTMEG copolymers exhibited excellent thermal behavior with a 5% decomposition temperature of ca. 370 °C. However, the incorporation of PTMEG significantly influenced the crystallization behavior of the copolymers. For instance, the crystallization temperature reduced from 182.3 to 135.1 °C, and the enthalpy of crystallization decreased from 47.0 to 22.1 J g^{-1} as PTMEG content increased from 0 to

40 wt%. This suggested a decrease in crystallinity due to the disruption of the ordered PBT chains by PTMEG. The crystal structure of PBT remained in α-form, but the X-ray diffraction's intensity of the characteristic peaks weakened with increasing PTMEG content, supporting the differential scanning calorimetry's crystallinity results.

2.4. Synthesis of block copolymer

The most often used approach for synthesizing the SIBS copolymer is the living cationic polymerization through the block copolymerization process.[6,43,95–98] Synthesis of well-defined block copolymers with narrow MWD and precise control over the block structure is made possible by this method's capacity to regulate the process. Vinylic monomer (styrene) and isobutylene are typically polymerized using a cationic initiator, such as AlCl$_3$ or TiCl$_4$, in the presence of a suitable solvent, such as toluene or hexane.[6,95,98] Isobutylene's weaker reactivity than styrene has been reported to make polymerization challenging, especially in cationic conditions, necessitating careful reaction condition control.[6,97,98] Even so, a triblock structure (i.e., styrene–isobutylene–styrene) is still formed by the sequential addition of styrene blocks to the isobutylene chain due to the living nature of the cationic polymerization, including the choice of a solvent and Lewis acid catalyst, which help facilitate controlled polymerization and thereby leading to the formation of thermoplastic elastomer with well-defined block structures.[95,96] Although fewer studies are devoted to the core synthesis of SIBS itself, a sizable body of literature concentrates, instead of the initial polymerization strategies, on the modification and processing of SIBS for specific purposes, such as improving its chemical properties or strengthening its functionality for specific end applications.[6,45,94,98] Nevertheless, the synthesis of SIBS for biocompatible materials, specifically for leaflet heart valve prostheses, was investigated by Rezvova et al.[99] The study produced SIBS with a narrow MWD ($M_w/M_n = 1.3$) via controlled cationic polymerization and demonstrated the resultant material's mechanical properties. This material showed greater elongation and Young's modulus (elastic modulus), but a lower strength when compared to xenopericard and expanded polytetrafluoroethylene (ePTFE). An investigation also illustrated that altering
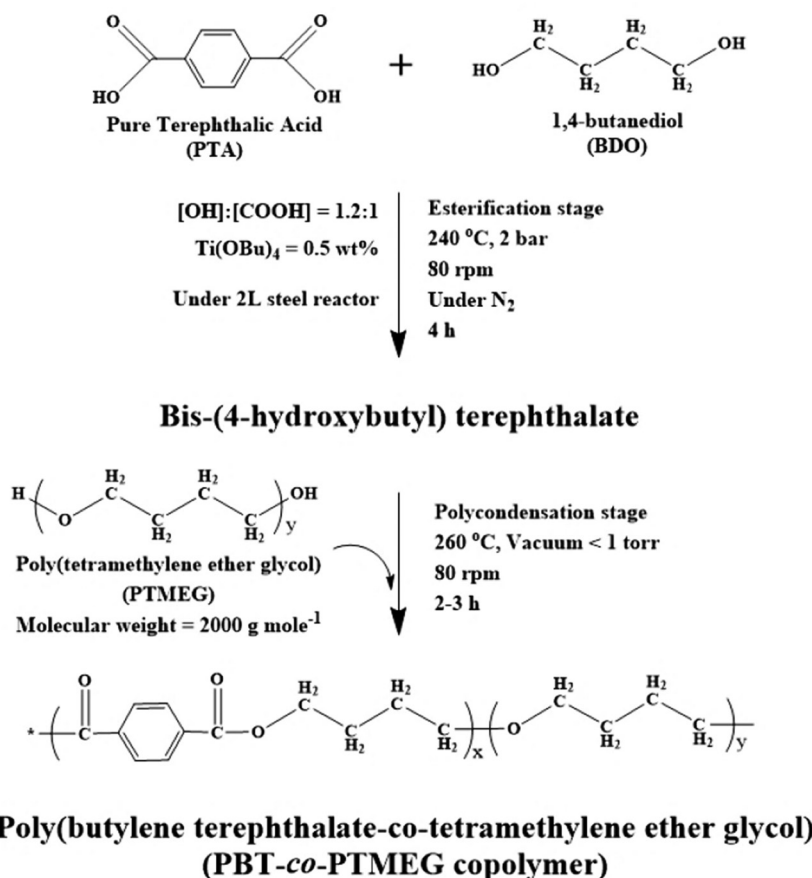
Fig. 9 Synthetic pathway for poly(butylene terephthalate-*co*-tetramethylene ether glycol) copolymer. Reproduced from ref. 94 with permission from MDPI, copyright 2020.

the core polyisobutylene block and varying the M_w could maximize the biocompatibility of SIBS, and accordingly, SIBS has promise for usage in biomedical applications, especially in prosthetic heart valves.[99] Makarevich *et al.*[95] also utilized the cationic polymerization method to synthesize SIBS, with a DiCumCl/TiCl₄/2,6-lutidine initiating system under open conditions. The work aimed to create a streamlined synthesis methodology for clearly defined SIBS without the need for the glove box method, which is commonly employed in cationic polymerization. The authors found that they could control the resultant copolymer's M_w and Đ by adding a proton trap. The ultimate tensile strength (UTS) of this SIBS was comparable to that of SIBS made in glove box conditions, demonstrating that SIBS copolymers with varying lengths of polyisobutylene and polystyrene blocks may be synthesized with minimal Đ. According to the results by both Makarevich *et al.*[95] and Rezvova *et al.*,[99] living cationic polymerization provides a practical way to create well-defined SIBS with favorable mechanical characteristics, which makes it ideal for a range of applications, in the biomedical sector and other industries.

2.5. Recent advances in synthesis

Synthesis of butene- and isobutylene-based polymers has advanced significantly as a result of the growing need for high-performance, environmentally friendly, and sustainable polymers. Exploring novel approaches and catalysts that can improve polymerization operations' efficiency while reducing their negative effects on the environment is, therefore, becoming more and more important. As noted previously, conventional catalysts, which may have limits in terms of selectivity, activity, sustainability, and economic aspects, are frequently used in traditional techniques of synthesizing certain butene- and isobutylene-based polymers. These methods also face numerous processing-related difficulties, such as high viscosity of reaction mixtures, limited control over molecular structure, high energy demands for thermal control, and the instability of catalysts under industrial-scale temperature and pressure conditions. In addition, scaling up from lab-scale to continuous industrial manufacturing typically presents challenges with heat monitoring, mixing efficiency, and real-time process management. To overcome these restrictions, current innovations like metallocene-based single-site catalysts (SSCs), continuous flow polymerization systems, green solvent utilization (such as scCO₂, ILs), and real-time reaction regulation strategies have been proposed (Table 4). These advances aim to enhance yield, control, and sustainability across the synthesis pipeline while addressing economic and environmental limitations.

2.5.1. Development of high-efficiency catalysts for sustainable production. Enhancing catalyst efficiency and selectivity

Table 4 Processing issues in the butene- and isobutylene-based polymer synthesis, along with proposed solutions

Issue	Example	Suggested solution	Ref.
High reaction medium viscosity	PIB and IIR polymerization	Utilizing diluent systems or ILs to decrease viscosity and improve mixing	30
High cost and toxicity of catalysts	AlCl$_3$ and TiCl$_4$ in conventional systems	Greener alternatives, including bio-based catalysts, earth-abundant metals, and SSCs	83
Inadequate thermal regulation at an industrial scale	Continuous synthesis of PIB	Heat exchangers-integrated continuous flow reactors	12
Poor control of MWD	PB and PIB polymerization	Utilization of metallocene SSCs, RAFT/ATRP methods for accuracy	46
Toxicity of solvents and environmental impact	Chlorinated hydrocarbons	Employing scCO$_2$ and ILs as green solvents	82
Deactivation of catalysts at elevated pressures	PIB synthesis through cationic polymerization	Modifications of a reactor; immobilized or supported catalysts	74
Upscaling batch processes	All common thermal polymerization processes	Transition to continuous flow synthesis, process intensification	75

for specific polymerization processes has been the primary focus of recent developments in catalyst design. These developments aim to lessen the use of hazardous materials, lower energy usage, and increase the yield of high-performance butene- and isobutylene-based polymers. Conventional catalysts that depend on metal halides (such as TiCl$_4$) and alkylaluminum compounds, like Ziegler–Natta and metallocene-based systems, present toxicity and environmental risks.[100,101] Green catalysts, on the other hand, including non-toxic metal complexes or biodegradable catalysts, have been developed to comply with environmental standards and minimize the usage of toxic materials. For instance, attention has been drawn to the development of biopolymer-based catalysts from sustainable feedstocks, such as proteins and polysaccharides.[102–106] Baranwal et al.[107] have provided a thorough analysis of the advancement of high-efficiency catalysts for the environmentally friendly synthesis of polymers, with an emphasis on their uses in the food packaging and medical industries. Bio-based catalysts that improve the synthesis of biodegradable polymers are essential in food applications to mitigate the environmental issues related to synthetic plastics.[102,104,105,107] Advanced catalytic techniques can be used to synthesize bio-based polymers, such as those made from renewable resources like starch, pectins, and alginates, to create materials that satisfy safety and integrity standards for food packaging while also being environmentally friendly.[102,105,107–110] In order to address the changing demands of biological systems and lessen dependency on artificial materials, these catalysts are essential for enhancing the synthesis of polymers that can be utilized in implantable and medical devices.[6,43,107,111] With these developments, the effective synthesis of bio-based polymers has enormous potential to transform food packaging and medical applications by offering more environmentally friendly substitutes for traditional materials. Like biopolymer-based catalysts, less toxic transition metal catalysts—such as those based on earth-abundant metals—have also been developed.[112–115] These catalysts provide better, environmentally friendly alternatives for conventional industrial catalysts, which are not entirely "sustainable" in the sense that they have relatively higher environmental impact.[112,113,115] However, Kahkeshi et al.[116] have claimed that these, especially the Al-based

catalysts, can also be made greener through innovative modifications. In their study, they introduced a novel IL compound supported on boehmite, used in conjunction with AlCl$_3$, to catalyze the polymerization of Raffinate 1 (C4-based mixed monomers) into PB for use as an oil viscosity improver. The work demonstrated that the supported ILs led to the production of PBs with comparable M_w and Đ to the blank AlCl$_3$ system, but with decreased exo-olefins content, which made the final product more suitable for the target application. Importantly, the key environmentally friendly advancement in their study was the halving of the dosage of AlCl$_3$ required in the polymerization process. By decreasing the quantity of this hazardous metal salt, the authors considerably minimized its environmental impact, supporting the idea that Al-based catalysts can be made greener with the right modifications. This adjustment not only helps decrease the toxicity associated with AlCl$_3$ but also aligns with the goals of sustainability in industrial catalysis, by decreasing the amount of potentially harmful materials involved in polymer production. This innovation provides a more eco-conscious alternative without compromising the performance of the polymerization process, thereby demonstrating that even Al-based systems can be modified to be more sustainable in the context of cationic polymerization.

Additionally promising for sustainable polymerization is the development of bimetallic catalysts, which combine two metals to increase catalytic activity, enhance the efficiency and selectivity of reactions, and reduce energy consumption.[113,117,118] These catalysts have the ability to improve selectivity towards desired polymer structures, raise M_w control, and increase the rate of polymerization.[113,119–121] Moreover, to increase the stability, reactivity, and sustainability of the catalytic system, hybrid catalysts—combinations of metal catalysts with organic ligands—have been used.[121–123] For instance, in the synthesis of high-density PB, bimetallic catalysts have demonstrated enhanced polymerization efficiency with superior control over stereoregularity and polymer architecture.[124] Also, high specificity and control over polymerization are provided by SSCs, which can create polymers with narrow MWD and controlled stereo-chemistry—two characteristics that are particularly important for the synthesis of isotactic PB or PB copolymers.[46,81,125,126] Metallocene catalysts are well-known SSCs. Recent developments

have concentrated on adjusting their functionality and structure to increase selectivity, sustainability, and efficiency.[127–131] Metallocene catalysts have demonstrated exceptional control over stereoregularity and MWD in the polymerization of butene-based monomers in some recent studies. For example, the use of *ansa*-zirconocene dichlorides bearing electron-rich ligands can improve isotactic selectivity in PB-1 synthesis while preserving narrow MWD.[132,133] Similarly, in the cationic copolymerization of Raffinate-1 monomers, increased catalytic activity and better tacticity have been observed when employing hafnocene-based systems.[9,134] These developments highlight metallocenes' ongoing significance as precise instruments for tailoring polymer structure, especially for high-performance applications where syndiotactic or isotactic structures are preferred. Furthermore, three key polymerization pathways—Ziegler–Natta, metallocene, and cationic polymerization—are shown in comparison in Fig. 10, with an emphasis on differences in active sites, control over polymer structure, and suitability for butene- and isobutylene-based polymers.

