# **REVIEW ARTICLE**

# **Organic polymers revolution: Applications and formation strategies, and future perspectives**

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#### ABSTRACT

The history of organic polymers is a remarkable journey from the discovery of natural materials like rubber and silk to the development of sophisticated synthetic polymers that have transformed industries and modern life. This comprehensive review article presents a detailed account of the evolution of organic polymers. It begins with the early uses of natural polymers and explores key breakthroughs, including the invention of Bakelite, nylon, and neoprene. The theoretical foundations of polymer science, laid by Hermann Staudinger, are discussed, and the post-war surge in polymer development is examined, including the introduction of polyethylene, polypropylene, and PVC. Notable advances in polymer chemistry, such as isotactic polypropylene and silicone polymers, are highlighted. The article also delves into the development of high-performance polymers like Kevlar and carbon-based materials, offering insights into their applications. Moreover, it discusses the current trends in polymer science, emphasizing sustainability and biodegradability. As the world continues to rely on polymers for numerous applications, this review provides a historical perspective and a glimpse into the future of organic polymers, where innovations are expected to shape various aspects of technology, healthcare, and environmental protection.

*Keywords:* tacticity; blending monomers; step-growth polymerization; condensation reactions; radical chain-growth polymerization

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## **1. Introduction**

Organic polymers, often referred to simply as polymers, are an incredibly diverse and indispensable class of materials that form the backbone of modern society. These compounds consist of long chains of repeated subunits, known as monomers, which are primarily composed of carbon, hydrogen, oxygen, and occasionally other elements. Organic polymers are known for their remarkable versatility, adaptability, and widespread use in various sectors, including industry, healthcare, and everyday consumer products<sup>[1]</sup>. The significance of organic polymers lies in their capacity to exhibit a wide range of physical, mechanical, and chemical properties, depending on the choice of monomers, their arrangement, and the synthesis process. This diversity enables them to serve an array of functions, from providing structural support in plastics and fibers to enabling electrical conductivity in semiconducting polymers. Organic polymers are the foundation of countless everyday items, from clothing and packaging materials to medical devices and electronic components. Their impact is felt across numerous fields,

including materials science, chemistry, and engineering. Furthermore, the development of innovative polymers with enhanced properties, such as improved biodegradability and conductivity, remains a focal point of ongoing research, promising even greater advancements in the future<sup>[2]</sup>.

The history of organic polymers is a tale of scientific discovery, innovation, and societal transformation. It begins with natural polymers that have been used for millennia, such as rubber and silk, and progresses to the development of synthetic polymers that have revolutionized various industries. This narrative unfolds in several key phases, highlighting fundamental moments and innovations. The story starts with natural polymers. Rubber, derived from the latex of the rubber tree *Hevea brasiliensis*, was used by indigenous peoples in Central and South America for centuries. In the early 19th century, Charles Goodyear accidentally discovered vulcanization, a process that cross-linked rubber molecules, making it more durable and versatile. In the 19th century, chemists began to explore the chemical nature of natural polymers. In 1833, French chemist Anselme Payen isolated cellulose, the primary component of plant cell walls. His work laid the foundation for the development of celluloid, one of the first synthetic polymers, by American inventor John Wesley Hyatt in the 1860s. Celluloid was used in photographic film, combs, and early motion picture film<sup>[3]</sup>.

