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Making polymers with low carbon content: a sustainable option

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To cope with the challenges posed by general polymer materials that rely on petroleum and generate pollution, we propose the partial substitution of carbon elements in polymers with oxygen (or other heteroatoms such as sulfur) and the use of biomass carbon to construct low-carbon polymers. The composition of natural cellulose can be used as a reference (O/C molar ratio of 5/6 and weight percentage of 49.4%) for low-carbon polymers that integrate non-edible biomass-based feedstocks, CO₂, and industrial carbon/sulfur waste (*i.e.* low-carbon monomers) through molecular design innovations, thereby balancing the performance/function with degradation/recycling potential. We discuss the unique characteristics of these low-carbon polymers in comparison to conventional “carbon-rich” polymers, highlighting the representative examples of PLA, PHA and PPC that are on the way to commercialization. This perspective also addresses the critical challenges of cost-effective synthesis, developing new catalysts/initiators, and the regulation of structure–property relationship, with particular emphasis on the industrialization of CO₂- and biomass-based polymers.

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1. Biodegradable polymers, recyclable polymers and bio-based polymers have been widely investigated as sustainable solutions for making general-purpose plastics.
2. Currently, general-purpose plastics such as PE and PET rely on petroleum and cause pollution when discarded; there is an urgent need for sustainable polymers with performance and cost comparable to those of traditional polymers.
3. Building on the inherently low-carbon nature of biomolecules like cellulose (O/C molar ratio of 5/6 and carbon weight percentage of 49.4%), we propose strategically designing synthetic general-purpose polymers targeting a similar composition-termed low-carbon polymers. These low-carbon polymers integrate non-edible biomass-based feedstocks, CO₂, and industrial carbon/sulfur wastes (*i.e.*, low-carbon monomers) with molecular design innovations, aiming to balance performance/function with degradation/recycling potential.

1 Introduction

Polymer research has entered its second century since Staudinger's first polymerization report published in 1920.¹ Polymer materials produced from petrochemical resources have excellent overall properties, such as light weight, ease of processing and corrosion resistance, and they are widely used in packaging films/foams, containers, pipes, clothing, medical equipment, auto parts and office equipment. General-purpose polymers like PE, PP, PS, PET and PVC cost less, are indispensable basic materials for societal development and have been significantly promoting the progress of human material

civilization for more than a hundred years.^{2,3} At present, the annual output of synthetic polymer materials in the world is more than 400 million tons. According to the current production methods of synthetic polymers, by 2050, the production and processing of polymer materials worldwide will consume more than 20% of crude oil and generate 15% of carbon emissions.⁴

On the other hand, the current general-purpose polymers (*e.g.* PE, PP, PS) have chemically stable carbon–carbon chain structures. Hence, improper post-use treatment causes long-term damage to the ecological environment.⁵ Statistical data reveal that approximately 19 to 23 million tonnes of plastic waste leak into aquatic ecosystems annually, contaminating lakes, rivers, and marine environments.⁶ Meanwhile, terrestrial microplastic pollution levels exceed marine concentrations by a factor of 4 to 23.⁷ Currently, less than 20% of plastic waste enters recycling systems, with the majority being processed through low-value pathways such as thermal re-

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cycling through waste-to-energy incineration and mechanical recycling that degrades material properties.⁸

To meet the challenges posed by traditional general polymer materials that are resource-dependent and pollute the environment, *making sustainable polymers* is a promising choice.^{9–11} The concept of sustainable polymers includes at least three aspects:^{12–14} (1) extraction of monomers from renewable, recycled, or waste carbon resources; (2) reduced environmental impact during production and use; and (3) promotion of a circular economy, in which polymers can be recycled, biodegraded, or composted after use. It should be emphasized that sustainable polymers should have comparable or improved properties to those of traditional plastics and should be cost-competitive. Therefore, the production of *sustainable polymers* is a huge challenge in polymer synthesis.