Metallocene catalysts provide single-site precision, generating polymers with distinct microstructures and narrow MWD, in contrast to the heterogeneous nature of Ziegler–Natta catalysts, which often produce broader MWDs and mixed tacticity.[136,137] On the other hand, cationic polymerization offers extremely rapid initiation, especially for isobutylene-derived systems like PIB; however, it usually lacks stereoregulation, though new hybrid and IL-supported systems are increasing its selectivity as well as sustainability.[138,139]

2.5.2. Strategies for polymerization to increase its efficiency. Green solvent, solvent-free, continuous flow, atom transfer radical polymerization (ATRP), and controlled radical polymerization have recently been important areas of focus for achieving more sustainable and efficient butene- and isobutylene-based polymer synthesis. Current approaches emphasize solvent-free polymerization or the use of green solvents, such as supercritical carbon dioxide ($scCO_2$) or ILs, to increase polymerization efficiency and reduce waste.[66,140–144] Since $scCO_2$ is affordable, recyclable, and environmentally

benign, it is being investigated as a sustainable solvent for the production of foam materials based on isotactic PB-1,[145–151] PBS/PBAT,[152] and PLA/PBS.[153] Similarly, it has been demonstrated that using ILs as reaction media can improve selectivity and polymerization rate while lowering the necessity for harmful organic solvents.[9,116,141,144] Furthermore, conventional polymerization techniques often involve batch operations, which can be energy-intensive and generate harmful waste.[66] A more environmentally friendly option is continuous flow polymerization, in which the reaction takes place in a continuous flow reactor, allowing for increased throughput, improved process control, and less waste generation.[154–156] Higher polymer yields and more consistent polymer characteristics are the result of precise temperature control made possible by continuous flow reactors with integrated heat exchangers. Strategies for continuous flow have also been modified for metallocene catalyst reactions. For the polymerization of α-olefins using metallocene/MAO systems, Zaccaria *et al.*[139] successfully implemented a continuous tubular reactor system, obtaining better heat and mass transfer rates, narrower MWD, and less batch-to-batch variability. This adaptation underpins the compatibility of advanced catalyst systems with contemporary sustainable reactor technologies.[157] The polymerization of medium molecular weight PIB has been accomplished with success using this approach[158,159] and offers a promise for the synthesis of other butene- and isobutylene-based polymers. Particularly, free radical polymerization (FRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization have gained disproportionate attention as a result of their simplicity and ability to tailor polymer properties and characteristics. These controlled radical polymerization techniques allow for the creation of polymers with low $Đ$ and controlled M_w.[45,56,160] RAFT, especially, presents compatibility with a broader range of functional monomers and conditions suited to isobutylene derivatives, while further contributing to sustainability by decreasing monomer waste generation and minimizing the formation of by-products.[56,160] While ATRP has also been explored, it is less typically applied to isobutylene itself and has commonly relied on commercial PIB macroinitiators rather than direct
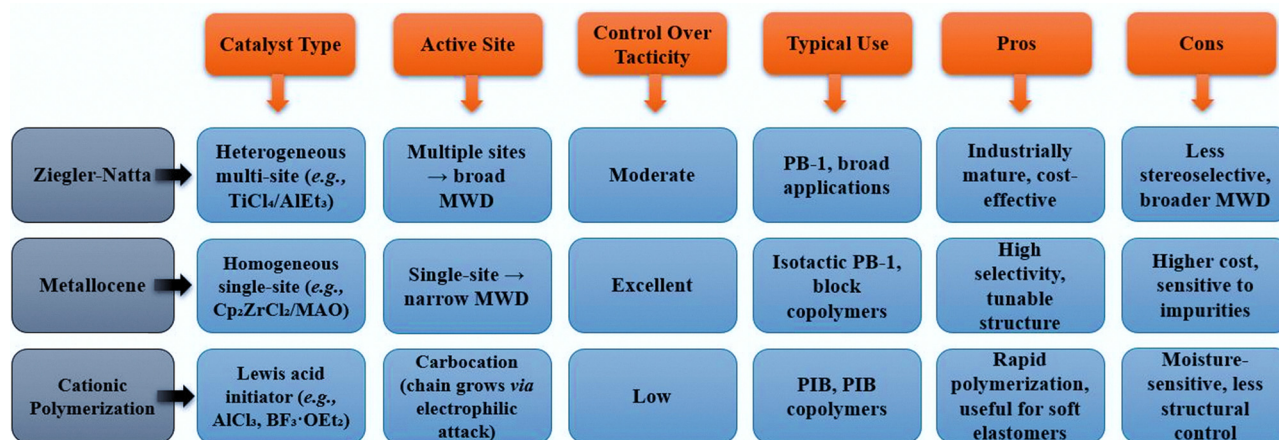

Catalyst Type	Active Site	Control Over Tacticity	Typical Use	Pros	Cons
Ziegler-Natta → Heterogeneous multi-site (*e.g.*, $TiCl_4/AlEt_3$)	Multiple sites → broad MWD	Moderate	PB-1, broad applications	Industrially mature, cost-effective	Less stereoselective, broader MWD
Metallocene → Homogeneous single-site (*e.g.*, Cp_2ZrCl_2/MAO)	Single-site → narrow MWD	Excellent	Isotactic PB-1, block copolymers	High selectivity, tunable structure	Higher cost, sensitive to impurities
Cationic Polymerization → Lewis acid initiator (*e.g.*, $AlCl_3$, $BF_3·OEt_2$)	Carbocation (chain grows *via* electrophilic attack)	Low	PIB, PIB copolymers	Rapid polymerization, useful for soft elastomers	Moisture-sensitive, less structural control

Fig. 10 Comparative pathways of Ziegler–Natta, metallocene, and cationic polymerization systems for butene- and isobutylene-based monomers.[135–139]

polymerization.[45,56] FRP and RAFT, therefore, remain more relevant methods for advancing the development of butene- and isobutylene-based functional copolymers.

2.5.3. Sustainable feedstock and waste management.

In the manufacture of polymers, sustainability goes beyond the choice of catalysts, polymerization methods, and solvents. Both the utilization of renewable feedstocks and the development of effective recycling strategies for post-consumer polymer waste are essential tools in enhancing the sustainability of butene- and isobutylene-based polymer production. For example, the transition toward bio-based monomers and sustainable feedstocks has become the focal point in the development of green polymerization processes. The use of renewable resources, like bio-based butene derived from bioethanol fermentation, can greatly lessen the need for raw materials derived from petroleum by becoming an alternative to petroleum-derived butene in the production of PB-1 and PB-2.[161–165] It is important to note that polyisoprene and polyisoprenoids are among the few truly sustainable polymers with butene/butadiene substructures, even though they are not the main topic of this review. Naturally occurring from renewable resources like *gutta-percha* or rubber trees (*e.g.*, *Hevea brasiliensis*, *Parthenium argentatum*, and *Taraxacum kok-saghyz*), polyisoprene offers bio-based origins while mimicking the structure of synthetic diene-based polymers. These bio-based polymers demonstrate the potential of bio-sourced butadiene analogues for the future development of sustainable butene- and isobutylene-related polymers and have a long history of industrial use, particularly in elastomeric applications. They are useful benchmarks for evaluating the sustainability of butene- and isobutylene-based polymer design because of their renewable nature and current large-scale production. Moreover, effective recycling methods, such as chemical recycling (*i.e.*, breaking down the polymers back into their original monomers) and mechanical recycling (*i.e.*, reprocessing polymers into new products), are crucial to enhancing the sustainability of butene- and isobutylene-based polymers. Conversion of end-of-life PB material into PB monomers like butene or isobutylene for use in new polymer synthesis fosters a circular economy, reducing the environmental impact of waste and promoting sustainable manufacturing practices. With an emphasis on recycling and upcycling its monomers, Ismail *et al.*[166] have recently created an effective enzymatic depolymerization method for PBAT (Fig. 11). Through membrane filtration and precipitation, they were able to fully hydrolyze PBAT films using the enzyme leaf-branch compost cutinase variant (LCC-WCCG), releasing monomer components (TPA, BDO, and adipic acid) rapidly and with >95% purity. The recycling loop was closed when the monomers were successfully repolymerized into fresh PBAT films (Fig. 11). By transforming BDO into 4-hydroxybutyrate and adipic acid into a polyamide, the work also investigated upcycling pathways and provided novel material alternatives. Compared to conventional techniques, this biocatalytic approach is more ecologically benign and energy-efficient, supporting a circular economy.

2.6. Environmental footprint and life cycle analysis

The sustainable development of polymer products requires careful consideration of the environmental impact of polymer synthesis. A common approach for assessing the environmental effects of various polymerization methods is life cycle assessment, or life cycle analysis (LCA).[167,168] From the extraction of raw materials to the disposal or recycling of products, LCA offers a methodical way to evaluate the overall environmental impact, considering factors like energy consumption, toxicity, waste production, and carbon emissions. Promoting more eco-conscious and sustainable production techniques for butene- and isobutylene-based polymers require an awareness of the effects that their polymerization processes have on the environment.

As summarized in Table 5, the comparative evaluation of different polymerization systems, such as the well-known Ziegler–Natta and metallocene-based catalysts, is made possible by LCA. Overall energy efficiency, environmental footprint, and sustainability of these two systems vary significantly. When compared to the Ziegler–Natta counterpart, the metallocene-based polymerization pathway often exhibits better environmental performance and sustainability because it is highly selective and controlled, generates fewer by-products and pollutants (greenhouse gas (GHG) emissions), and consumes less energy because it operates under milder conditions throughout the polymer synthesis process.[74,75,79,127,129,130,169] As highlighted before, the metallocene-based systems are those like MAO-activated metallocenes that convert butene into ethylene–butene copolymers, propylene-butene copolymers, *etc.* The more complex Ziegler–Natta systems have a higher carbon footprint because of both their production of higher amounts of waste and their higher reactor energy consumption resulting from the higher temperature and pressure requirements.[170–174] Also, in addition to improving product quality, the decreased polymer structural variation offered by metallocene catalysts reduces the necessity for excess reagents and solvents, which are frequently required in less efficient methods like Ziegler–Natta polymerization.[172] The selectivity of the metallocene catalyst also makes this system a more sustainable choice for large-scale polymer manufacturing.[129,130,169] When taking into account the broader life cycle of butene- and isobutylene-based polymers, the disparity in environmental impact between the two systems becomes particularly evident. For example, because of their superior material properties, such as greater UTS and improved chemical resistance, metallocene-catalyzed polymers typically have a longer service life.[175–177] This extended lifespan of products created from these polymers means that their contribution to environmental waste is prolonged, further lessening their overall environmental footprint.

Furthermore, metallocene-based polymerization processes relatively allow for the recycling of butene- and isobutylene-based polymers at the end of their life cycle.[172,178] Because of their controlled molecular architecture and consistent properties, the polymers generated by the metallocene catalysts tend to be simpler to recycle. For instance, it has been shown that ethylene–butene copolymers synthesized with metallocene catalysts are more recyclable than common ethylene–butene copolymers, which are made *via* Ziegler–Natta systems.[179–183] This improved recyclability is essential for encouraging a circular economy and lowering the demand for the manufacturing of
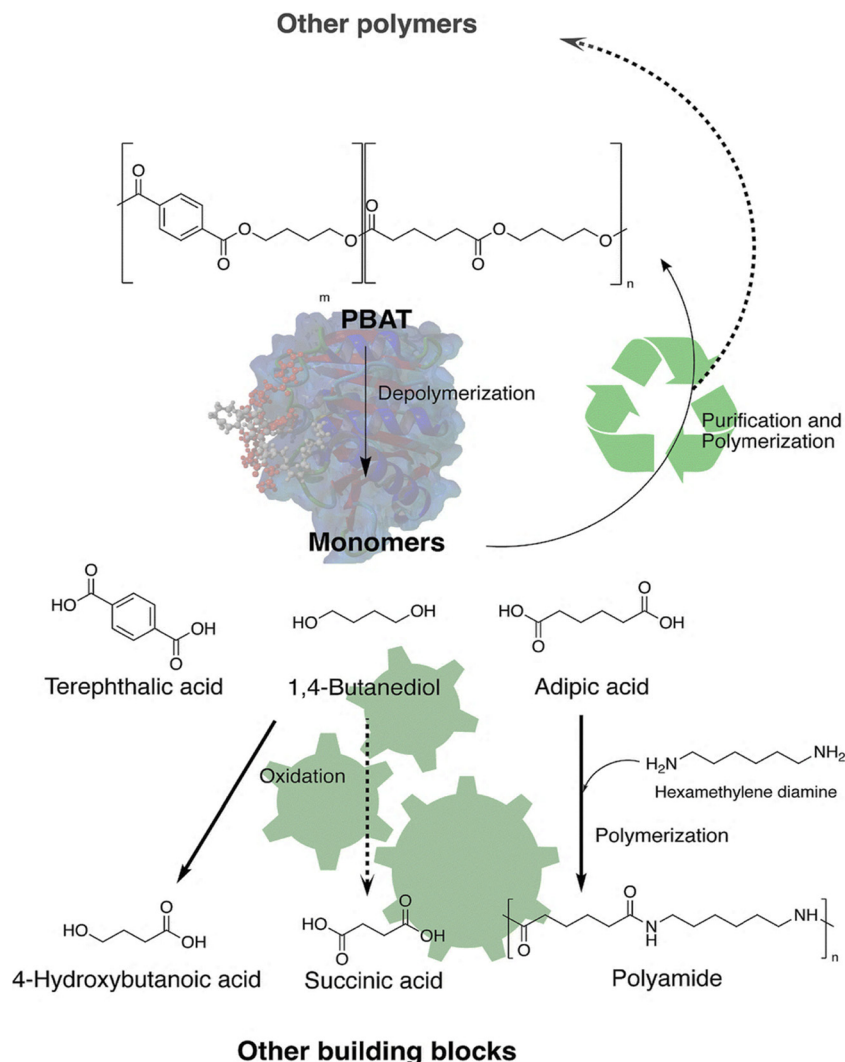
Fig. 11 Chemical recycling of PBAT *via* enzymatic hydrolysis to break it down into its monomer components, followed by their separation, recycling, and possible upcycling. Reproduced from ref. 166 with permission from Royal Society of Chemistry, copyright 2024.

virgin polymers, which further lessens the impact on the environment. The greater complexity and lesser selectivity of Ziegler–Natta catalysts would then be the primary reasons for this system to produce butene- and isobutylene-based polymers that are more challenging to recycle.[10,70,80,100,179,183] Impurities and structural variations in polymers often lead to lower-quality recyclates, which may need to be blended with virgin material or undergo further treatment to meet product specifications. This additional processing can decrease the overall life cycle's efficiency and increase the environmental effect of recycling.

Nonetheless, Ziegler–Natta systems are still often utilized in the polymerization of butene- and isobutylene-based polymers because of their well-established industrial infrastructure and lower costs,[70,80,100] even though metallocene catalysts have substantial environmental advantages. Therefore, future widespread use or adoption of these more environmentally friendly technologies is anticipated to be driven by continued developments in catalyst design, metallocene system process optimization, and sustainable polymer synthesis. The efficiency of metallocene catalysts is still

superior, but recent research on the development of SSCs to produce polymers has shown a decrease in the energy consumption and waste generation of Ziegler–Natta systems.[184] Ultimately, the overall decrease in carbon footprint and energy consumption is essential for both the sustainability of polymer synthesis and the mitigation of the environmental effects of the polymer's use in consumer goods. For industries looking into lessening their environmental impact while satisfying the increasing demand for butene- and isobutylene-based polymers in a variety of applications, energy-efficient and cleaner processes of metallocene catalysts are essential. Accordingly, one important step in the direction of more environmentally friendly synthesis methods in the butene- and isobutylene-based polymer sector could be the shift to metallocene-based polymerization technology. However, whilst metallocene-based polymerization systems have several advantages, the impact that the final product has on the environment is just as important, especially when considering biodegradability.