The next significant leap in polymer history came with the isolation of protein-based polymers. In 1841, German chemist Justus von Liebig discovered that the silk cocoon's fibers consisted of a protein he named fibroin. This finding advanced the understanding of natural polymers. Protein-based polymers play a crucial role in the textile and biomedical industries. The late 19th century and early 20th century witnessed pivotal advancements in polymer science. In 1909, Belgian-American chemist Leo Baekeland invented Bakelite, the first entirely synthetic polymer. Bakelite, known as the "material of a thousand uses", was a heat-resistant and insulating material used in electrical equipment, telephones, and various consumer products<sup>[4,5]</sup>. In the 1920s, German chemist Hermann Staudinger proposed the concept of macromolecules. He suggested that long chains of repeating units, now known as polymers, formed the basis of these materials. This breakthrough laid the theoretical groundwork for modern polymer science. Polymer development surged in the 1930s. The American chemists Wallace Carothers and Julian Hill invented nylon, a versatile synthetic polymer with applications in textiles, toothbrush bristles, and more. Meanwhile, American chemical company DuPont introduced neoprene, a synthetic rubber with remarkable resistance to oil and temperature variations<sup>[6]</sup>. Both materials played vital roles in World War II. The 1950s brought forth the polymer revolution, led by the discovery of polyethylene, polypropylene, and polyvinyl chloride (PVC). Polyethylene, developed by British scientists Eric Fawcett and Reginald Gibson in 1933, became a cornerstone in packaging materials, from plastic bags to containers. Polypropylene, discovered by Italian chemist Giulio Natta and German chemist Karl Ziegler, revolutionized the plastics industry, while PVC, created in 1872 by German chemist Eugen Baumann but commercially produced in the 1930s, found widespread use in construction, piping, and medical applications. In 1954, American chemist Robert H. Natta and Italian chemist Giulio Natta developed isotactic polypropylene, a variation of polypropylene with higher crystallinity, stability, and strength<sup>[7]</sup>. This discovery significantly improved the material's properties and its applications. The 20th century also saw the emergence of silicone polymers, invented by American chemist Eugene Rochow in the 1930s. Silicones, with their remarkable heat resistance, flexibility, and non-stick properties, found applications in lubricants, sealants, and medical devices. The late 20th century and early 21st century have seen the development of high-performance polymers like Kevlar, a strong and lightweight material developed by American chemist Stephanie Kwolek in 1965. Kevlar is used in bulletproof vests, tires, and aerospace components. In the 1980s, the discovery of fullerenes, including the iconic Buckminsterfullerene (C60), marked a new class of carbon-based polymers, spurring interest in nanomaterials. Today, the polymer industry continues to evolve, with a focus on sustainability, biodegradable materials, and advanced applications in electronics, healthcare, and environmental protection.

The field of organic polymers has come a long way since the accidental discovery of vulcanized rubber and the invention of Bakelite, and it continues to shape our world in remarkable ways<sup>[8]</sup>.

# 2. Structural diversity and properties

Polymers, the macromolecules that constitute the building blocks of materials in our everyday lives, exhibit remarkable diversity in their structural arrangements. This structural diversity, which encompasses aspects like tacticity, copolymerization, and cross-linking, plays a fundamental role in shaping the properties of polymers, making them suitable for a wide array of applications. In this comprehensive discussion, we will explore these structural aspects and their profound effects on the properties and applications of polymers.

## 2.1. Tacticity: The influence of arrangement

Tacticity, the regularity or arrangement of monomer units along the polymer chain, stands as a fundamental determinant of a polymer's physical and chemical properties. Its impact is particularly evident in the crystallinity, mechanical strength, and thermal behavior of polymers. The significance of tacticity is most evident in its influence on crystallinity<sup>[9]</sup>. Crystalline regions in polymers are characterized by a highly ordered and closely packed arrangement of polymer chains. This ordered structure results in increased stiffness, strength, and resistance to deformation. Thus, the degree of crystallinity is a key factor in a polymer's mechanical properties. Isotactic polymers exemplify the impact of tacticity on crystallinity. In isotactic polymers, the monomer units are consistently arranged on the same side of the polymer backbone. This regular arrangement leads to a high degree of crystallinity, resulting in increased tensile strength, rigidity, and hardness. Prominent examples include isotactic polypropylene (iPP) and isotactic polyethylene (iPE). These polymers find applications in a wide range of industries, from packaging materials to engineering plastics, where mechanical strength and rigidity are paramount<sup>[10]</sup>.