Current sustainable polymers fall into three key categories: biodegradable polymers capable of environmentally benign decomposition, recyclable polymers designed for infinite material recovery through industrial reprocessing, and bio-based polymers derived from renewable biomass feedstocks. This study briefly explains the definitions, main systems, and characteristics of biodegradable polymers, recyclable polymers, and bio-based polymer materials, along with recent research progress in polymer synthetic chemistry. On this basis, this article proposes the concept of *low-carbon polymer* that focuses on using chalcogen (O, S) elements to partially replace carbon elements in polymers for making sustainable polymers (Fig. 1). Although the term “*low carbon polymer*” has appeared in prior discussions related to sustainability,¹⁵ we herein define a *low-carbon polymer* as a synthetic general-purpose polymer strategically designed to have a reduced carbon content, specifically targeting an oxygen-to-carbon (O/C) molar composition ratio approaching that of natural cellulose ($\approx 5/6$),

corresponding to a carbon weight percentage of approximately 50%. This reduction is achieved primarily through the partial substitution of carbon elements in the polymer backbone or side chains with oxygen (and/or other heteroatoms like sulfur) and the utilization of carbon derived from biomass, CO₂, or industrial waste molecules.

2 Sustainable polymers

Significant research efforts have focused on developing synthetic strategies for sustainable polymers,¹⁶ with current systems conceptually categorized into three dominant paradigms: biodegradable polymers,^{17–20} recyclable polymers,^{21–23} and biomass-based polymers.²⁴ Although these categories exhibit conceptual overlaps, they retain distinct priorities, ranging from structural design principles to feedstock sourcing considerations.

2.1 Biodegradable polymers

Biodegradable polymers typically degrade into non-toxic and harmless small molecules through biodegradation, especially under forced composting conditions, and are thus often referred to as environment-friendly polymers.^{17–20} Most biodegradable polymers are oxygen-containing aliphatic polyesters or polycarbonates, which can decompose in the natural environment within a short period of time (Fig. 2).

Typical commercially available biodegradable aliphatic plastics include polylactide (PLA) and propylene oxide (PO)–CO₂ copolymer (PPC).^{25–27}

The development of PLA dates back to the 1930s,²⁸ with its industrialization process accelerating as a result of breakthroughs in catalyst technology. The evolution from early-stage