Biodegradable butene- and isobutylene-based polymers seem promising for lessening the impact of plastic waste on

Table 5 LCA comparison of Ziegler–Natta vs. metallocene-based pathways in the polymer synthesis

Aspect	Ziegler–Natta polymerization pathway	Metallocene polymerization pathway	Ref.
(1) Preparation of raw materials	Feedstock: butane derivative	Feedstock: butane derivative	74 and 80
(2) Preparation of a catalyst	Preparing Ziegler–Natta catalysts necessitates higher temperatures (70–90 °C) and pressures (10–30 bar)	Lower temperatures (40–60 °C) and pressures (2–10 bar) are employed in the manufacture of metallocene catalysts, meaning the process is less complex, more controlled, and inexpensive	75 and 100
(3) Polymerization reaction as well as by-products and waste production	Synthesis of broader MWD polymer	A narrower MWD polymer is produced through more selective polymerization	130 and 179
	More by-products and waste, such as solvent waste and excess reagents, are produced because of less precise control of the process	Fewer by-products and less waste are generated because of a more controlled process, meaning more efficient use of resources	
(4) Energy consumption and gas emissions	Higher GHG emissions from solvents and excess reagents because of high temperatures	Lesser energy consumption and GHG emissions because of meticulous catalyst selection, precise control, and milder reaction conditions	74 and 100
	Significant energy input because of complex steps that necessitate high temperatures and pressures		
(5) Polymer product	Broader MWD results in less material recyclability	Higher recyclability as well as better UTS and other material properties	75 and 130
(6) Sustainability (generally)	Sustainability is reduced by higher energy consumption, pollutants, and waste production	Sustainability is strengthened by small energy requirements, lesser pollutant emissions, and lower waste production	130 and 179

ecosystems when taking into account the entire life cycle, including end-of-life degradation. For example, as compared to traditional petroleum-based plastics, PBS, a biodegradable polyester synthesized similarly to PBT using BDO and succinic acid (instead of DMT or TPA), provides notable environmental advantages. It is much less harmful when it decomposes in natural settings because it produces non-toxic metabolites that lessen its long-term persistence in landfills and waterways.[13–16,185,186] Compared to conventional techniques like Ziegler–Natta, the manufacture of PBS utilizing metallocene catalysts also uses less energy and produces fewer by-products, making it a more environmentally and industrially sustainable option.[38,39,187] The growing need for eco-friendly materials is effectively served by this combination of energy-efficient manufacture and biodegradability. Similarly, PBAT is another isobutylene-based copolymer that combines biodegradability with advantageous life cycle characteristics. Because it decomposes naturally in industrial composting environments, it is a more environmentally friendly option for packaging applications than traditional plastics.[16,38,39,187] The PBAT synthesis, when carried out using metallocene-based systems, also benefits from a more precisely controlled route that uses less energy and produces fewer emissions. These characteristics highlight the potential of metallocene-based catalysts to generate materials that help lessen environmental plastic pollution in addition to high-performance butene- and isobutylene-based polymers. Accordingly, PBS and PBAT both exemplify how combining biodegradability with advanced polymerization methods can result in the manufacture of more sustainable materials, with definite benefits when assessed via life cycle analyses.

3. Processing characteristics of butene- and isobutylene-based polymers

Key processing characteristics of butene- and isobutylene-based polymers are essential for efficiently transforming them into final, high-quality products. These, which primarily include ease of processing, flow behavior, and formability, depend on several factors such as molecular structure, viscosity, as well as thermal and crystallization behaviors.[24,188,189] Additionally, the processing characteristics also influence the final cost and performance of the material in its intended application. Therefore, it is important to understand and control the factors they depend on to optimize processing methods—i.e., extrusion, injection, and blow molding, as well as film casting—and ensure that the finished product meets desired application specifications but is also cost-effective. This section examines these characteristics, along with how each characteristic influences the processing efficiency and final performance of the material.

3.1. Ease of processing, flow behavior, and formability

The ease of processing refers to the simplicity of transforming polymers into their respective, final forms using traditional processing methods.[103] A viscosity, which varies with temperature, is directly correlated with how well a polymer flows. Generally, better flow from a decreased viscosity makes it easier for a polymer to fill extruders or molds.[190] Because higher M_ws typically results in higher viscosities, which slow down the flow and necessitate higher temperatures or pressures to facilitate processing, M_w and shear sensitivity also have a substantial impact on flow behavior. Accordingly, because they require less energy to flow and mold, polymers with lower M_ws, lower crystallinity, and moderate viscosity are generally easier to process.[190,191] Conversely, because of their greater flow resistance, the high M_w and crystalline polymers are typically more challenging to process.[190,191] For instance, the moderate M_w and semi-crystallinity of PB (particularly isotactic PB-1) necessitate rather high processing temperatures (usually 180–200 °C) for better flow behavior and extrusion or molding.[29,192] In addition, because of its rigid and regular chain structure, both

of which cause it to flow less easily, PB-1 may be more challenging to process, especially at lower temperatures, than more amorphous butene- and isobutylene-based polymers.[193–196] When cooled too rapidly, for example, PB tends to show slower flow rates, which can lead to defects in the finished product, particularly in applications like pipelines where dimensional stability—a material's ability to retain its size and form under varying environmental factors including temperature, mechanical stress, or chemical exposure—and uniformity are crucial.[193–199] Nonetheless, in the study by Li et al.,[200] effective melting and extrusion of PB-1 pellets into filaments was made possible by the melt-spinning system, which included a spin pack and a single-screw extruder (Fig. 12(a)). According to the authors, processing was made easier by the comparatively mild extrusion temperatures (i.e., 110–260 °C), which promoted favorable flow characteristics and reduced thermal degradation. Similarly, uniform melting and smooth film formation were guaranteed by the hot-pressing method (Fig. 12(b)) employed to make PB-1 films at 180 °C. These processes worked well for processing PB-1, providing good control over material properties and characteristics, including mechanical performance and crystallinity. They also made it possible to produce high-quality filaments and films that could be used for intended testing and applications.

In addition to its greater amorphousness, PIB, on the other hand, is generally easier to process at lower temperatures (150–170 °C) due to its lower M_w.[24,52,201,202] It is especially well-suited for the extrusion of flexible products like adhesives, sealants, medical tubing, coatings, and packing films because of its low T_g, which permits it to flow more readily at lower processing temperatures.[201–209] Moreover, PIB exhibits shear-thinning behavior, meaning that as shear forces rise, its viscosity drops.[23,202,203,206,209] This makes it easier to process under high shear conditions, which makes it easier to fabricate thin, flexible products. However, PIB is typically not applicable for

applications needing high-dimensional stability because it lacks the structural rigidity of PB.[210]

Furthermore, specialized machinery, like extruders and Banbury mixers, is typically used for IIR processing under high-shear conditions to overcome the material's intrinsic flow resistance despite its amorphousness.[211–213] Because of its cross-linkable structure, it is less flowable than thermoplastic polymers like PB and PIB under typical molding or extrusion conditions, necessitating the use of more precise control over the processing conditions.[211,213] This structure is a result of a highly reactive monomer (isoprene) that adds double bonds to the polymer chain, enabling crosslinking—a crucial process for the material's ultimate functionality. IIR's elastic properties, in spite of its poor flowability, are made better by the presence of isoprene in the polymer structure, which makes it ideal for uses requiring great strength and flexibility under stress, where stretchability and durability are crucial.[214] Also, in contrast to materials based only on isobutylene, the addition of isoprene makes the IIR have a higher viscosity, which has an impact on the melt flow characteristics of the polymer.[26] Because IIR may need higher temperatures, between 140 and 180 °C for Banbury mixing, ca. 160–200 °C for extrusion, and ca. 180–220 °C for injection molding, to obtain significant flow during processing, this increase in viscosity might make processing more challenging.[211,212] However, after being crosslinked, the isoprene units contribute to the formation of a network structure that gives the finished product enhanced wear resistance, dimensional stability, and chemical resistance.[214,215] It is important to strike a balance between the amounts of isoprene and isobutylene since too much of the former can diminish the M_w and processability, while too little can limit the crosslinking capability and jeopardize the final mechanical properties.

Some isobutylene-based copolymers alter the material's properties and processability by combining isobutylene with
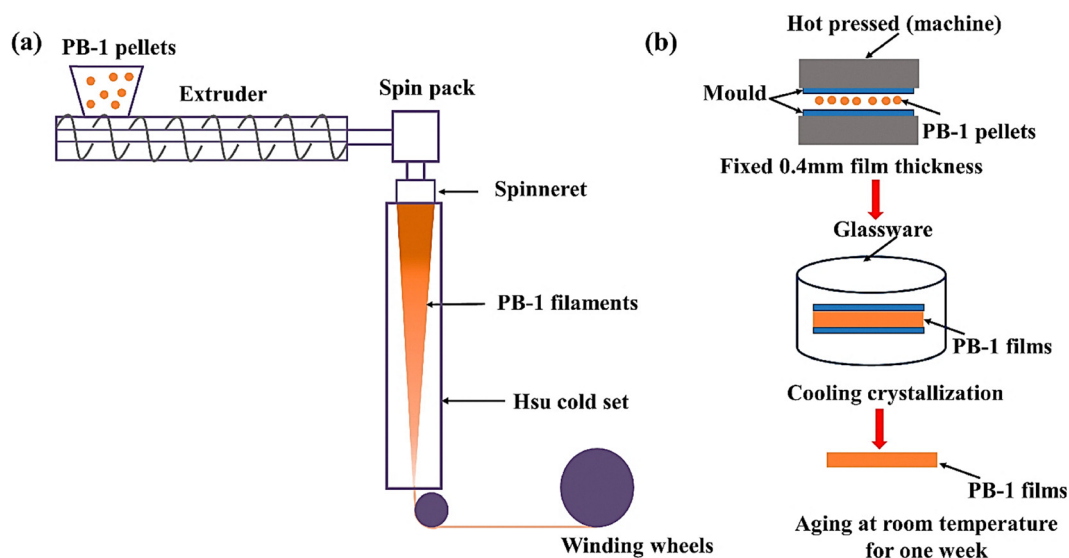

Fig. 12 Schematic of the melt-spinning (a) and hot-pressing (b) processes for the production of polybutene-1 filaments and films. Reproduced from ref. 200 with permission from MDPI, copyright 2023.

styrene. One important aspect of this alteration is the impact of styrene on isobutylene's processability, particularly when it comes to SIBS block copolymers. The addition of styrene to isobutylene improves the polymer's melt strength and viscosity, among other processability characteristics.[95,97] Higher melt strength enables the polymer to retain its structure and shape throughout fabrication, which is especially advantageous in techniques like extrusion, as well as injection and blow molding.[95,216,217] Better phase separation between the hard styrene blocks and the soft isobutylene segments is made possible by styrene's compatibilizing role in the polymer blend.[43,95,217] The isobutylene segments retain flexibility and rubberiness, but the stiff, crystalline styrene blocks give the polymer structural stability, creating a material that is easy to process while balancing rigidity with elasticity and maintaining the necessary mechanical properties for demanding applications like coatings and films. Adding styrene, however, also presents certain challenges. Because styrene is stiffer than isobutylene, it can elevate the melting point and viscosity of the polymer. To handle the changed material efficiently, greater processing temperatures and specialized equipment may be needed. Additionally, depending on the polymerization conditions, block copolymerization of styrene and isobutylene could result in branched architectures, which can affect the process consistency as well as the mechanical performance of the final material.[97,216] The amount of styrene must also be carefully regulated because too much of it might cause the finished product to become brittle, which will lessen its flexibility and resistance to impact. Similar to the case with IIR, to guarantee that the material works as well as it can for a given application, styrene must be balanced even if it enhances the processability and mechanical properties of isobutylene-based copolymers. PBS is another type of copolymer, but different from isobutylene-based copolymers, where Ewurum et al.[218] have recently studied its different processing techniques, including extrusion and molding, with the former making it possible to incorporate lignin into the PBS matrix effectively (Fig. 13). According to the authors, the PBS-lignin materials were processed smoothly and with good flow

characteristics and uniform lignin dispersion throughout the polymer thanks to the use of a single-screw extruder and a hot press at relatively moderate temperatures (140 °C for extrusion and 120 °C for molding). By altering PBS's structure and enhancing its compatibility with lignin, the processing techniques—specifically, reaction extrusion with DCP and molding—further improved the polymer's processability. These methods demonstrated the viability and simplicity of working with lignin-filled PBS systems for the production of copolymers with different lignin contents.

The ease of processing of a butene- and isobutylene-based polymer can also be achieved by blending it with another polymer. The properties of two polymers together can reveal important information about how the materials can be treated in different applications. By optimizing the blend composition to meet desired processing characteristics, this approach can assist in addressing processing-related issues like temperature sensitivity in addition to viscosity and flow behavior. For example, PB-1 can be made more processable by mixing it with a more flexible polymer. This will make it easier to handle during extrusion, injection molding, and other fabrication processes. The material's overall flow characteristics and melt viscosity can all be improved by the interaction between the two polymers. The resultant mixture may exhibit enhanced flexibility, toughness, or thermal stability, depending on the polymer selected for blending. This will facilitate processing into finished products such as films, fibers, or molded components. The study by Palai et al.[219] offers a pertinent example to support the notion that polymer blending improves ease of processability and material properties. In their study, they prepared PLA/poly(butylene succinate-co-adipate) (PBSA) blend-based films by mixing these two polymers with a fixed wt% of epoxy-functionalized styrene acrylate (ESA), using a single-step blending process followed by a blown film extrusion process (Fig. 14). The material's integrity was maintained by the effective blending of PLA, PBSA, and ESA during the dry blending process, which was conducted at 50 °C and 80 rpm without causing undue shear. The melt blending procedure, carried out in a co-rotating twin-screw
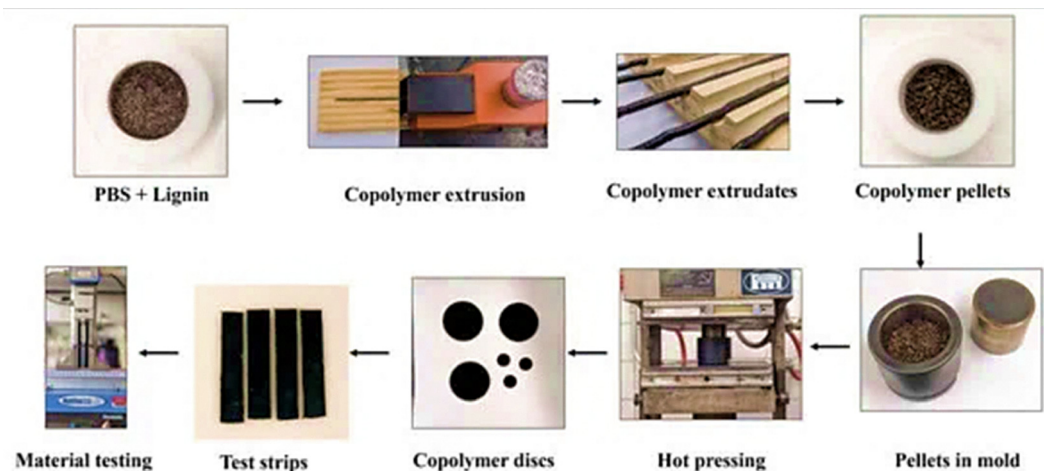

Fig. 13 Schematic illustration of the processing of biodegradable PBS-lignin copolymers via extrusion and molding. Reproduced from ref. 218 with permission from MDPI, copyright 2025.