Conversely, syndiotactic polymers display an alternating arrangement of monomer units on opposite sides of the polymer chain. This arrangement contributes to increased crystallinity, improved thermal stability, and well-defined melting points. Syndiotactic polystyrene (sPS) is a well-known example, with applications in areas where its distinct melting points and high chemical resistance are advantageous. Atactic polymers, in contrast, exhibit a random arrangement of monomer units along the polymer chain. The lack of regularity in atactic polymers results in reduced crystallinity and increased flexibility. This flexibility is desirable in applications where the polymer needs to be malleable and conformable. Atactic polypropylene (aPP) and atactic polystyrene (aPS) are examples of atactic polymers that find use in a variety of products, from medical devices to consumer goods, where flexibility is valued<sup>[11]</sup>. Tacticity also significantly affects the melting and glass transition temperatures of polymers. Isotactic and syndiotactic polymers, with their high degrees of crystallinity, generally have higher melting temperatures and exhibit distinct melting points. In contrast, atactic polymers, with their reduced crystallinity, often have lower melting and glass transition temperatures, which make them more suitable for specific applications. In essence, tacticity provides polymer scientists and engineers with a versatile tool to tailor the properties of polymers, enabling them to meet specific requirements across a multitude of industries. Understanding and controlling tacticity stand as essential aspects of polymer design and synthesis, contributing to the vast array of materials we encounter daily<sup>[12]</sup>.

#### 2.2. Copolymerization: The versatility of blending monomers

Copolymers, the product of blending two or more different monomers during polymerization, offer an extraordinary degree of versatility in tailoring polymer properties to meet specific needs. The ability to combine monomers with diverse properties and characteristics allows for the creation of materials that possess a wide range of physical and chemical attributes<sup>[13]</sup>. One notable example of the versatility of copolymers is styrene-butadiene rubber (SBR). This copolymer is synthesized by blending the monomers styrene and

butadiene<sup>[14]</sup>. The combination of these monomers results in a material that exhibits an excellent balance of properties, including elasticity, resilience, and resistance to abrasion. SBR is commonly used in tire production, footwear, conveyor belts, and various other applications that require durability and flexibility. The ability to engineer copolymers with precise properties makes them invaluable in industries that demand materials with specific attributes, such as the automotive and industrial sectors. Another example of the versatility of copolymers is acrylonitrile-butadiene-styrene (ABS), a copolymer comprising acrylonitrile, butadiene, and styrene monomers. ABS is known for its high impact strength, good chemical resistance, and ease of processing. It finds applications in a wide range of products, including consumer goods, automotive parts, and 3D printing. The blend of these three monomers results in a material with properties that make it adaptable to various requirements. ABS demonstrates the capacity of copolymers to offer tailored solutions for different industries and applications, enhancing the efficiency of material design. Copolymers enable the fine-tuning of properties by selectively incorporating monomers with desirable characteristics. This approach offers an extensive range of materials that can meet specific requirements, whether they involve flexibility, rigidity, or resistance to environmental factors<sup>[15,16]</sup>.

# **3.** Formation strategies

## 3.1. Step-growth polymerization

Step-growth polymerization is a fundamental process in the creation of organic polymers, involving the linking of monomers through condensation reactions. This method, in contrast to chain-growth polymerization, results in the growth of the polymer molecule by the elimination of small molecules, such as water or methanol. In this comprehensive discussion, we will inquire into the intricate process of step-growth polymerization, with a focus on condensation reactions and the formation of two key classes of organic polymers: polyesters and polyamides<sup>[17]</sup>. Step-growth polymerization, often referred to as polycondensation or polyaddition, is a polymerization mechanism characterized by the formation of covalent bonds between monomers, resulting in the gradual growth of the polymer chain. This growth occurs through the stepwise reaction of monomer units, accompanied by the release of a small molecule as a byproduct. In the case of condensation reactions, this byproduct is typically water (H<sub>2</sub>O), while in the case of addition reactions, it can be any small molecule like methanol (CH<sub>3</sub>OH) or ammonia (NH<sub>3</sub>). The formation of high molecular weight polymers from relatively low molecular weight monomers is a hallmark of step-growth polymerization<sup>[16,17]</sup>.