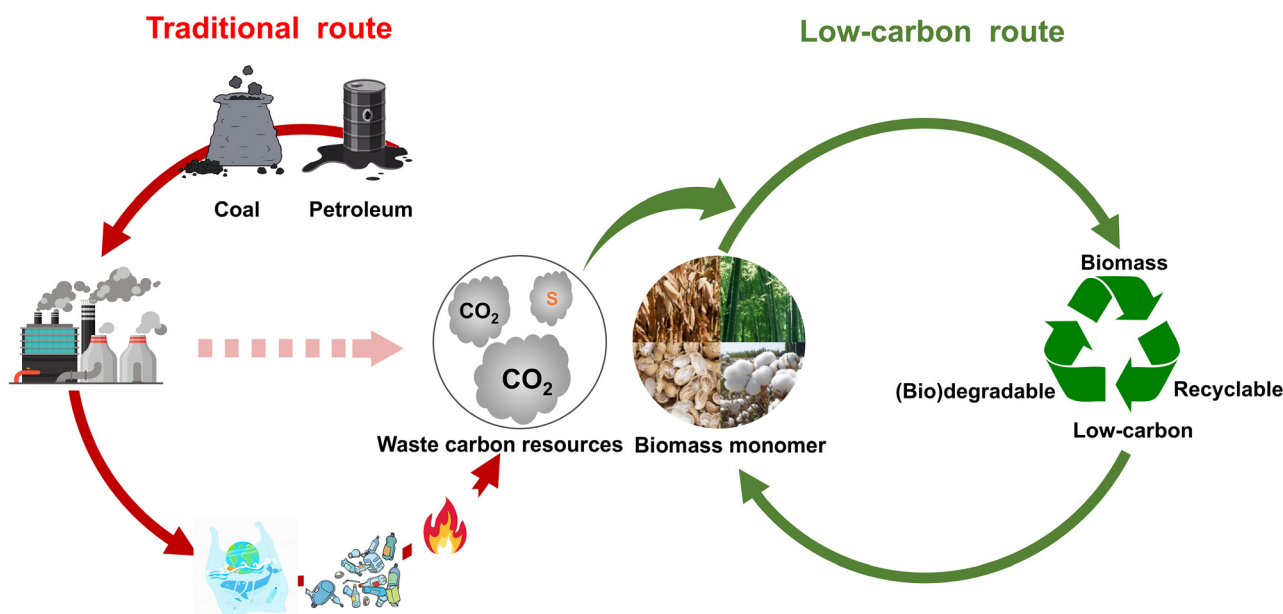


Fig. 1 Innovation in synthetic chemistry towards sustainable polymers, with low-carbon composition as an option.

Through molecular design strategies incorporating pre-installed ester bonds in monomer architectures, we developed a series of novel sulfur-containing polyesters. These materials exhibit both satisfactory mechanical properties and inherent chemical recyclability.^{52–55}

Polyacetals and poly(acetal-ester)s are emerging recyclable polymers that can be synthesized *via* the ring-opening polymerization of 1,3-dioxolane,⁵⁶ 1,4-dioxolane-2-one,^{57,58} and the ring-opening copolymerization of cyclic anhydrides with aldehydes^{59–61} or cyclic acetals.⁶² Geoffrey W. Coates *et al.* employed indium bromide-catalyzed reversible deactivation cationic ring-opening polymerization (RD-CROP) of cyclic acetals to synthesize high-strength poly(1,3-dioxolane) (PDXL), achieving near-quantitative monomer recovery *via* acid-catalyzed depolymerization.⁵⁶ We have reported cationic alternating copolymerization of cyclic anhydrides and aldehydes and obtained a library of polyesters with alternating acetal-ester linkages. The copolymerization exhibited chemical reversibility attributed to its relatively low enthalpy. They achieved not only efficient monomer recovery in a sublimation unit at 180 °C without any solvents and catalysts, but also rapid depolymerization of the polymer at 100 °C in dichloromethane using Lewis acids as catalysts.^{59–61}

Recyclable polymers are expected to follow an infinite cycle of “monomer–polymer–monomer”, thereby preventing environmental damage and monomer loss. However, in reality, most polymers need to be added with multiple additives or blended for practical use. A key challenge is to balance energy and material consumption throughout the entire life cycle, including production, processing, recycling, degradation and separation.

2.3 Biomass-based polymers

Biomass-based polymers are derived from starch, cellulose, lignin, protein, and vegetable oil as raw materials and are produced by biological fermentation or chemical synthesis (Fig. 4).^{63–65}

At present, bio-based polymers are mainly divided into two types: natural polymers and bio-based synthetic polymers. Natural polymers have been widely used in the preparation of bioplastics and composite materials, such as cellulose, lignin, hemicellulose, starch, protein and modified bio-based polymers.^{66–69} For example, Hu *et al.* produced an ultra-strong and dense wood with orderly arranged cellulose nanofibers by removing lignin and hemicellulose from the wood and collapsing the wood cell walls through high-temperature compression.⁷⁰ Another prominent example is starch-based plastic, a biodegradable material predominantly composed of natural starch. By combining it with other degradable components through composite modification, this material retains mechanical properties comparable to conventional plastics while exhibiting environmentally friendly biodegradability.⁷¹

Biomass-based synthetic polymers are mainly derived from various small-molecule biomass sources, such as vegetable oils, fatty acids, furans, terpenes, rosin acid and amino acids through biorefinery processes. Typical biomass-based polymers, such as PLA (made from corn starch),⁷² furandicarboxylate-based polyesters,⁷³ and biomass-based polyethylene, have been developed. Chen *et al.* reported an intramolecular multi-nuclear catalyst to achieve precise stereochemical control in PLA synthesis and successfully achieved the industrial production of PLA in China.^{74–76} Zhu *et al.* designed high-barrier