Fig. 14 Schematic of the processing steps for PLA/PBSA/ESA blend-based films: dry blending and blown film extrusion. Reproduced from ref. 219 with permission from Elsevier, copyright 2020.

extruder with regulated screw speeds (*i.e.*, 80–100 rpm) and temperature profiles (from 155–175 °C), guaranteed a consistent dispersion of ESA throughout the polymer blend matrix, thereby enhancing PLA and PBSA compatibility. Additionally, by precisely controlling the residence duration (2–4 minutes), this approach ensured that the polymers were processed under optimal conditions and optimized the flow behavior, allowing the components to blend efficiently without degrading. Stable PLA/PBSA/ESA blend-based film manufacturing with strong optical qualities and effective control over material thickness and blow-up ratio was made possible by the blown film extrusion method, which used a conventional mixing screw and controlled temperatures (160–175 °C) to preserve favorable flow behavior. This is similar to a recent study by Zhang *et al.*,[220] who created PLA/PBAT blend- and PLA/PBS blend-based films through melt blending and extrusion cast processing, and Choi *et al.*,[221] who created PLA/PBS blend-based fibers by blending PLA and PBS using a melt-spinning technique, from twin screw extrusion to fiber spinning process.

The polymer's ability to be shaped into the desired finished product—a sheet, film, fiber, or three-dimensional (3D) object—without failure is referred to as formability.[192,222] This characteristic is also influenced by the molecular structure.[222] For instance, since they soften more readily when heated and may be molded into a variety of shapes without cracking or breaking, isobutylene-based polymers like PIB with low crystallinity (low T_g) and high amorphous nature (flexible molecular chains) are often more formable.[223,224] Thus, formability is somewhat more challenging for PB, which normally leads to issues like warping during rapid cooling.[192,225,226] However, when processed under optimized conditions, PB also shows good formability.[192,226] For instance, the crystalline nature of PB means that higher temperatures and pressures, as well as longer processing durations, are required to ensure that it flows into molds sufficiently and maintains its shape while cooling, thereby achieving optimal formability, especially during the manufacture of PB pipes.[192,198,199,226] As expected, IIR is less formable than PB and PIB because of its cross-linkable architecture, which limits its melt-processability.[227] However, just like PB, IIR can be processed into molds or shapes *via* specialized molding and vulcanization methods, although moldability and formability are limited in conventional thermoplastic processes. On the other hand, because additional monomers often enhance the balance of flexibility and stiffness, isobutylene-based copolymers normally show higher formability when compared to pure PIB.[42,64,228] When PIB is blended with a polymer like PE, the resultant PIB/PE blend also provides a more highly formable material than pure PIB and PE because of the synergistic effects of both polymers.[206,229,230] Because of their better formability, such blends can be processed into films, coatings, and other products that need both flexibility and strength. Table 6 provides a summary of the butene- and isobutylene-based polymers' processing characteristics while also contrasting them with those of common polymers.

4. Properties of butene- and isobutylene-based polymers

Butene- and isobutylene-based polymers have drawn a lot of interest recently because of their unique set of properties and

Table 6 Comparison of processing characteristics of different polymers

| Polymer | Processing characteristic | | | | |
	Ease of processing	Flow behavior	Formability	Suitable processing method	Ref.
PB-1	Moderate	Moderate at high temperatures	Ideal for rigid products	Extrusion, as well as injection and blow molding	192 and 199
PIB	High	Excellent at low temperatures	Excellent for films	Extrusion and film casting	224 and 225
IIR	Moderate to low	Restricted due to crosslinking	Limited	Molding, hot-press vulcanization, and extrusion	208
PE	High	Good at high temperatures	Moderate	Extrusion, injection molding, and blown film	230
PP	High	Moderate to good	Good	Extrusion, injection molding, and thermoforming	231

competitive costs.[22,38,52,95,227,232] These desirable properties make them useful in a variety of applications, from packaging materials to electronics. Moreover, the growing focus on sustainability has driven the development of biodegradable and recyclable butene- and isobutylene-based polymers, positioning them as a viable alternative to conventional plastics. This section offers an overview of the key properties of butene- and isobutylene-based polymers, building upon their section on synthesis, and setting the context for their section on applications. By examining these properties, we hope to highlight the potential of butene- and isobutylene-based polymers in addressing both functional and environmental challenges in contemporary material science.

4.1. Mechanical properties

Butene- and isobutylene-based polymers exhibit good mechanical properties that can be harnessed for specific applications. For instance, IIR, CIIR, and BIIR have been demonstrated to have excellent mechanical properties because of the polymer's isobutylene backbone, which offers inherent flexibility, low gas permeability, and high resilience, as well as the halogenation in CIIR and BIIR (chlorine and bromine), which improves their strength, wear resistance, and overall mechanical performance.[214,233–236] Also, PBT exhibits good mechanical properties, including high strength, rigidity, good impact resistance, dimensional stability, low creep, and excellent wear resistance, making it suitable for applications requiring both mechanical strength and heat resistance.[17,237–239] On the other hand, because of aromatic units found in the molecule chains, PBAT exhibits good mechanical properties such as elastic modulus, UTS, and flexibility.[240–242] Furthermore, PBAT is biodegradable; however, this characteristic greatly depends on the process variables chosen during synthesis.[240,242] PBS polymers have been shown to exhibit a good compromise of mechanical endurance, ductility, toughness, and impact resistance. Studies have shown that the mechanical properties of PBS are comparable to those of PE and PP.[13,38,243] The mechanical behavior of PB and PIB has been studied extensively, and compared to traditional polyolefins, these butene- and isobutylene-based polyolefins possess unique chain and helical structures that result in excellent mechanical properties.[199,207,208,244–246] Furthermore, functionalized PB and PIB exhibit beneficial properties concerning toughness.[45,208,247–249] Block copolymers like SIBS exhibit exceptional UTS and elongation properties because of the phase separation between the

hard styrene blocks and the soft isoprene/butylene blocks, as well as their characteristic M_w.[95,99,250,251] A comparison of tensile properties of different types of butene- and isobutylene-based polymers is presented in Table 7. It is evident that the structure and composition of butene- and isobutylene-based polymers greatly affect their mechanical characteristics. PBT has a higher elastic modulus and is considerably stiffer than polymers like PB-1 and PBS, which show high elongation, indicating good elasticity or flexibility. PIB exhibits high elongation and low stiffness, indicating exceptional flexibility. When compared to unmodified PBS, modified PBS (e.g., PBS-0.03M and PBS-0.2TMP, where M and TMP are malic acid and tri-methyl propane, respectively), exhibit better strength, underscoring the advantages of surface modification. Depending on their structure, block copolymers such as poly(styrene–isobutylene–styrene) (PS–PIB–PS) exhibit different properties; the star block version offers good strength, while linear versions offer both superior strength and high elongation. The trade-offs between strength, flexibility, and how changes affect these polymers' performance are demonstrated by this comparison.

4.1.1. Factors influencing the mechanical properties. Generally, the UTS of a polymer increases with an increase in M_w up to a certain extent. At lower M_w, the polymer chains can move easily because they are loosely bonded by weak van der Waals forces. In the case of large M_w polymers, the chains are entangled, giving strength to the polymer.[259,260] Burford et al.[242] have reported that UTS increases whilst elongation at break (ε_b) decreases with an increase in M_w of PBAT. Moreover, secondary bonds (also known as non-covalent interactions), such as van der Waals forces, dispersion forces, dipole–dipole interactions, induced dipole interactions, and hydrogen bonds, are intermolecular forces that can be broken by applying an external force, leading to physical changes without modifying the chemical structure of the molecules.[261,262] Therefore, secondary bonding has a strong bearing on physical properties. Strong secondary bonds, which contribute to the overall intermolecular forces between polymer chains, found in a polymer material, promote mechanical resistance, and such polymers display higher UTS, low volatility, low elastic deformation, brittleness, etc.[263,264] Crystallinity is another factor that typically influences the mechanical properties of polymers. The degree of crystallinity of a polymer is an indication of the strength of the intermolecular bonding. A given polymer's tendency toward being crystalline or amorphous is determined by its chemical

Table 7 A comparison of tensile properties of different butene- and isobutylene-based polymers and blends

Polymer	Composition/trade name	Young modulus^a (MPa)	Tensile strength^a (MPa)	Elongation at break^a (%)	Study
PB-1	Toppyl PB 8340M	270	30	300	252
PIB	—	1.6	14	650	253
CIIR	—	2	2	400	254
BIIR	—	—	15	566	213
PBT	—	925	47	—	255
PBAT	—	126	21	670	240
Starch/PBAT	KINGFA	—	20	287	
PLA/PBAT	KINGFA	—	22	258	
PBS	—	—	19	375	13
PBS	Bionelle 1020 MD	707	34	—	38
PBS-0.03 M	0.03 mol% branching ratio by M	160	23	100	256
PBS-0.2TMP	0.2 mol% branching ratio by TMP	200	37	130	
PBS/15%SRF	15%SRF	—	15	48	257
PS–PIB–PS	Linear block copolymer	1	24	906	258
PS–PIB–PS	Linear block copolymer	19	13	460	
PS–PIB–PS	Star block copolymer	52	10	339	

^{a} Approximate values, —: not reported.

structure. The mechanical properties of a semicrystalline polymer, especially UTS, ductility, and brittleness, are influenced by the tie chains that connect the lamellar regions, creating a mechanically integrated structure through intermolecular bonding. An increase in crystallinity can enhance the strength of the polymer, but it may decrease its toughness, as it can make the material more rigid and less able to absorb energy before fracture or rupture. The degree of crystallinity is generally reduced by copolymerization, which involves the mixing of two different forms of monomers in the same polymer chain, through the introduction of irregularities.[265] However, it has also been found that if the monomer units of a copolymer have similar chemical structures, isomorphism may occur, meaning that the polymer chains align more uniformly at the molecular level, and this can enhance mechanical strength due to better packing and organization of polymer chains.[266,267]

Furthermore, crosslinking, which involves chemically connecting polymer molecules by primary valence bonds, introduces stability to a polymer because of the imposed restrictions on molecular mobility. The rigidity of a polymer is increased by crosslinking, depending on the degree of crosslinking. The length of the crosslink and the distance between crosslinks vary. The shorter the crosslinks, or the smaller the separation between them, the stronger and more rigid the polymer becomes. While more significantly crosslinked materials are rigid and may be brittle, the minimally crosslinked polymers are typically rubbery. Dziemidkiewicz et al.[268] have examined the influence of different curing agents for the BIIR crosslinking process on the mechanical behavior of the vulcanizates, which were cured with metal acetylacetonates and showed good mechanical properties with UTS in the range of 9–14 MPa and better damping properties. The chemicals and materials, known as additives and fillers, that are typically added into polymer formulations to obtain the properties required for desired end applications, also affect the mechanical properties of the resultant polymer product.[13,14,28,269,270] Adding additives like fillers to polymers can significantly affect their strength, often enhancing it by increasing stiffness, improving impact resistance, or creating a more durable internal structure, depending on the amount and whether it is a reinforcing filler or not. However, some additives can weaken a polymer depending on their interaction with the polymer chains, like plasticizers, as low-vapor liquids that lower the T_g of polymers, thus increasing flexibility at the cost of UTS and elastic modulus.[237,271,272] This decrease in UTS and modulus is because the introduction of plasticizers results in polymer chains in the amorphous regions being forced apart, thereby decreasing the intermolecular forces between chains and allowing them to slip more readily over one another.[264,273] Nonetheless, reinforcing butene- and isobutylene-based polymers with fillers like synthetic materials (e.g., glass fibers, carbon black (CB), and carbon nanotubes (CNTs)) and natural materials (e.g., clay, coffee husk, and natural fibers) can significantly increase their mechanical properties, such as UTS, modulus, hardness, and impact resistance.[18,20,23,232,233,271]

4.2. Thermal stability

PBS has been reported to have good thermal stability in addition to excellent mechanical properties, and due to these properties, injection or blow molded and extruded items have been effectively made from PBS.[38,274–276] Furthermore, blending a butene- or isobutylene-based polymer with another butene- or isobutylene-based polymer or a different type of polymer can induce structural changes in the resulting polymer, such as differences in sequence distribution and phase morphology, which significantly impact its thermal properties.[277,278] For example, blending PBS with PBT[38,279,280] or polycarbonate (PC)[281,282] can enhance the thermal stability of PBS, as both PBT and PC have higher T_g and melting temperatures or points (T_ms) than PBS, which contributes to improved thermal properties. Additionally, PBAT has been reported to have good crystallization and thermal stability. As a result, it has good processing stability to be used alone or blended with other materials through conventional manufacturing processes like extrusion, injection molding, and blowing film.[240,283] It has been reported that the melting point

of PBAT is *ca.* 120 °C and has a crystallization point of 60 °C, a 5% weight loss temperature of 350 °C, and a heat distortion temperature of 55 °C.[240] Hence, although PBAT may not function well in elevated-temperature applications due to its relatively low melting and heat distortion temperatures, its high 5% weight loss temperature indicates good thermal stability and resistance to degradation at moderate temperatures. On the other hand, IIR and its halogen-functionalized counterparts are unique in that they have a high percentage of methyl groups (–CH$_3$) attached to the polymer chain. This structure makes the polymer chains more rigid and contributes to their excellent resistance to thermal and UV oxidation as well as environmental aging.[284–287] As for SIBS, it exhibits high thermal and oxidative stability due to its saturated polyisobutylene mid-block, performing well in applications with temperatures up to *ca.* 200 °C; however, it is not suitable for high-temperature environments above this threshold.[6,95,288] A comparison of thermal properties of different types of butene- and isobutylene-based polymers is presented in Table 8. Similar to tensile properties, this comparison demonstrates how blends, additives, as well as polymer structure and composition, affect the thermal behavior of butene- and isobutylene-based polymers. Good thermal stability is indicated by the comparatively high melting and crystallization temperatures of polymers like PB-1 and polyethylene terephthalate (PET)/PBT (PET/PBT) blends. In contrast, PIB exhibits a high heat distortion temperature and a very low T_g, indicating superior flexibility at low temperatures and resistance to high heat. Their melting and crystallization temperatures are higher when PBS is modified (for example, by adding M or TMP as a branching agent) to enhance its thermal properties. PBS/15%SRF (*i.e.*, PBS with 15% sugarcane rind fiber) exhibits T_m similar to that of PB-1, probably due to the influence of SRF on the crystallization behavior and polymer chain interactions since pure PBS and PBS with lower SRF contents had lower T_m values in the study. Moreover, linear block copolymers maintain high heat distortion temperatures

while displaying low glass transition temperatures (T_gs), which suggests flexibility at low temperatures.

4.2.1. Factors influencing thermal stability. The relationship between the molecular weight of the polymer and its T_g is given by the Fox–Flory equation (eqn (1)), which generally describes that T_g increases with the number-average molecular weight (M_n). However, the Fox–Flory relationship suggests that there is no considerable increase in T_g for molecular weights above 20 000 g mol^{-1}.[293,294] This is because the polymer chains get sufficiently large that further molecular weight increases do not substantially alter how the chains move.[293,294] As a result, not much more heat is needed to make the transition from a rigid, glassy state to a more flexible, rubbery state. The Fox–Flory equation is as follows:[293,294]

$$T_g = T_{g,\infty} + \left[\frac{K}{M_n}\right] \tag{1}$$

where, $T_{g,\infty}$, in °C or K, symbolizes the asymptotic T_g that the polymer would approach as its molecular weight increases indefinitely, and K, in °C mol g^{-1}, is a constant that is dependent on the type of polymer and its structure, where its value reflects how strongly the molecular weight influences the T_g. Eqn (2) provides this constant as follows:[293]

$$K = 2V_c\rho N_A/\alpha \tag{2}$$

where, V_c, in cm^3, is the free volume contributed by chain ends; ρ, in g cc^{-1}, symbolizes polymer density; N_A is Avogadro number 6.023×10^{23} molecules per mole; and α symbolizes thermal expansion coefficient per °C.