## 3.1.1. Condensation reactions in step-growth polymerization

1). Esterification: Ester formation, a common condensation reaction, occurs when a carboxylic acid reacts with an alcohol. The resulting covalent bond is called an ester linkage, and water is eliminated as a byproduct. Esterification plays a crucial role in the formation of polyesters, a class of organic polymers known for their versatility and wide range of applications<sup>[18]</sup>. Polyesters are prominent in the textile industry, particularly in the production of fabrics like polyester and PET bottles used for packaging. Polyesters are a group of organic polymers formed through esterification, a condensation reaction. The monomers involved typically consist of a dicarboxylic acid and a diol (a compound containing two hydroxyl groups). These two monomers react to produce the polyester polymer, with the elimination of a water molecule for each repeating unit. The formation of polyesters plays a critical role in various industries, particularly in textiles, packaging, and plastics. Poly(ethylene terephthalate) (PET): Perhaps the most well-known polyester, PET is widely used in the production of bottles, textiles, and films. The reaction involves the dicarboxylic acid terephthalic acid and the diol ethylene glycol, resulting in the creation of PET. This polymer is celebrated for its exceptional mechanical properties, clarity, and resistance to moisture, making it ideal for applications such as beverage containers and synthetic fibers<sup>[19]</sup>.

2). Amide Formation: In amide formation, a carboxylic acid reacts with an amine compound to produce an amide linkage, releasing water as a byproduct. This reaction is central to the formation of polyamides, a class of polymers celebrated for their exceptional strength and durability<sup>[20]</sup>. Polyamides are extensively used in the production of various materials, including nylon and Kevlar, both of which have a wide array of applications, ranging from textiles and clothing to high-strength, lightweight materials in the aerospace and military sectors. Polyamides, often referred to as nylons, are organic polymers formed through amide linkages. The fundamental monomers in polyamide formation consist of a dicarboxylic acid and a diamine, with water as the byproduct. Polyamides are celebrated for their mechanical strength, toughness, and thermal stability. These properties have led to their extensive use in various industries, including textiles, engineering, and even aerospace. Nylon-6,6: Nylon-6,6 is a widely recognized polyamide formed by the condensation reaction between adipic acid and hexamethylene diamine. The resulting polymer exhibits remarkable mechanical strength, making it a favored choice for applications like ropes, fabrics, and engineering materials. Nylon-6: This polyamide is formed through the polymerization of caprolactam and is known for its exceptional elasticity and durability. It is used in various products, from clothing and carpets to automotive parts and industrial components<sup>[21]</sup>.

## 3.1.2. Advantages and challenges of step-growth polymerization

Step-growth polymerization offers several advantages. It can be used to create a wide range of polymers with diverse properties, including high thermal stability, mechanical strength, and chemical resistance. However, it is important to acknowledge the challenges associated with this process. One significant challenge is the potential for side reactions, which can result in undesired branching or cross-linking within the polymer structure. These side reactions can affect the polymer's properties and molecular weight distribution. Step-growth polymerization through condensation reactions is a fundamental process in the formation of organic polymers. This mechanism, exemplified by the creation of polyesters and polyamides, has significantly impacted various industries. Polyesters and polyamides, with their unique properties and applications, showcase the versatility of step-growth polymerization. While the process offers the advantage of creating polymers with diverse properties, challenges such as side reactions must be carefully considered and managed to achieve the desired results. Overall, step-growth polymerization continues to be a cornerstone in the development of innovative materials across numerous fields, from textiles and packaging to aerospace and engineering<sup>[21,22]</sup>.

## 3.2. Chain-growth polymerization

Chain-growth polymerization is a pivotal mechanism for creating organic polymers characterized by the growth of a polymer chain through the successive addition of monomers. This process is known for its versatility and is primarily governed by three major mechanisms: radical, anionic, and cationic polymerization. In this discussion, we will explore each of these mechanisms, emphasizing their roles in the formation of common polymers, including polyethylene and polypropylene.