Biomass-based polymers

Natural polymers

Bio-based synthetic polymers

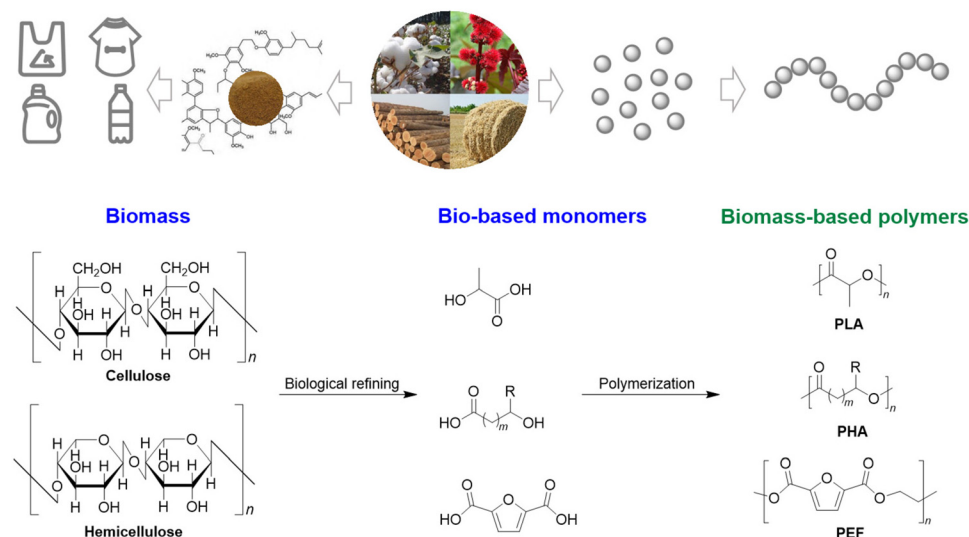


Fig. 4 Illustrations of biomass-based polymers.

biomass-based polyesters by incorporating degradable components (short-chain diacids, lactic acid, and PEG) into furan-dicarboxylate-based polyesters (PEFs), systematically investigating the structure–property relationships governing barrier performance, mechanical strength, and degradation behavior.^{77–79} Another typical example is bio-derived PE, which is obtained from ethylene produced by ethanol fermentation, although PE is non-biodegradable and difficult to chemically recycle.⁸⁰ Alternatively, microbial fermentation processes employing bacteria/cyanobacteria can convert renewable carbon sources (sugars, waste oils) into PHA for biomass-based plastic production.⁸¹ Chen *et al.* have achieved high-efficiency, low-cost, industrial-scale production of PHA by employing synthetic biology techniques to engineer microbial strains and optimize fermentation processes, culminating in the commissioning of China's inaugural 10 000-ton PHA production line in Yichang, Hubei Province.⁸²

Biomass-based polymers emphasize the use of biomass-derived and renewable raw materials, which are not necessarily biodegradable, and represent an important low-carbon approach to addressing the excessive dependence of polymer materials on petroleum resources. The main challenges of biomass-based polymer materials are high production costs, and environmental pollution is still not fully addressed.

2.4 Low-carbon polymers

Although current biodegradable polymers focus on end-of-life degradation, they often use non-bio-based monomers, face performance/cost challenges compared to conventional plastics, and lack consideration of monomer sourcing. Recyclable polymers struggle with energy-intensive depolymerization cycles complicated by additives and blends. Meanwhile, biomass-based polymers offer a low-carbon alternative but are limited by high costs, unresolved pollution issues, and competition for feedstock.

The ideal sustainable polymers should, first of all, meet the performance requirements while ensuring sustainability of the resources and less impact on environment during the entire life cycle. Herein, we define low-carbon polymers as polymers with low carbon content, representing a sustainable option. The key feature of low-carbon polymers is the partial substitution of carbon elements in polymers with oxygen and/or other heteroatoms (sulfur, even nitrogen). It is proposed that the O/C composition ratio in a low-carbon polymer should be close to that of cellulose (C₆H₁₀O₅), *i.e.*, 5/6; correspondingly, the weight percentage of carbon in low-carbon polymers is approximately 50 wt%. It is noted that other polymer classes, such as polyphosphoesters, polyphosphazenes, and polyorganosiloxanes, inherently possess low carbon content due to their elemental composition. Although they share the broad goal of sustainability, their distinct chemical nature and synthetic paradigms place them beyond the primary scope of this perspective, which focuses on strategically reducing carbon content within traditionally carbon-rich organic chain polymers through heteroatom substitution and alternative carbon sourcing. Therefore, low-carbon polymers will subvert the syn-

thetic methods, structure and properties, processing and applications for traditional carbon-rich polymers.