Similar to mechanical behavior, the thermal properties of a polymer can also be influenced by the secondary bonds, where the strong intermolecular forces in polymer units result in higher T_gs because they have the potential to limit polymer chain mobility but increase stiffness.[2,295] T_gs for halogenated IIRs, such as CIIR and BIIR, have been found to typically be higher than those of non-halogenated butyl rubber.[284,296,297]

Table 8 A comparison of thermal properties of different butene- and isobutylene-based polymers and blends

Polymer or blend	Composition/trade name	Melting temp.[a] (°C)	Crystallization temp.[a] (°C)	Glass transition temp.[a] (°C)	Heat distortion temp.[a] (°C)	Study
PB-1	Toppyl PB 8340M	97	111	−21	—	29
PIB	—	—	—	−63.2	260	253
PIB-PTMO-TPU[b]	80% PIB diol	—	—	−25	—	289
BIIR	—	—	—	−55	—	290
PBT	—	224	198	51	—	291
PET/PBT	80/20	238	188	63	—	
PET/PBT	60/40	211	165	58	—	
PET/PBT	80/20	254	216	—	—	292
PBAT	—	115	60	—	55	240
PBS	Bionelle 1020 MD	115	—	−32	—	38
PBS	—	—	19	—	375	13
PBS-0.03 M	0.03 mol% branching ratio by M	160	23	—	100	256
PBS-0.2TMP	0.2 mol% branching ratio by TMP	200	37	—	130	
PBS/15%SRF	15% SRF	97	57	—	—	257
PS-PIB-PS	Linear block copolymer	1	24	−61	906	258
PS-PIB-PS	Linear block copolymer	19	13	−61	460	

[a] Approximate values. [b] A thermoplastic polyurethane (TPU) composed of PIB diols (hydroxyallyl telechelic PIBs) and poly(tetramethylene oxide) (PTMO), where PTMO serves as a compatibilizer.

This is mostly because of the halogen atoms, which, because of the polarity of the C–Cl and C–Br bonds, can produce stronger intermolecular interactions, like dipole–dipole forces. The T_g rises as a result of these interactions, which limit the mobility of polymer chains. Also, the T_g rises due to the decreased flexibility of the chains caused by the larger size of the halogen atoms and possible steric hindrance.[298] Therefore, in addition to any dipole–dipole forces, the higher T_g of halogenated IIRs is primarily caused by a combination of increased intermolecular forces and steric effects. However, the addition of plasticizers results in polymer chains in the amorphous regions being forced apart, thereby decreasing the intermolecular forces between chains and allowing them to slip more readily over one another.[264,275,299–302] As a result, the T_g is lowered. One of the common plasticizers that have been used with butene- and isobutylene-based polymers, particularly PBS and PIB, is oligomeric poly(ethylene glycol) (PEG M_w = 4000).[56,301] Furthermore, it has been shown that a certain degree of chain stiffness affects the degradation of polymers, *i.e.*, the degradability of the polymer decreases with an increase in the thermal stability, which explains the non-degradability of high thermally stable butene- and isobutylene-based polymers like pure PB, PIB, IIRs, PBT, and SIBS. Nonetheless, the rigidity of a polymer is also increased by crosslinking, depending on the crosslinking system used and thereby the degree of crosslinking; *e.g.*, higher crosslinked polymers will exhibit a higher T_g than those with lower crosslinked molecules. Because they form dense network structures, epoxy crosslinking, radiation crosslinking, and isocyanate crosslinking are the systems that typically result in the highest degree of crosslinking and higher T_g.[303,304] On the other hand, the thermal stability of IIR vulcanizates is not significantly affected by crosslinking agents like metal acetylacetonates.[268] Moreover, blending with PBT could improve the thermal stability of PBS, as the former contributes to a more rigid and thermally stable structure because it exhibits a higher T_g and T_m than the latter. This can be shown by comparing the T_ms of the reactants (*i.e.*, PBT and PBS) to that of the resultant product (*i.e.*, a biodegradable plastic called poly(butylene succinate-*co*-butylene terephthalate) (PBST)). For example, when compared to PBS alone, which has T_m generally ranging from *ca.* 115–125 °C, the higher T_m (*ca.* 220–250 °C) of PBST is comparable to that of PBT alone (*ca.* 225–250 °C), depending on the specific formulation, composition, molecular weight, crystallinity, and processing conditions.[305–307] Reinforcing butene- and isobutylene-based polymers with reinforcing fillers like glass fibers, CB, silica, or talc, could also significantly improve their thermal stability.

4.3. Chemical stability

The chemical stability of a polymer directly impacts the material's performance, durability, and suitability for specific applications. For example, polymers used for medical devices must be able to resist body fluids and the various sterilization processes. Polymers used for food packaging must not react with food or leach chemicals. In aerospace and automotive industries, polymer materials used must be able to endure fuels, oils, and extreme temperatures. PIB-based elastomers provide superior oxidative and chemical stability.[208,308] For specific applications, PIB-based tri-blocks are expected to yield barrier and damping properties that cannot be obtained with diene-based materials.[258] These unique properties make PIB-based materials ideal for use in industries where chemical resistance and durability are critical. On the other hand, although IIR exhibits excellent resistance to a wide range of chemicals, including aliphatic hydrocarbons, oxygenated solvents (*e.g.*, alcohols and ketones), as well as oils, it remains susceptible to degradation when exposed to environmental conditions that involve aromatic hydrocarbons, chlorinated solvents, and strong acids (*e.g.*, sulphuric and nitric acids).[213,233,269,309] Consequently, unmodified IIR is typically not suitable for applications in environments with prolonged exposure to these substances, such as in automotive fuel systems, chemical processing, and highly acidic environments, where chemical resistance is critical.[213,269,309] As for other butene- and isobutylene-based polymers, PB is susceptible to aromatic hydrocarbons, chlorinated solvents, and oxidizing agents.[9,73,310] PBT is highly resistant to acids and alkalies; however, it has limitations with oxidizers and high pH.[18,311] The modified versions (*i.e.*, PBAT and PBST) perform well in specific applications but are limited by chlorinated solvents and strong acids.[312,313] PBS is suitable for environments without exposure to aromatic solvents and strong acids,[14,314] and SIBS is resistant to aliphatic hydrocarbons but not suitable for specific aromatic solvents or strong acids.[315]

Furthermore, the chemical composition of butene- and isobutylene-based polymers play a key role in determining their resistance to chemical degradation. PB and PIB have saturated hydrocarbon chains, which provide inherent resistance to different chemicals (acids, bases, and water).[9,52,64,73] Because these polymers do not contain reactive functional groups like amines or esters, they are less likely to oxidize or hydrolyze. However, the presence of unsaturation in PIB makes it more susceptible to oxidative degradation. IIR is also characterized by a combination of saturated (isobutylene) and unsaturated (isoprene) units. Though susceptible to aromatic hydrocarbons, *etc.*, the unsaturation in the isoprene segment enables crosslinking, and the resulting crosslinked network enhances the chemical resistance of the polymer by reducing chain mobility, which makes it less vulnerable to chemical attack.[285,316] However, extreme conditions like exposure to strong oxidizing agents have been found to still compromise the chemical resistance of IIR, especially when non-halogenated.[284] Similarly, although the presence of ester functional groups in the polymer backbone contributes to its resistance to a variety of acids, bases, and oils, PBT, much like PET, is more prone to hydrolysis when exposed to strong acids and bases, leading to possible degradation over time.[317,318] PBS, another ester group-containing polymer, is susceptible to hydrolysis, mainly in the presence of moisture or acids, which then limits its chemical resistance, particularly in environments exposed to oils or solvents.[319,320] On the other hand, SIBS benefits from the presence of styrene blocks in the copolymer, which enhances its chemical resistance properties. However, as stated previously, SIBS may be more vulnerable to oxidizing agents and aromatic solvents due to the phenyl groups in the styrene units.[315] Overall, the ability of these

butene- and isobutylene-based polymers to withstand chemical degradation under various environmental conditions is largely determined by their chemical makeup, which includes the type of bonding (saturation *vs.* unsaturation), functional groups, as well as crosslinking or halogenation.

Nonetheless, a variety of additives can be incorporated into butene- and isobutylene-based polymers to enhance their chemical properties. For PB and PIB, antioxidants, such as phenolic antioxidants and phosphites, are often utilized to improve their oxidative stability.[321,322] Plasticizers, such as esters and paraffinic oils, are commonly added to enhance flexibility in these materials.[323] For IIR, crosslinking agents (sulphur or peroxides) are used to introduce crosslinks in the polymer chain and resistance to chemicals. Halogenation agents like chlorine or bromine are also introduced to get CIIR or BIIR, respectively, with modified chemical resistance properties. Antioxidants, such as butylated hydroxytoluene (BHT), phosphites, and aminic antioxidants, can also be utilized to increase the chemical durability of IIR under harsh conditions. In PBT, specific additives, including dioctyl phthalate, epoxidized soybean oil, di(2-ethylhexyl) adipate, and trioctyl trimellitate, can be included in their formulations to improve resistance to chemical degradation from oils, solvents, and strong acids. For PBS, plasticizers and stabilizers (especially antioxidants and biostabilizers) are employed to enhance its thermal stability, particularly for biodegradation formulations.[324,325] SIBS benefits from the incorporation of antioxidants, especially non-staining and non-discoloring ones, like BHT and many phenolic types to enhance its chemical attack, especially oils, aromatic solvents or acids, and oxidizing agents.[6,270,288]

5. Applications of butene- and isobutylene-based polymers

Due to their unique, exceptional properties, butene- and isobutylene-based polymers are finding use across diverse industries. Along with a comprehensive overview that follows, Table 9 presents a summary of the applications of butene- and isobutylene-based polymers studied, highlighting the specific properties that render them suitable for these applications. These unique, properties-driven applications highlight the significant versatility of butene- and isobutylene-based polymers. They make them highly adaptable for use in various sectors, from automotive to medical, packaging, and even emerging technologies. The ability of each polymer to meet the specific demands of its application, whether it be low gas permeability in automotive tyres or biocompatibility in medical devices, guarantees that these materials are performing optimally in diverse environments and under different conditions. Moreover, the importance of this versatility cannot be overstated. In addition to the continual emergence of challenges in the field, having a polymer base that can be tailored for specific applications becomes crucial as industries evolve, including the need for sustainable materials, enhanced performance in challenging environments, or the development of advanced medical treatments. The ability to modify and optimize properties and biodegradability allows for continuous innovation. Because of this adaptability, butene- and isobutylene-based polymers are anticipated to remain essential components in advancing various industries and enabling better, more effective products that satisfy both functional and environmental requirements.

5.1. Packaging

Approximately 146 million tonnes, or *ca.* 36% of the world's total plastic production, are used in packaging.[326,327] The most common polymers employed for packaging include polyvinyl chloride (PVC), which is found in cling films, bottles, and non-food packaging; low-density PE, which is used for grocery bags, food wraps, and squeezable bottles; PP, which is found in yogurt containers, straws, and bottle caps; PET, which is found in beverage bottles and food containers; high-density PE, which is used in milk jugs, detergent bottles, and grocery bags; and polystyrene, which is used in disposable cutlery, plastic cups, and food containers.[328] These polymers contribute significantly to plastic pollution because they are not naturally degradable and can persist in the environment for hundreds of years.[328] Additionally, only *ca.* 9% of plastic waste is recycled worldwide. This striking disparity draws attention to the difficulties in managing plastic waste and the pressing need for initiatives to address the growing environmental concerns associated with packaging waste. Accordingly, biodegradable plastics are gaining popularity in packaging applications. Because of their biodegradability and distinct physical properties, PBAT and PBS are increasingly being utilized in the packaging industry to address the growing concerns regarding plastic waste.[186,301] PBS has gained significant traction for compostable packaging like food containers, films, and wraps.[154,301] Its capacity to break down organically in the environment without leaving harmful residues is in line with the increasing demand for compostable packaging. Although it shows great promise for single-use applications, the low melting point and relatively low stiffness limit the use of PBS in more demanding packaging. Therefore, to more effectively compete with conventional plastic alternatives, recent developments have concentrated on enhancing the ease of processing, mechanical properties (*e.g.*, increased stiffness), and heat resistance of PBS by blending it or forming composites with other biodegradable polymers for more specialized packaging applications.[301,324] Additionally, because it provides a suitable strength, flexibility, and reduction of plastic waste environmental footprint, PBAT has emerged as the material of choice for compostable plastic bags and single-use packaging like agricultural films.[186,242] While PBS and PBAT are the most prominent options, PBT is also making strides in the packaging sector, especially for rigid, lightweight packaging applications like bottle caps and food containers where durability and performance under high heat or chemical exposure (*e.g.*, cosmetic packaging) conditions are essential.[19,94]

5.2. Automotive

In the automotive industry, IIR remains a staple due to its unique properties like low permeability, heat resistance, and

Table 9 A summary of the properties-based applications of butene- and isobutylene-based polymers