## 3.2.1. Radical chain-growth polymerization

Radical polymerization is one of the most prevalent methods for synthesizing polymers. The process begins with the initiation step, where an initiator molecule, often a peroxide or azo compound, undergoes homolytic cleavage, yielding two radicals (**Figure 1**)<sup>[23]</sup>. These radicals are highly reactive and initiate the polymerization of monomers. In the propagation step, monomers, typically vinyl monomers like ethylene or propylene, react with the growing radical chain to form a covalent bond, extending the polymer chain. Importantly, this step continues iteratively, resulting in a polymer chain of significant length. One of the most common polymers produced through radical chain-growth polymerization is polyethylene. In the case of polyethylene, the monomer ethylene ( $CH_2 = CH_2$ ) undergoes polymerization to create a polymer with a high

degree of branching, high crystallinity, and excellent mechanical properties. Polyethylene finds widespread use in various applications, including packaging materials, plastic bags, and containers<sup>[23]</sup>.



Figure 1. Metal-catalyzed living radical polymerization<sup>[23]</sup>.

#### 3.2.2. Anionic chain-growth polymerization

Anionic polymerization is another chain-growth mechanism, where the process begins with the formation of anions through the use of a strong base or initiators, such as organolithium compounds or alkaline metals. In the propagation step, these anions react with monomers, such as styrene or butadiene, to form a covalent bond, extending the polymer chain. Anionic polymerization is highly controlled and can result in polymers with precise structures and narrow molecular weight distributions (**Figure 2**)<sup>[24]</sup>.



Figure 2. Preparation of the Br-TNDIT-Br/Zn radical-anion monomer and its catalyst-transfer polymerization to Ph/H P(TNDT)<sup>[24]</sup>.

#### 3.2.3. Cationic chain-growth polymerization

Cationic polymerization is the third major mechanism for chain-growth polymerization (Figure 3)<sup>[25]</sup>. This process initiates through the use of strong Lewis acids or other initiators that generate cations. The cations interact with monomers, such as isobutylene or vinyl ethers, leading to polymer chain growth. Polypropylene (PP): One of the most prominent polymers produced through cationic chain-growth polymerization is polypropylene. In the case of polypropylene, propylene ( $CH_s = CHCH_3$ ) is polymerized using a cationic initiator. The resulting polymer exhibits outstanding mechanical properties, resistance to high temperatures, and excellent chemical stability. Polypropylene is commonly used in applications such as packaging, automotive components, and textiles. Each of these chain-growth polymerization mechanisms has its advantages and challenges. Radical polymerization is versatile but can result in relatively broad molecular weight distributions. Anionic polymerization provides excellent control over polymer structures but may require highly reactive and air-sensitive initiators. Cationic polymerization offers the synthesis of unique polymers but can be sensitive to impurities and side reactions. Chain-growth polymerization is a versatile and powerful tool for creating a wide range of polymers. The choice of mechanism depends on the desired properties and applications of the polymer. Polyethylene, polypropylene, and various other polymers exemplify the flexibility of chain-growth polymerization in addressing diverse industrial and technological needs.



Figure 3. Chain-growth cationic polymerization of 2-halogenated thiophenes promoted by Bronsted acids<sup>[25]</sup>.

#### 3.3. Ring-opening polymerization

Ring-opening polymerization (ROP) is a versatile and widely employed mechanism for the creation of organic polymers. This process involves the cyclic opening of monomers, such as cyclic esters (lactones) or cyclic carbonates, to form linear polymer chains. In this discussion, we will delve into the mechanisms and synthesis routes of two significant classes of polymers produced through ring-opening polymerization: polycarbonates and polyesters<sup>[25]</sup>. Polycarbonates: Polycarbonates are a class of polymers renowned for their exceptional transparency, impact resistance, and thermal stability<sup>[26]</sup>. They are used in a variety of applications, from optical lenses and medical devices to high-performance engineering materials. The synthesis of polycarbonates primarily occurs through the ring-opening polymerization of cyclic carbonates. A prominent example is the reaction between propylene oxide and carbon dioxide: The cyclic carbonate, such as propylene oxide, opens under the influence of an initiator, often an alcohol, to form a covalent bond with the monomer, leading to the elongation of the polymer chain. This reaction results in the formation of a carbonate linkage within the polymer structure, with the elimination of small molecules, such as methanol or ethanol<sup>[26]</sup>. Poly(ethylene carbonate) (PEC): In the case of poly(ethylene carbonate), the cyclic carbonate ethylene carbonate undergoes ring-opening polymerization, yielding a polymer with high flexibility and dielectric properties. PEC has applications in the production of battery separators and flexible electronics. Polycarbonates like poly(ethylene carbonate) and poly(propylene carbonate) are notable examples. These polymers are known for their biocompatibility and have applications in drug delivery systems and biodegradable materials. Polyesters are a diverse class of polymers with applications spanning from textiles and packaging to biodegradable plastics. They are commonly synthesized through the ring-opening