Firstly, low-carbon polymers require monomers containing oxygen (and other heteroatoms). Oxygen is highly abundant on Earth and is a key element in forming organic molecules. Its critical role in low-carbon polymers lies in enabling the formation of esters, carbonates, ethers and other functional groups through well-established organic synthesis methodologies. Sulfur, a member belonging to the same family as that of oxygen and often a by-product of fossil resource processing, is difficult to utilize. The oil refining industry produces about 80 million tons of “waste sulfur” each year, highlighting the urgent need to develop new value-added strategies for its utilization (Fig. 5). The carbon content in low-carbon polymers can be sourced either from *waste* molecules (*e.g.* CO₂) in petrochemical resources or from biomass, such as sugar-derived and lignin-derived molecules (Fig. 5). Through biorefinery processes using biomass resources, especially non-edible agricultural and forestry waste, a series of sugar-based derivatives such as 1,3-propanediol, succinic acid, furfural, fumaric acid (and CO₂) can be produced, which serve as highly promising monomers for low-carbon polymers. Traditional general-purpose polymers, in contrast, rely on carbon-based olefins, aromatic diacids, *etc.*, as monomers and are dependent on petroleum resources (Table 1). It is proposed that a general polymer contains ~50 wt% oxygen content and bio-derived carbon, thereby eliminating dependence on petroleum resources.

Secondly, a small variation in polymer composition, from carbon-rich to low-carbon, can lead to dramatic changes in regulating structure and properties. A comparison of the composition, structure and properties of low-carbon polymers and “carbon-rich” polymers is presented in Table 1. For instance, PLA, with an oxygen content of 44.4 wt% (O/C ratio of 2/3), is a typical biodegradable polymer with a high melting point but is brittle, has high water absorption and shows poor thermal stability during use. PPC is also a biodegradable ductile polymer with an oxygen content of 47.1 wt% (O/C ratio of 3/4) but struggles with low thermal stability due to its amorphous state and low glass transition temperatures (*ca.* 30 °C). Poly(1,3-dioxolane)⁵⁶ (O/C ratio of 2/3; oxygen content of 43.2 wt%) and poly(acetal-ester)⁶² (O/C ratio of up to 6/7; oxygen content up to 50.5 wt%) exhibit reduced carbon content and recyclability; however, they are just in the lab phase and have poor overall properties. These polymers often have high density, high water absorption and are difficult to be applied individually. To date, the reported polymers with low-carbon content have exhibited superior degradability, recyclability compared to traditional carbon-rich counterparts (*e.g.*, polyolefins), but suffer from compromised processing adaptability, mechanical robustness and high costs. It is still a huge challenge to develop low-carbon polymers that combine both high performance and sustainability.

What gives us hope is that polyoxymethylene (POM, O/C ratio is 1/1, with an oxygen content of 53.3%) is a commercially available low-carbon polymer, which is a high-performance