Polymer	Properties-based application	Study
PB	Especially PB-1, used as lubricants, adhesives, sealants, coatings, tubing, flexible films, and appliance parts because of its high tackiness; low density (0.91 g mL^{-1} at 25 °C); good dimensional stability; low dielectric constant (2.2–2.5 at 25 °C); high transparency (generally translucent to opaque); low gas permeability (5–20 cc per (m^2 day atm) for oxygen); and good adhesion that is due to its low surface energy	29,192,199 and 225
PIB	Because its dielectric constant (2.2–2.3 at 25 °C) and gas permeability (10^{-12}–10^{-9} cm^3 (cm^2 s cm Hg)$^{-1}$ for oxygen) are low, and it offers excellent anti-aging, creep resistance, and adhesive properties as well as high tackiness, it can be used in lubricant formulations, automotive parts, tubing, and as an insulation and encapsulant material in photovoltaic modules and other electronic devices. Especially PIB-HMW, it can be used in stretch films and eyewear or optical devices because of its high strength (15 to 30 MPa); excellent transparency; low moisture diffusivity (10^{-13}–10^{-12} cm^2 s^{-1}); high flexibility (ε_b up to 600%); and low T_g (−70 to −60 °C). It is also used in coatings, linings, as well as pressure-sensitive adhesives (PSAs) and sealants, due to its high adhesive strength, non-reactivity under ambient conditions, and solubility in hydrocarbons, along with its flexibility and easy removability	23,24,43,202,206,207 and 229
IIR	Its excellent air retention properties; good resistance to both heat (up to 150, 160, and 170 °C for IIR, CIIR, and BIIR, respectively) and chemicals; low gas permeability; good flexibility; good damping properties; and excellent sealing performance explain its typical use in automotive tyres (inner liners of tubeless tyres and inner tubes), vibration dampers, gaskets, ball bladders, footwear, protective wear, and other domestic and industrial applications. Particularly, a low molecular weight polymer, chlorinated butyl, is used as a sealant and adhesive	2,28,215,227,254 and 269
PBT	Its applications in engineering, biomedicine, conductive microfibers, electrical connectors, and appliance parts are made possible by its excellent moldability (250–280 °C molding temp.) and properties like high strength (50–80 MPa); modulus (2.5–4 GPa); good dimensional stability; and good electrical resistance or insulation capability (*i.e.*, high dielectric strength, 15–20 kV mm^{-1}). When blended with PC, the resultant thermoplastic blend is used in the automotive (*e.g.*, bumpers, relays, sockets, switches), aerospace, electronics, consumer goods (like packaging), *etc.* because of the blend's enhanced notched Izod impact strength (4–8 kJ m^{-2} of pure PBT *vs.* 15–40 kJ m^{-2} at 25 °C of PBT/PC blend); dimensional stability (due to the reduced moisture absorption and higher thermal resistance from PC); and resistance to stress cracking, chemicals, fuel, heat, and weather. Its outdoor electrical insulation is also possible when copolymerized with PTMEG	18,19,27,94,239,255 and 291
PBAT	Used in cable insulation because of its flexibility; good chemical resistance; good UTS (15–35 MPa); high ε_b (from 200–600%); low T_g (−20 to −10 °C); and good electrical properties. Its biodegradability (occurring both in aerobic and anaerobic environments), along with compostable capabilities and good barrier properties against moisture, makes it ideal for food containers and disposable cutlery. When blended with PLA, the resultant PBAT/PLA blend is used in packaging films because of enhanced tensile properties (UTS (higher at higher PLA content), elastic modulus (higher at higher PLA content), and ε_b (higher at higher PBAT content))	153,186,240,242,283 and 312
PBS	It is ideal for packaging, agricultural films, and biodegradable plastics because of its environmental impact reduction combined with flexibility, high UTS (40–50 MPa), flexural modulus (*ca.* 100–300 MPa), and ε_b (up to 500%)	5,14,37,154,219,301 and 324
SIBS	It finds use in medical applications, such as drug-eluting coronary stents, ophthalmic implants, artificial heart valves, tissue scaffolds, wound dressings, hydrophobic mats, *etc.* due to its hemocompatibility, hydrophobicity, biocompatibility, high flexibility, ability to support cell growth for medical use, and suitable UTS (3–25 MPa), tear strength (15–50 kN m^{-1}), ε_b (up to 700%), elastic modulus (0.5–10 MPa), and strain at yield (5–15%)	6,99,217,250 and 315

chemical durability. Specifically, it plays a crucial role in inner tubes and tyre linings, where it retains air pressure, resists damage from environmental factors, and provides durability throughout the long service life of a tyre.[28,215,254,269] IIR is resilient enough to be also used in vehicle seals to protect against dust, water, and specific chemicals. Its use in more durable forms, like CIIR and BIIR, which have enhanced chemical resistance, has recently gained popularity. Additionally, PIB, with its strong adhesive properties, continues to be used as a base polymer in PSAs.[206,207,329] However, there has been significant attention focused on more recyclable rubber and plastic materials and greener alternatives to conventional IIRs and PIB in some automotive parts due to the rising demand for electric vehicles (EVs). The automotive industry's transition to sustainable rubber and plastic materials in an attempt to meet environmental goals has been covered in detail by Vieyra *et al.*[330] Their analysis highlights how important it is to replace plastics made from fossil fuels with those derived from renewable resources in order to reduce plastic waste, lighten automobiles, and facilitate the switch to electric and driverless vehicles. They also discussed the challenges and

opportunities of using recycled and biodegradable plastics, emphasizing the significance of addressing material selection and guaranteeing durability throughout the lifecycle of a vehicle. Furthermore, materials like IIRs and PIB exhibit more complex chemical structures that make them generally not considered widely recyclable in most standard recycling streams, which generally focus on more commonly recycled materials like PE, PP, and PET.[331,332] SIBS, with its excellent properties combined with high biostability and biocompatibility, is increasingly used for medicinal devices as well as automotive sealants and adhesives, responding to the industries' demands for more versatile and high-performance but also sustainable materials that can withstand various harsh environmental conditions.[6,217] Meanwhile, PBT is making a significant mark in automotive bumpers, engine components, and interior parts like electronics (*e.g.*, switches and connectors) because of its excellent dimensional stability and resistance to mechanical wear and tear as well as to elevated temperatures (up to 140 °C).[94,239,333–335] Also, by incorporating IL moieties, nanofillers, or improving the material's chemical resistance through particular functional groups, the surface-modified PBT

has improved performance in automotive sensors and control units, guaranteeing increased durability and resistance to environmental challenges.[335–337]

5.3. Healthcare

Similar to SIBS, PIB (particularly, the crosslinked form) has long been used in the medical field because of its suitable properties combined with biostability and biocompatibility.[43,224,338] Recent trends in medical adhesives, surgical drapes, drug delivery systems, implantable devices, and wound care focus on PB (particularly, in its hydrogenated form) and PIB, as they remain favored materials where their bio-adhesive strength, inertness, and low toxicity ensure safe and effective contact with human tissues.[224,339] The suitability for drug delivery systems is further increased by the ability of the particularly biocompatible butene- and isobutylene-based polymers to be functionalized with different molecules.[340,341] In response to the growing demand for biodegradable medical materials with favorable mechanical properties, PBS has been explored for tissue engineering and biomaterial scaffolds, with research emphasizing its degradation rate and mechanical performance to match the specific needs of biological tissues.[13,14,38,342] Similarly, because of its biocompatibility and chemical resistance, PBT is being used in medical applications, especially for injection molded connectors in health-related devices like tips for electrosurgical instruments, pulse oximeters, and clips for breathing masks.[343,344] Another biocompatible polymer used in medicinal applications, particularly in biodegradable drug-eluting stents, drug delivery systems, and different temporary implants that naturally degrade in the body thereby decreasing the need for surgical removal, is SIBS.[270,345–347]

5.4. Other

As research and development efforts continue, the applications of butene- and isobutylene-based polymers are expected to be diversified, driven by advancements in polymer science and engineering as well as the need for innovative materials in various industries. For instance, PIB, like other addition polymers, is a material that can undergo depolymerization under controlled conditions to yield original isobutylene monomers, making it possible to produce new and recycled thermoplastic elastomers for use in domestic and industrial products, such as the automotive, electronics, and specific consumer goods.[348] Moreover, the versatility of PIB and PBT in next-generation energy technologies is demonstrated by their development for use in energy storage systems, including as possible components of polymer electrolytes.[349] Research into functionalizing these polymers with ILs and other materials shows promise for enhancing the performance of energy storage systems, even though these materials are not typically the main electrolytes used in supercapacitors and batteries.[350] These advancements aim to improve characteristics like stability, ionic conductivity, and flexibility, which may make them useful for future energy storage applications.[350] Stretchability and resilience are crucial for next-generation electronic applications, and polymers like SIBS are gaining prominence for flexible electronics, smart textiles, and wearable technology because of their exceptional balance of flexibility, mechanical strength, and durability.[6,7,351]

New avenues for advanced applications have been made possible by recent advancements in hybrid materials based on polymers derived from butene and isobutylene. For example, because of the synergetic combination of PIB's inherent flexibility and graphene's electrical conductivity and thermal stability, polymer–graphene nanocomposites have shown exceptional electromagnetic interference (EMI) shielding capabilities. These hybrids show promise as lightweight shielding materials for aerospace and flexible electronics applications.[352] Similar to this, PBS reinforced with nanocellulose has demonstrated noticeably better mechanical strength and oxygen barrier performance, making it appropriate for environmentally friendly food packaging films. In keeping with the objectives of green packaging, these PBS–nanocellulose composites also maintain their biodegradability.[353] Despite these benefits, there are still issues, especially with dispersion and compatibility between polymers and fillers. To increase interfacial adhesion, compatibilizers or surface functionalization of nanofillers are frequently required. For these hybrids, the most common processing techniques are still the melt blending and solvent casting, with the former being preferred due to its scalability and industrial viability. These hybrid systems are anticipated to be crucial in packaging, electronics, and biomedical applications as the need for sustainable, multifunctional materials grows.

5.5. Emerging applications

Butene- and isobutylene-based polymers are being investigated more and more for many cutting-edge and novel applications in the high-tech and sustainable innovation fields, in addition to their well-established uses. The functional potential of these polymers is being expanded by recent studies that show their increasing relevance in domains like energy storage, additive manufacturing, and soft electronics.

Energy storage systems: isobutylene-based polymers such as PBS, PBAT, and PBT are gaining significant interest as structural or membrane components in biodegradable batteries and polymer electrolytes as a result of their processability, compatibility with ILs, and chemical inertness. Particularly, PBT functionalized with IL moieties has been studied to enhance ionic conductivity and mechanical integrity in flexible energy storage devices.[354,355]

3D printing and additive manufacturing: biodegradable polymers like PBS and PBAT are emerging as customizable filaments for fused deposition modeling 3D printing, owing to their thermal stability, low warpage, and biodegradability.[356] They offer an important potential for manufacturing eco-friendly parts for prototyping, medical models, and lightweight consumer goods.[357]

Flexible and wearable electronics: elastomeric isobutylene-based copolymers such as SIBS and modified PIB have been suggested as substrates or dielectric layers in stretchable electronics and soft robotics.[358] Their flexibility, chemical resistance, and ability to retain properties under cyclic strain make

them feasible for utilization in wearable sensors, actuators, and biomedical electronics.[359]

6. Narrowing the focus to biodegradability and recyclability

6.1. Biodegradability

As partly highlighted before, researchers are becoming increasingly concerned about the environmental effects of bio-based plastics, as well as their capacity to degrade. While both biodegradable and non-biodegradable bio-based plastics are predicted to minimize environmental plastic pollution, neither is genuinely sustainable.[360] Bio-based plastics like bio-PE, bio-PP, and bio-PET are considered not biodegradable, have extended disposal timeframes, and can be detrimental to the environment in a way that compares to their fossil-fuel counterparts.[361] They break down into microplastics, which are consumed by aquatic and terrestrial species and contain hazardous chemicals and microbes unless properly disposed of in a designated composting facility. Chemicals added to increase the material's functioning cause nonspecific toxicity, and their migratory processes are poorly understood. A recent study discovered that bioplastics and plant-based polymers were just as harmful to the environment and individuals as traditional plastics.[362] On the other hand, researchers have been working on producing biodegradable, non-volatile, and nontoxic additives to significantly increase the mechanical, thermal, and physical characteristics of bioplastics, as well as their biodegradability, with minimum concomitant leaching.[363,364] As evidenced by the papers retrieved, incorporating polysaccharide or lipid-based plasticizers into conventional plastics such as PVC has become more appealing than traditional phthalate plasticizers, demonstrating competitive performance with potential in industrial applications.[365,366] Combining such studies on the chemical modification of bio-based polymers with studies on the potential risks of additives will aid the design of a greener product with better performance while minimizing potential damage both to the end users and the environment.

Furthermore, bioplastics' biodegradability is determined more by their chemical structure rather than their biobased origin. In contrast to other biodegradable polymers such as PLA, PBS, and polyhydroxyoctanoate, biodegradability studies using polyhydroxyalkanoates and their blends have shown success in aqueous and soil testing.[367,368] Nevertheless, most degradation experiments are performed on a laboratory scale, and inconsistencies may occur owing to suboptimal circumstances in the natural environment.[369–371] Moreover, PBAT and PBST, while being biodegradable and more easily dispersed in the environment, their natural degradation capacities are highly modest. As a result of their increasing usage, significant amounts of waste have accumulated, potentially causing a significant environmental burden. Thus, establishing strategies to minimize and recycle PBAT and PBST waste is vital for their long-term use.[372,373] This demands considerable studies into environmental parameters that influence bioplastic degradation, such as pH, salinity, nutrient content, and microbial population, in order to better understand degradation pathways and processes. Blending certain bio-based plastics with other biodegradable or non-biodegradable polymers can have both antagonistic and synergistic effects on biodegradability. Recent research has identified marine biodegradable bio-based polymers with potential uses in a variety of fields. However, merely creating biodegradable materials may not be sufficient; manufacturing should include a practical strategy for recovery and treatment using the current infrastructure. Also, genetically engineered organisms, persistent bio-accumulative and toxic compounds, and petroleum-based co-polymers utilized in some bio-based plastics are causing environmental concerns, especially in terms of pollution and long-term ecological effects. Accordingly, although bio-based plastics provide several environmental benefits, there is rising worry regarding their inputs, GHG emissions, and end-of-life management. Concerns about chemical stability have an impact on the lifecycle and performance of butene- and isobutylene-based polymers in addition to biodegradability. For instance, it has been demonstrated that PBS degrades hydrolytically in humid environments, losing over 10% of its mass after 30 days at 60 °C and 90% relative humidity.[374] In contrast, PIB is vulnerable to oxidative degradation when exposed to UV light; without stabilizers, molecular weight reductions of up to 40% have been documented following several hours of exposure at specific nm.[375] To improve environmental resistance while maintaining functionality, these vulnerabilities can be lessened by adding UV stabilizers (such as hindered amine light stabilizers), incorporating inorganic nanoparticles like titanium dioxide (TiO_2) or zinc oxide (ZnO), or copolymerizing PIB with PBAT or other biodegradable segments.[376] These consequences are quantified through life cycle evaluations (as previously discussed), which can also include biological carbon content analysis and carbon isotope assays. Ultimately, while bio-based plastics benefit the environment, production and end-of-life choices should be improved. Switching to renewable energy and innovative feedstocks can result in higher emission reductions and cheaper prices.

The overall environmental performance of butene- and isobutylene-based polymers is largely determined by sustainable supply chain factors. These materials can be derived from renewable feedstocks like 1,4-butanediol or succinic acid derived from plants, or they can be made from fossil-based monomers (like butenes in petrochemical streams). The feedstock selection has a direct impact on these polymers' cost structure, long-term viability, and carbon footprint. Although bio-based sources typically emit lower GHGs, their sustainability can vary greatly based on factors like land-use change, water needs, and agricultural inputs. Additionally, LCA tools like SimaPro and GaBi should be used to assess the energy intensity of polymer synthesis routes, including the use of high-pressure reactors, specialized catalysts, and purification steps. Researchers can use these tools to measure effects at every stage of the supply chain, from the procurement of raw materials to recycling or end-of-life disposal. Closing the loop and lowering reliance on virgin resources in this situation requires the use of circular economy models, especially those that incorporate mechanical recycling, chemical depolymerization, and renewable energy inputs. Researchers and industry stakeholders can more effectively

optimize the economic and environmental trade-offs of these polymer systems by implementing such multi-metric LCA approaches.