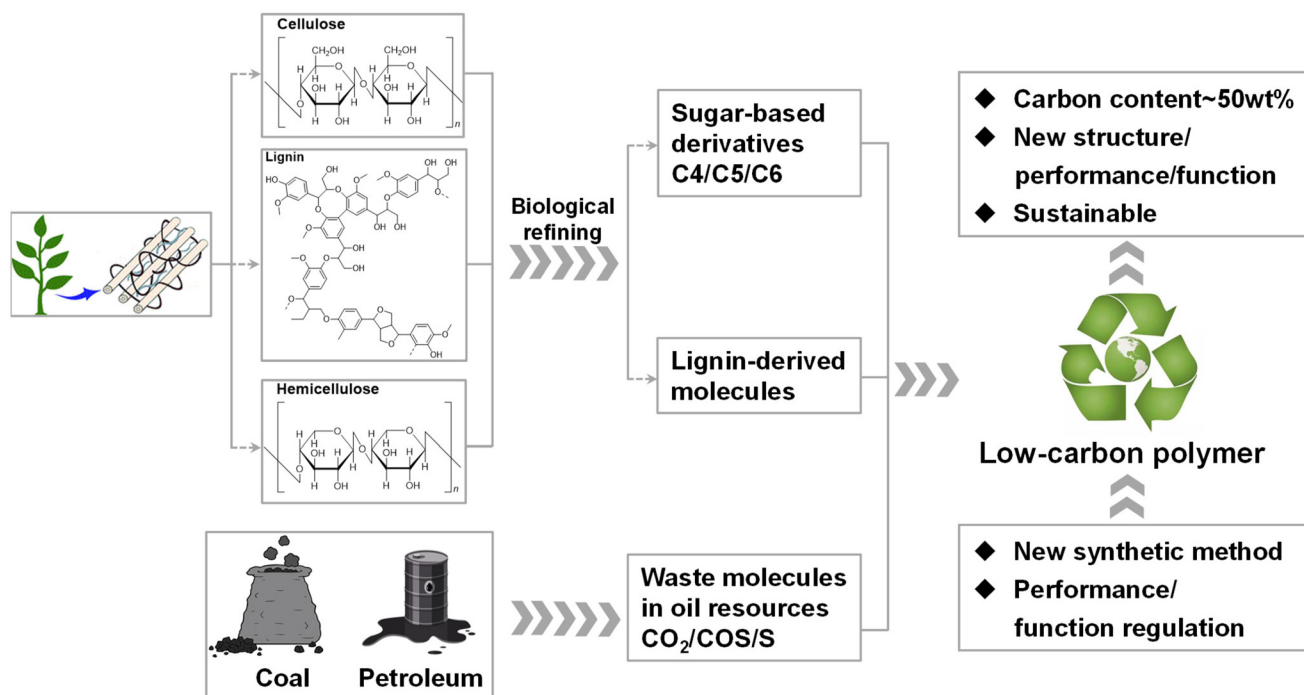


Fig. 5 Chemically created general-purpose synthetic polymers with low-carbon composition.

Table 1 Comparison of the composition, structure and properties of low-carbon polymers and "carbon-rich" polymers

Category	Low-carbon polymers	Carbon-rich polymers
Carbon content	Expected ~50 wt%	Close to 100 wt% (PET: 67 wt%)
Monomer	Oxygen (heteroatom)-rich monomers	Carbon-based olefin monomers (aromatic diacid)
Structure	Multiple functional groups Low chain regularity Unsuitable crystallinity and/or glass transition temperatures	No or few functional groups High chain regularity Suitable crystallinity and/or glass transition temperatures
Performance and application	Poor or good thermal and mechanical properties High density High water absorption Difficult to apply alone	Good or excellent thermal and mechanical properties Low density Low water absorption Apply alone or blended
Representative varieties	PLA, PHA, PPC, etc.	Polyolefins, polyacrylates, polyesters (PET), polyurethanes, etc.
	Less than one million tons global	About 400 million tons global

Note: High-performance engineered plastics such as polyoxymethylene (with an oxygen content of 53 wt%) and some common oxygen-containing polymers such as polymethyl acrylate (with an oxygen content of 37 wt%) are not included in this table due to their limited total production globally.

engineering plastic with excellent mechanical strength and dimensional stability. This suggests that there is a lot of potential for making low-carbon polymers with excellent performance by regulating their structures. However, when oxygen in aliphatic oxygen-containing polymers was replaced with sulfur, the resulting sulfur (often coexisting with oxygen)-containing polymers have exhibited improved thermal and mechanical properties, according to previous reports.^{83,84} As shown in Fig. 6, poly(γ -thiobutyrolactone) has a melting point of 100 °C, higher than that of P(γ -BL) (~50 °C).⁸⁵ Poly(thiolactone) has 130% elongation at break, outperforming its oxygen counterpart (PLA) in ductility.⁸⁶ In addition, sulfur-containing polymers exhibit low water absorption owing to the hydrophobicity of sulfur atoms, provide a different oxidative degradation mechanism and are recyclable. Crucially, the environmental impact of sulfur appears minimal: as evidenced by a century of tire production, natural sulfur cycles ultimately convert sulfur into geochemically stable sulfates or elemental sulfur, forms that are ubiquitous in nature. Another pathway is to introduce multiple hydrogen bonds to regulate the chain conformation and even the aggregate structure of the polymer (like nylon) for strengthening the performances.^{87,88}

Thirdly, low-carbon polymers require innovation in polymerization systems. The inherent complexity of alternative feedstocks (e.g., biomass derivatives or industrial waste molecules) demands catalysts/initiators with exceptional selectivity and impurity tolerance, in contrast to the standardized reactivity of petrochemical monomers under exceptionally pure conditions. In fact, it is difficult to synthesize high molecular weight (e.g., M_n more than 100 kg mol⁻¹) oxygen-rich polymers



Fig. 6 Sulfur substitution strategy.

such as PLA and PPC, as reported in the literature.^{39,89,90} In terms of polymerization methods, the oxygen-rich architecture required for low-carbon polymers fundamentally conflicts with conventional polymerization strategies developed for carbon-rich monomers, necessitating precise control over side reactions and chain stability. For example, it remains very difficult to realize a perfect stereoselective polymerization for PLA⁷⁶ and CO₂/epoxide copolymers.⁹¹ Therefore, new polymerization methods involving oxygen-rich monomers and catalysts/initiators that will enrich the theory of polymerization must be developed. Recent advances in organic catalysts and light-metal catalysts (such as sodium) are highly promising due to their potential for low toxicity, high activity, and tolerance towards heteroatoms and impurities. For example, we have developed a novel class of catalysts capable of catalyzing the rapid and controllable ROP of cyclic esters.³⁴ We integrated (thio)urea and alkyl borane (sodium alkoxide) moieties into a single molecule, creating a catalytic ROP initiator.

As described above, we propose the concept of low-carbon polymers from the perspective of altering the basic composition of polymers. Low-carbon polymers exhibit distinct characteristics while maintaining interconnected and complementary relationships with biodegradable polymers, recyclable polymers, and biomass-based polymers, as shown in

Table 2. Biodegradable polymers emphasize biodegradability, low environmental impact after their use, and end-of-life safety through eco-friendly degradation products.¹⁸ Polymers containing ester and/or carbonate linkages are often biodegradable. Indeed, these polymers often have low carbon content, such as PLA and PPC. Recyclable polymers can be selectively degraded into their original monomers (closed-loop recycling), useful compounds or other polymers under certain conditions through chemical or biological recycling methods, thereby achieving material circularity.⁹² However, it is a small cycle involving only the polymerization and depolymerization processes. In parallel, low-carbon polymers emphasize carbon efficiency within the global carbon cycle. This focus is also demonstrated by their significantly low life cycle carbon emissions – approximately 13.53% to 62.19% less than those of conventional petroleum-based plastics.⁹³ This reduction is primarily driven by differences in the production and waste treatment stages, with notable carbon reduction potential residing specifically in the raw material acquisition phase. In terms of raw material sources, both low-carbon polymers and biomass-based polymers utilize biomass resources to reduce dependence on conventional petroleum. However, the low-carbon polymers described herein further expand carbon feedstocks (*e.g.*, repurposed petroleum-derived waste molecules) and use

Table 2 Differences among various sustainable polymers

Types	Chain structure	Source	Degradation	End of life
Biodegradable polymers	Biodegradable groups	Petroleum or biomass	Biodegradable	Environmentally friendly molecules
Recyclable polymers	Chemically reversible covalent bonds	Petroleum or biomass	Chemical depolymerization or conversion	Pristine monomers, the useful compounds or other polymers
Biomass-based polymers	No special requirements	Biomass only	No attention	No attention
Low-carbon polymers	Low carbon and oxygen-rich in composition	Biomass or underutilized carbon from petroleum	Chemical degradation or biodegradation	Environmentally friendly molecules, pristine monomers, useful compounds or other polymers

oxygen to partially replace carbon, thereby integrating carbon footprint management into renewable sourcing strategies. Therefore, low-carbon polymers integrate multiple sustainability approaches and broaden the scope of carbon feedstocks while complementing biodegradation and recycling technologies. By leveraging biomass feedstocks, optimizing carbon sources, and engineering precise molecular structures, these materials deliver comprehensive environmental solutions spanning the entire lifecycle from “feedstock-production-use-recycling/degradation”.