6.2. Recycling and reuse

Polymer recycling involves a sequence of well-defined steps designed to recover and repurpose end-of-life plastic products. The process typically includes the collection and sorting of waste, followed by identification using spectroscopic or density-based techniques, thorough washing to remove contaminants, and subsequent size reduction through shredding. The shredded material is then pelletized to produce uniform granulates, which can be reprocessed into new polymeric materials.[51] Among recycling methods, mechanical recycling remains the most widely implemented due to its relative simplicity and cost-effectiveness. It relies mainly on the effective separation of single-polymer streams and requires clean, uncontaminated feedstock to maintain polymer properties after reprocessing. Chemical recycling, on the other hand, offers an alternative route by breaking down polymers into their monomeric units or other value-added chemicals using heat, solvents, catalysts, and/or pressure.[377] This approach is particularly beneficial for dealing with complex or contaminated plastics that are unsuitable for mechanical recycling. Technologies under chemical recycling include solvent-based dissolution processes, which preserve polymer chains, and depolymerization approaches that cleave the covalent bonds within polymer backbones—an especially relevant technique for butene- and isobutylene-based elastomers. Both mechanical and chemical recycling methods can be adapted to recover and reuse butene- and isobutylene-derived polymers (Fig. 15), such as polyisobutylene and its derivatives.

Presently, most polymer waste is recycled mechanically, which is only successful for uniform, contaminant-free plastic waste that is challenging to collect. However, using chemical recycling techniques to complete the mechanical recycling of polymers can considerably increase recycling rates and assist in revitalizing the whole petrochemical industry. Furthermore, depolymerization is a process that is commonly used to recycle synthetic polymers, such as addition and condensation polymers. This process not only enhances sustainability but also supports the circular economy by enabling the recycling and reuse of butene- and isobutylene-based polymers. Heat is frequently used to depolymerize addition polymers like PB, PIB, IIR, and SIBS, but hydrolysis is required for condensation polymers like PBT, PBAT, and PBS.[51] Pyrolysis, a process in which waste polymers are heated and pressed in an oxygen-free environment, is one example of thermochemical recycling of polymer waste. It may be modified to produce considerable volumes of monomeric compounds for reuse from a specific polymer waste stream. However, pyrolysis is not without its significant drawbacks, which include environmental concerns, high energy requirements, and potential challenges in waste management. Therefore, other recycling processes with less environmental impact have been developed. For instance, Watson et al.[348] carried out the depolymerization of PIB at room temperature in the presence of trifluoromethanesulfonic acid and an arene solvent such as benzene. This enthalpically driven process formed tert-butyl carbocations, which were stabilized by the solvent, resulting in stable products like tert-butylbenzene. The depolymerization occurred in minutes, with the extent dependent on the end groups of the PIB and the solvent utilized. This method lowered the ceiling temperature of the polymer, offering a new approach to polymer recycling. On the other hand, PBT has been successfully depolymerized in supercritical methanol[378] and hot compressed water-containing reactors,[379,380] as well as via enzymatic pathways.[381] By utilizing and/or advancing these approaches, the butene- and isobutylene-based polymer wastes could be effectively addressed, lowering their contribution to the overall polymer waste concerns.

The widespread adoption of efficient recycling techniques for butene- and isobutylene-based polymers is hampered by a number of challenges, despite encouraging developments. The requirement for pure, single-polymer streams, which is rarely met because of contamination and multilayer packaging, limits mechanical recycling. After multiple reprocessing cycles, polymer degradation also results in a loss of thermal stability and mechanical integrity, rendering materials unsuitable for high-performance reuse. Regarding chemical recycling, the recovery and purity of monomers are still hampered by the separation of copolymer components, additives, and catalysts. Moreover, several chemical depolymerization methods are still energy-intensive and reliant on harmful solvents or high pressures, which makes them less sustainable. These limitations are being addressed by recent innovations. For example, under mild conditions, selective depolymerization techniques show tailored breakdown of polymer chains, such as acid-mediated room-temperature degradation of PIB[348] or supercritical and enzymatic depolymerization of PBT and PBAT.[378–381] Compared to conventional pyrolysis, these techniques increase selectivity and have a lower environmental impact. Additionally, separation-enhanced procedures, such as membrane filtration and tandem enzymatic depolymerization, demonstrate how biocatalytic and hybrid systems can increase recycling yield and material purity, particularly for condensation polymers like PBAT.[166]

6.3. Environmental impact and recyclability

Understanding the environmental fate of butene- and isobutylene-based polymers is crucial, especially when it comes to their performance in different environmental conditions, hydrolysis behavior, and degradation kinetics. Although biodegradable polymers like PBS and PBAT have potential benefits, environmental factors like temperature, microbial diversity, and moisture content have a significant impact on how quickly they degrade. PBS films, for instance, degraded up to 60% in 180 days under industrial composting conditions, according to Borelbach et al.,[382] while only 90 days of controlled composting conditions showed 60.7%, as Shin et al.[383] stated. Similarly, PBS showed hydrolytic degradation rates exceeding 50% weight loss in controlled marine mesocosms within 90 days, according to Suzuki et al.,[384] indicating partial marine degradability. However, broad environmental integration is still hampered by chemical stability under particular conditions. Despite being
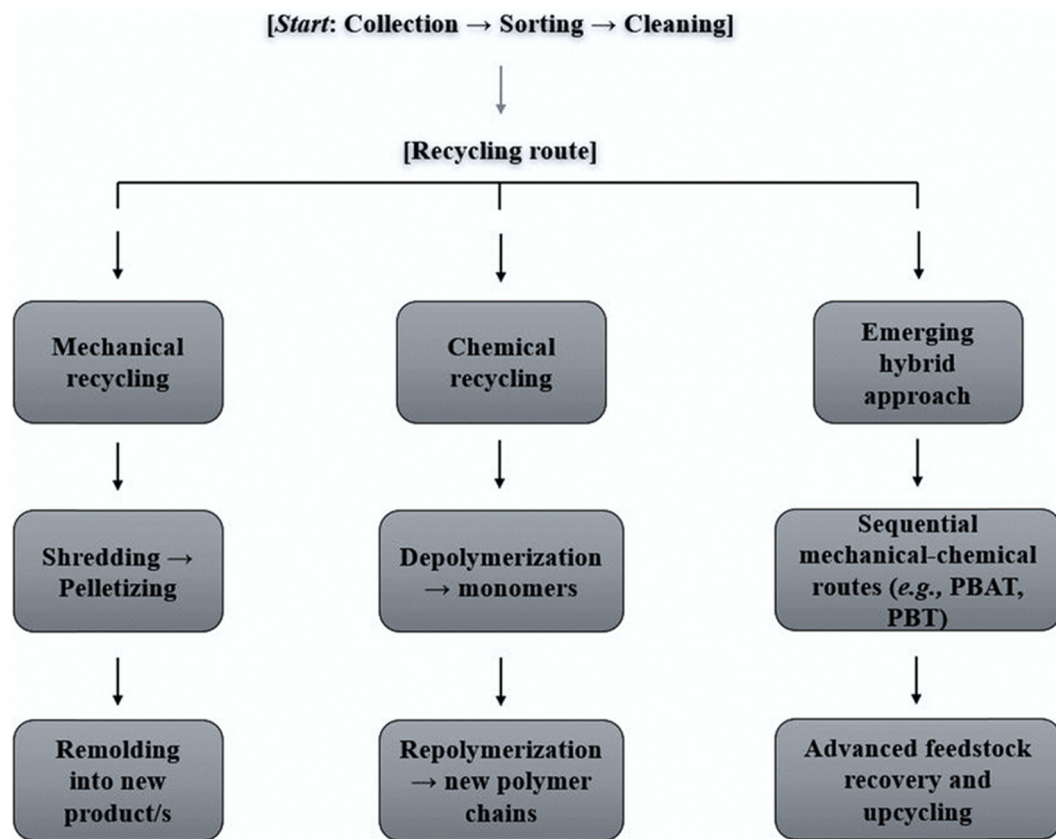
[*Start*: Collection → Sorting → Cleaning]

↓

[Recycling route]

| Mechanical recycling | Chemical recycling | Emerging hybrid approach |

| Shredding → Pelletizing | Depolymerization → monomers | Sequential mechanical-chemical routes (*e.g.*, PBAT, PBT) |

| Remolding into new product/s | Repolymerization → new polymer chains | Advanced feedstock recovery and upcycling |

Fig. 15 Overview of mechanical and chemical recycling pathways for butene- and isobutylene-based polymer materials.[166,348,377–381]

biodegradable under ideal conditions, PBT and PBAT exhibit strong resistance in landfills and freshwater systems.[283,385] High temperatures and steady enzymatic activity are necessary for their degradation, which is not always feasible in open environments.[386,387] Also, chemical additives like plasticizers and UV stabilizers that are frequently used in commercial formulations may disrupt the kinetics of degradation and present a risk of leaching during breakdown, which could result in ecological toxicity.[388,389] Regarding recyclability, the environmental trade-offs of mechanical and chemical methods must be taken into account. Despite its effectiveness in recovering monomers, pyrolysis has significant energy requirements and emissions. However, new solvent-based and enzymatic depolymerization processes present viable, low-impact substitutes. For example, a recent study by Yang *et al.*[390] reports on the enzymatic depolymerization of PBAT film using engineered cutinases, and reveals 55% gel formation after UV exposure for 24 h and immersing in a solvent (trichloromethane) for 48 h. However, the majority of solvents used are toxic as well. These findings underscore the need for a multifaceted approach when assessing the life cycle of butene- and isobutylene-based polymers. To promote the sustainable use of these polymers, more case-specific environmental impact analyses and scalable recycling techniques are essential. Ultimately, directing policy and design decisions for more environmentally friendly polymer solutions will depend on combining LCA data with actual degradation behavior.

7. Future directions and research opportunities

Despite recent significant advancements, there are still several promising research prospects in the field of butene- and isobutylene-based polymers discussed in this review. More research into cutting-edge synthesis methods, novel copolymers, and the sustainability of these materials will ensure their widespread adoption as they evolve. Creating new butene- and isobutylene-based copolymers that combine the desirable qualities of different monomers to achieve distinctive performance characteristics is a primary avenue for future studies. For instance, butylene has been incorporated into copolymers like PBS, PBAT, and PBST to produce polymers that combine material biodegradability and enhanced mechanical properties. Future research can concentrate on broadening the variety of renewable resource-based monomers added to butene- and isobutylene-based copolymers, which may produce more biodegradable polymers with unique properties for a wider range of applications.

Specific butene- and isobutylene-based copolymer systems are beginning to show promise in meeting application-specific requirements, in keeping with current trends in material innovation (Table 10). PBS and polycaprolactone copolymerization (PBS–PCL), for instance, may provide improved elasticity and delayed degradation, making it ideal for medical applications like drug delivery scaffolds and bioresorbable implants.[391] Similar to this, combining PIB and PBAT (PIB–PBAT) may result in flexible, semi-biodegradable films with increased toughness, making them desirable options for agricultural and flexible food packaging applications.[392] Such studies highlight how crucial strategic monomer selection is for tuning mechanical and environmental performance. Future research should build upon these by integrating copolymer architectures for advanced and sustainable applications with functionality, responsiveness, and compatibility.

The characteristics and performance of butene- and isobutylene-based polymers could be greatly enhanced by advanced processing methods. For example, to get more control over the MWD and polymer architecture, the application of metallocene-based catalysts in the synthesis of PB can be investigated further. New methods for adjusting the structure and characteristics of butene- and isobutylene-based polymers are provided by recent advancements in the use of supercritical fluids in polymer processing. PBS and PBAT, in particular, have been made highly porous by the use of scCO$_2$, which may make it appropriate for use in drug delivery systems or as a bio-based substitute for synthetic polymers in packaging applications.[144,145,232,297] In addition, investigating the use of other innovative polymerization processes like plasma and microwave-assisted polymerization could open the door to more effective, scalable, and ecologically friendly ways to synthesize these polymers.[396,397]

Another crucial area for further study is the role of butene- and isobutylene-based polymers in the context of the circular economy. In addition to the biodegradability, the recyclability of these polymers will become a crucial characteristic to investigate as the need for sustainable materials grows. Creating methods to enhance the mechanical and chemical recycling of these materials is a promising direction of study. PBS, PBAT, and PBST are biodegradable, but further studies are still needed to determine how quickly they break down in different environmental settings. This might be the main strategy in which their roles in the circular economy can be more clearly defined. Moreover, PB, PBT, and IIR recycling procedures are currently not maximized. Future studies could concentrate on developing more effective depolymerization and re-polymerization processes to make these materials viable contenders for circular product life cycles. Biodegradable butene- and isobutylene-based polymers should also have their LCA extended to incorporate a wider range of environmental metrics, such as carbon sequestration, water use, and land use. These comprehensive assessments will shed more light on the true environmental advantages of these polymers (in contrast to traditional plastics) and direct their continued use across a range of sectors.