3 Conclusions and perspectives

In summary, we proposed an idea for creating low-carbon polymers, focusing on using oxygen to partially replace carbon in polymer structures, as an option for achieving sustainability. As an ambitious substitute for current general-purpose polymers, low-carbon polymers have the potential to promote economic and social development in a green and sustainable manner. However, in synthetic polymer chemistry, low-carbon polymers have overturned the design concepts and polymerization methods used for traditional “carbon-rich” monomers (such as olefins). The design and synthesis of low-carbon polymers are more challenging.

Regarding the future development of low-carbon polymers, the following issues should be considered:

(i) Chalcogen-rich monomers. The direct use of chalcogen-rich one-carbon feedstocks such as CO, CO₂, COS and CS₂ for the synthesis of low-carbon polymers is highly desired,^{38,52} and H₂O^{53,94} and sulfur^{95,96} should be seriously considered. At the same time, the direct use of bio-derived alcohols and aldehydes for synthesizing low-carbon polymers is promising.^{54,55,59–62,97} In addition, it is necessary to explore low-cost routes to synthesize new chalcogen-containing monomers from biomass molecules or above-mentioned industrial wastes; for example, developing low-cost methods to use sugar for making polymers,^{98–100} and lignin-derived polymers is of great importance because lignin is the only resource to produce aromatic structures in nature.¹⁰¹

(ii) New catalysts/initiators and new polymerization methods. How to use these monomers to design and synthesize polymers with good properties similar to those of conventional carbon-rich polymers remains a gap that needs to be explored. Given the limited monomer repertoire available, developing effective polymerization strategies requires suitable catalysts/initiators and related polymerization methods. Organocatalysts and light metal catalysts are very promising for making low-carbon polymers because they have the advantages of easy availability, low toxicity, high activity and tolerance to chalcogen-containing monomers and impurities like water and oxygen during polymerizations.^{11,34,102–104}

(iii) Low-carbon polymers have good performance and specific functions. Currently, the types of low-carbon polymers are still limited, the relationship between their structure and performance remains unclear, and their processing and rheo-

logical properties have not been systematically studied. There is an urgent need for continuous efforts to establish systematic structure–property relationships in preparation for their large-scale application. These low-carbon polymers can be initially used like traditional general-purpose polymers; we also should make full use of their advantages related to the incorporation of chalcogen elements, which may endow these polymers with intrinsic functions such as high refractive index, good biocompatibility and degradability, photoluminescence^{105–108} and electrolyte properties.^{109,110}

(iv) CO₂-based polymers. We emphasize the utilization of CO₂ for making low-carbon polymers because CO₂ is inexpensive and abundantly available, and CO₂-based polymers are predicted to have strong potential as general-purpose polymers in the future.¹¹¹ In recent years, CO₂-based polymers have been successfully industrialized and have demonstrated polyolefin-like properties, along with excellent barrier performance and biodegradability.

Last but not the least, by sustainable polymers (including low-carbon polymers), we refer to the general-purpose polymers rather than engineered polymers or other special polymers whose global production remains limited. Sustainable polymers that are produced and applied on a large scale can demonstrate their impact on the environment and resources. However, it must be noted that challenges such as imperfect standards and certification systems, strict industrial production requirements for sustainable low-carbon polymers, and the lack of end-of-life treatment facilities still require joint efforts from the scientific community, industry and even the whole society.

Author contributions

Xinghong Zhang and Chengjian Zhang conceived, designed, and directed the project and revised the manuscript. Yanni Xia wrote the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

No primary research results, software or code have been included, and no new data were generated or analysed as part of this review.

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