Further studies could also explore the copolymerization, functionalization, and nanoparticle reinforcement of butene- and isobutylene-based polymers to fabricate smart materials that react differently to environmental stimuli. For example, to make PBAT well-suited for high-tech uses like environmental sensors and self-healing materials, it might be developed to have improved features like stimuli-responsiveness (for example, in response to temperature, light, or pH) (Fig. 16).[398,399] A glimpse of these smart functionalities can be found in recent case studies. For instance, because of their low T_g and intrinsic segmental mobility, self-healing coatings derived from PIB-based elastomers have shown exceptional mechanical integrity recovery following minor damage.[24,400] In aerospace and marine applications, where microcracks often form during cyclic stress, these materials could be ideal for long-term protective coatings. In addition, controlled shape recovery and responsiveness to external stimuli like heat and moisture have been demonstrated for PBS-based nanocomposites embedded with thermo-responsive fillers like graphene oxide or poly(N-isopropylacrylamide).[401] These systems are becoming sustainable alternatives in high-tech automotive, electronics systems, and temperature-sensitive sensors, as well as in the medical field (e.g., biomedical scaffolds and current use of SIBS in drug delivery systems) and smart packaging (e.g., packaging that effectively responds to environmental factors like temperature and humidity).[348,391]

The investigation of butene- and isobutylene-based polymers for high-performance applications in sectors like aerospace is another important area of research. For such a demanding sector in terms of components' properties, where some require high strength, others need high rigidity, and some demand both and more, great effort is necessary to

Table 10 Selected emerging butene- and isobutylene-based copolymer systems: monomer combinations, target properties, and potential applications

Copolymer systems	Monomer combination	Target property/benefit	Potential application	Ref.
PBS–PCL	Butylene succinate + ε-caprolactone	Increased biocompatibility, reduced rate of biodegradation, and improved elasticity	Medical devices like scaffolds, sutures, and implants	391
PIB–PBAT	Isobutylene + butylene adipate/terephthalate	Improved toughness, flexibility, and partial biodegradability	Flexible packaging and agricultural films	392
PB–PLA	Butene + lactic acid	Balance of flexibility, rigidity, and biodegradability	Compostable containers and semi-rigid packaging	393
PBS–starch	1,4-Butanediol/succinic acid + glucose	Increased biodegradability and reduced cost	Disposable food packaging and mulch films	394
PBAT–PEG	Butylene adipate/terephthalate + ethylene glycol	Stimuli responsiveness and water uptake control	Smart materials and controlled drug release	395

[Stimulus applied (Heat, pH, Light)]

Polymer matrix → Self-healing *via* microphase mobility

Nanocomposite system → Controlled swelling, shape-memory, and drug release

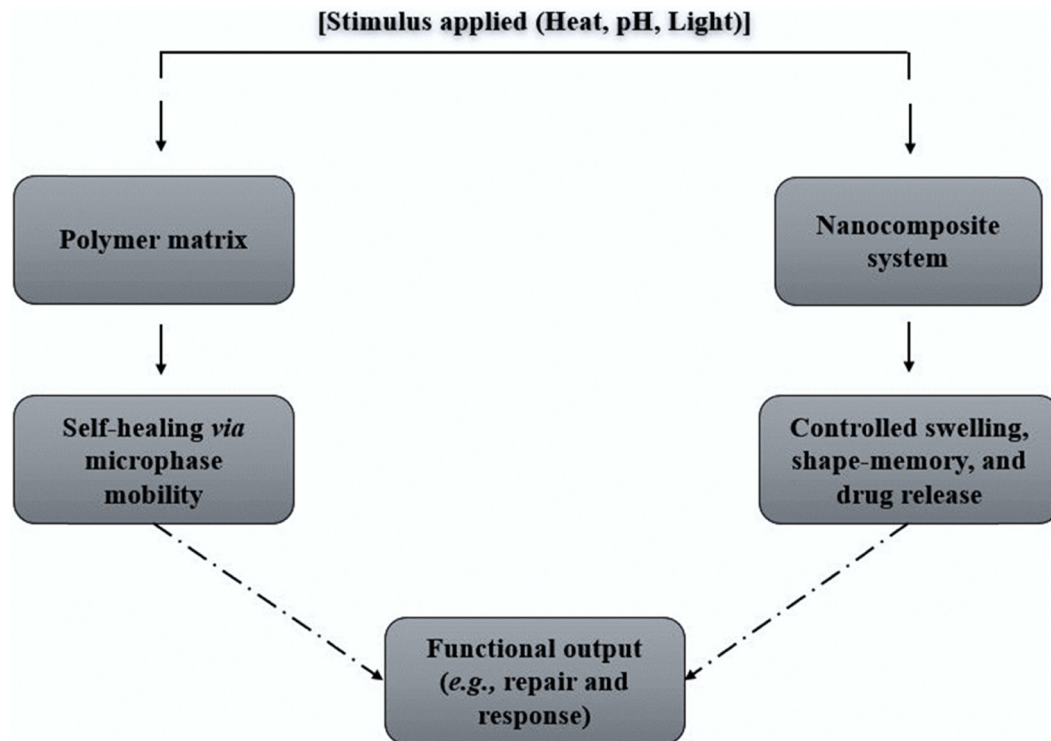Functional output (*e.g.*, repair and response)

Fig. 16 Conceptual representation of stimuli-responsive behavior in smart butene- and isobutylene-based polymer systems.[398–401]

enhance the processing capabilities, mechanical behavior, dimensional stability, and heat resistance of butene- and isobutylene-based polymers. Future studies could concentrate on the creation of hybrid materials, which combine the qualities of butene- and isobutylene-based polymers with inorganic fibers or fillers, like graphene or CNTs, to fabricate high-strength and ultra-lightweight materials that can be used in next-generation electronics, vehicles, or systems. This is particularly because butene- and isobutylene-based polymers have demonstrated a basic solution for the automotive industry's increasing need for lightweight, durable, and environmentally friendly materials in areas like external components, interior panels, and under-the-hood applications.[265,316,330,333]

Another relevant field for research is the incorporation of renewable feedstocks into the production of butene- and isobutylene-based polymers. Currently, some of these polymers, *i.e.*, PBS, PBAT, and PBST, are made from plant-based feedstocks and renewable resources. The carbon footprint of these polymers may be further reduced with additional studies into alternate biomass sources like algae or lignocellulosic materials for their synthesis. Optimizing the synthesis process will require an understanding of how different feedstocks affect the finished polymer's performance. Therefore, to ensure that the environmental advantages of butene- and isobutylene-based polymers are optimized, researchers might have to look into the sustainability of the whole supply chain, from the sourcing of feedstock to polymerization and end-of-life management.

Developing advanced blends and composites comprising butene- and isobutylene-based polymers and other biodegradable

materials is a notable research opportunity. Materials with improved mechanical properties and increased biodegradability may result from further blending PBS with materials like starch and PLA, opening up a wider range of packaging industry applications.[176,402,403] Similarly, the creation of composite materials made up of PBS, PBAT, or PBST and natural fibers may provide a more environmentally friendly substitute for traditional plastics in automotive and construction applications. This means that researchers can reduce reliance on fossil-based plastics by developing novel materials that meet new market demands by combining the special properties of butene- and isobutylene-based polymers with other biopolymers.

As PBS, PBAT, and PBST, in particular, gain traction in the market, there is an increasing demand to make their synthesis methods more scalable. Optimizing the methods for these polymers is crucial to satisfy the growing demand for sustainable polymer products. For instance, although PBAT is made from a variety of renewable feedstocks, its complex synthesis pathway makes it costly to produce on a commercial scale.[403] Future studies could concentrate on increasing the synthesis process's efficiency for PBAT as well as other isobutylene-based copolymers and polymers. Improvements in reactor technology, reaction kinetics, and catalyst design may make it possible to produce biodegradable plastics on a larger scale and at a lower cost.[403,404] To summarize and promote further research on overcoming challenges related to processing, Fig. 17 illustrates a flow diagram outlining current processing restrictions and emerging strategic solutions for enhancing the efficiency, scalability, and sustainability of butene- and isobutylene-based polymer synthesis and applications.
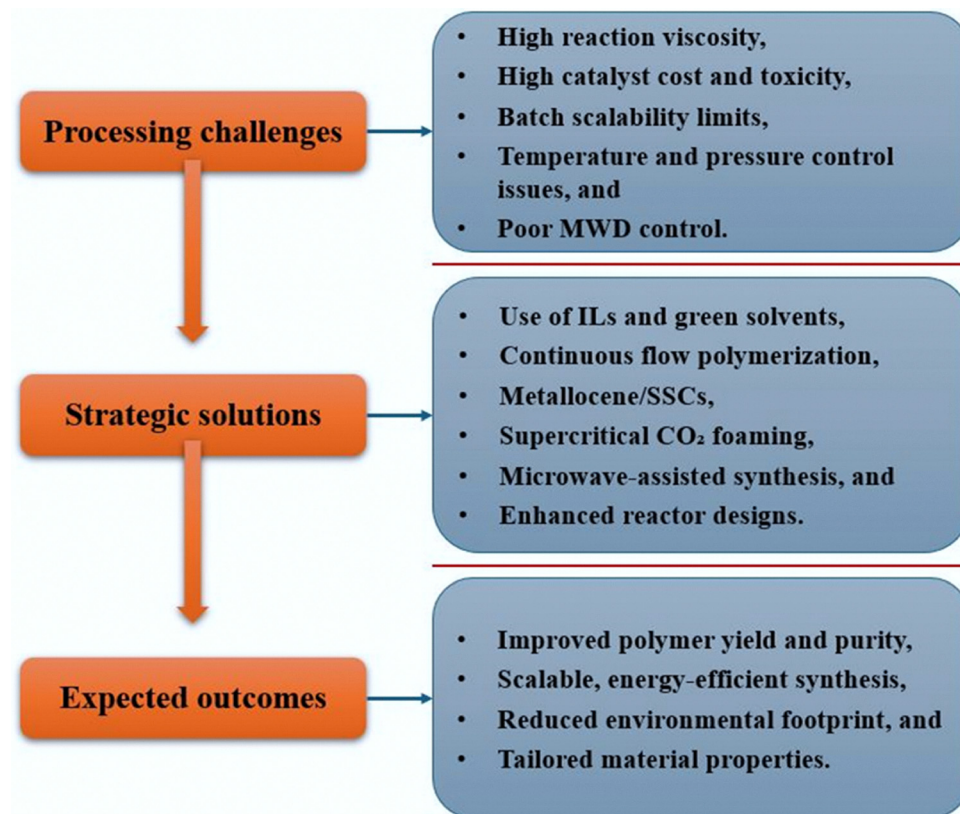
Fig. 17 General flow diagram of processing challenges and proposed strategic solutions for butene- and isobutylene–based polymers.[241,274,398,406]

Researchers should explore the role of butene- and isobutylene-based polymers in energy-efficient applications in keeping with sustainability. PBT, for example, has good electrical and thermal properties, making it an ideal option for energy-efficient electronics.[405] The use of this material in energy harvesting, storage, and even as part of photovoltaics or energy-efficient windows may be the subject of future research. In line with the expanding trend of sustainability in electronics, PBS, PBAT, and PBST may also be viable materials for use in biodegradable energy storage devices due to their biodegradability and mechanical strengths. In general, the ongoing development of the applicability and sustainability of butene- and isobutylene-based polymers will be essential in widening their usage while tackling environmental issues and furthering the green chemistry agenda as awareness of plastic pollution and its effects grows worldwide.

7.1. Proposed experimental methodologies and evaluation frameworks

This subsection describes particular experimental techniques and evaluation instruments to direct the real-world application of the research directions suggested in this review. For butene- and isobutylene-based polymers, these approaches facilitate the implementation of innovative processing methods, environmental evaluations, and application-focused advancements.
  ● For renewable feedstocks:

o Explore bio-based butene synthesis from glucose by *Clostridium acetobutylicum* fermentation.

o Use gas chromatography-mass spectrometry and nuclear magnetic resonance (NMR, ^{1}H/^{13}C) to characterize fermentation outputs.

o Use high-performance liquid chromatography, elemental analysis, and Fourier transform infrared spectroscopy (FT-IR) to assess purity and conversion.
  ● For scalable synthesis:

o Assess continuous flow reactors at different temperatures (*e.g.*, 50–120 °C) and contact times.

o Use size-exclusion chromatography, thermogravimetric analysis, and in-line FT-IR to monitor polymer conversion.

o Assess throughput and stability by optimizing catalyst loading and flow rates.
  ● For circular economy integration and recyclability:

o Employ supercritical methanol or enzymatic digestion to perform chemical depolymerization.

o Use techniques like liquid chromatography-mass spectrometry, NMR, and respirometry to characterize degradation products.

o Employ differential scanning calorimetry (DSC), dynamic mechanical analysis, and other mechanical testing to assess recyclability after multiple thermal cycles.
  ● For the development of smart material:

o Use nanoparticles, including ZnO, CNTs, and graphene, to functionalize polymers through melt blending or *in situ* polymerization.

o Employ UV-Vis spectroscopy, DSC, and dynamic mechanical analysis to test stimuli-responsiveness under pH, light, and thermal stimuli.

o Use electrochemical impedance spectroscopy and gas permeability testing to assess conductivity or barrier properties, more especially for electronics and packaging.

• For environmental impact and degradation evaluation:

o Use tools like SimaPro or GaBi to conduct LCA, covering cradle-to-grave metrics, which typically include GHG emissions, water consumption, and land-use change.

o Employ respirometry, mass loss tracking, and scanning electron microscopy imaging to assess polymer degradation in marine, composting, and soil conditions.

o Utilize carbon isotope ratio analysis to measure renewable content.

8. Conclusion

Significant progress has been achieved in the synthesis of butene- and isobutylene-based polymers, with several approaches improving polymerization efficiency, processability, material properties, and applicability. With precise control over molecular weight distribution and polymer design, metallocene-based catalyst systems have demonstrated notable efficacy in the synthesis of high-quality PBT, PBAT, and PBS. In addition to producing materials with enhanced mechanical and thermal properties, these synthesis process advancements have also lessened the environmental impact of polymerization by using less energy and generating fewer by-products than traditional Ziegler–Natta catalyst systems, which are typically used to synthesize PB, PIB, and IIR. On the other hand, the core synthesis of SIBS itself has received less attention.

Properties of butene- and isobutylene-based polymers have been crucial to their expanding use in various industries. For example, PB and PIB find use in adhesive applications because of their high bonding strength. On the other hand, as an alternative to conventional, non-biodegradable polymers, PBAT and PBS, are notable for their biodegradability and have demonstrated significant potential in eco-friendly packaging solutions, agricultural films, and medicinal uses. Like PBS, the applications of SIBS extend to the healthcare sector, where its biocompatibility makes it an ideal fit for controlled-release drug delivery systems. Meanwhile, because of its good resistance to both heat and chemicals, low gas permeability, and excellent sealing performance, IIR finds use in protective wear, automotive tyres, seals, and gaskets. Ultimately, the growth of these polymers in various industries is anticipated to accelerate as the need for high-performance and ecologically friendly materials keeps increasing and research advances.

Benefits for the environment from isobutylene-based polymers, especially PBS, PBAT, and PBST, are essential for addressing the rising issues of plastic waste and pollution. These biodegradable polymers contribute significantly to the transition to more sustainable materials as they present a viable biodegradable substitute for conventional plastics derived from petroleum-based resources. Notwithstanding these promising characteristics, the synthesis costs of the overall butene- and isobutylene-based polymers are high. Additionally, even though the synthesis process optimization has advanced, more may be done to lessen the environmental impact of polymer synthesis, particularly concerning energy use and GHG emissions. Future studies should, therefore, concentrate on investigating different, more sustainable catalytic methods and enhancing the scalability of metallocene-based systems. There are also still concerns with the full biodegradability of PBS and PBAT and their ability to be completely integrated into the circular economy. On the other hand, PB, PIB, PBT, IIR, and SIBS recycling procedures are currently underexplored. This can be addressed by improving the degradation rates of PBS and PBAT under various environmental conditions and enhancing the recyclability of the other butene- and isobutylene-based polymers, both of which will maximize the polymers' environmental benefits and thereby their adoption across various domestic and industrial sectors.

Author contributions

J. I. Mnyango: conceptualization, methodology, literature investigation, writing – original draft, writing – review & editing, visualization, validation; B. Nyoni: writing – original draft; N. Mama: writing – review & editing; B. G. Fouda-Mbanga: writing – original draft; Z. Tywabi-Ngeva: writing – review & editing; S. P. Hlangothi: conceptualization, supervision, writing – review & editing, validation.

Conflicts of interest

The authors declared no potential conflicts of interest concerning the research, authorship, and/or publication of this article.

Data availability

As this paper is a literature review, no original research data or datasets were generated or analyzed during the study. All data and information presented in this paper are derived from publicly available scientific literature, research articles, and academic sources. References to the relevant studies are provided throughout the paper. Any additional data, if required, would have to be accessed by consulting the cited sources in the reference list.

Acknowledgements

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