polymerization of cyclic esters, often referred to as lactones. A well-known example of polyesters is poly( $\varepsilon$ -caprolactone) (PCL)<sup>[27,28]</sup>. The synthesis of polyesters involves the ring-opening polymerization of cyclic esters. The process typically utilizes an initiator, such as alcohol, which opens the cyclic ester ring and forms a covalent linkage, extending the polymer chain. As a byproduct of this reaction, a small molecule, such as methanol, is eliminated. Poly( $\varepsilon$ -caprolactone) (PCL): Poly( $\varepsilon$ -caprolactone) is a common polyester formed by the ring-opening polymerization of  $\varepsilon$ -caprolactone. PCL is celebrated for its biodegradability and flexibility, making it suitable for applications like biodegradable packaging, drug delivery systems, and tissue engineering scaffolds. Polyesters like PCL have gained prominence in the medical field. They are used for the controlled release of drugs, as their biodegradability ensures gradual drug delivery while minimizing the need for repeated interventions<sup>[28]</sup>.

#### Advantages and challenges of ROP

Ring-opening polymerization offers precise control over polymer structures and molecular weight distribution. The process is versatile, allowing the synthesis of polymers with tailored properties, such as biodegradability and thermal stability. However, it may require careful consideration of initiators, reaction conditions, and potential side reactions to achieve the desired results. Ring-opening polymerization is a valuable mechanism for the synthesis of polymers with diverse properties and applications. Polycarbonates and polyesters, produced through ROP, illustrate the flexibility and versatility of this process, addressing the evolving needs of various industries. Whether in the production of biodegradable materials, medical devices, or high-performance engineering polymers, ROP continues to play a vital role in polymer science and technology<sup>[29]</sup>.

# 4. Applications of polymers: From packaging to fashion

Polymers, with their diverse range of properties and versatility, have found applications in a multitude of industries and products. This section delves into some of the key areas where polymers play a crucial role, from food packaging to biomedical devices and the world of fashion.

#### 4.1. Packaging materials: Preserving freshness and convenience

The use of polymers in packaging materials is ubiquitous, and two standout examples are polyethylene and polypropylene. These polymers are extensively employed in food packaging and storage, primarily due to their exceptional barrier properties, cost-effectiveness, and ease of processing. Polyethylene, a widely used polymer, is valued for its durability and ability to create a barrier that protects food from moisture and external contaminants<sup>[30]</sup>. High-density polyethylene (HDPE) is commonly used for rigid packaging, such as bottles for milk and detergent. Low-density polyethylene (LDPE) is more flexible and is often used in plastic bags and wraps, providing a convenient and cost-effective solution for food storage. The versatility of polyethylene extends from its use in single-use plastic bags to durable containers for long-term storage, highlighting its adaptability to various packaging needs. Polypropylene (PP) is another polymer of choice for food packaging. It offers a balance between strength and flexibility, making it suitable for a wide range of applications, including microwave-safe containers, food storage containers, and bottle caps. PP's excellent heat resistance and sealing properties have led to its use in microwaveable food containers, ensuring that convenience does not compromise safety. Moreover, the recyclability of both polyethylene and polypropylene contributes to sustainable packaging solutions<sup>[30]</sup>.

## 4.2. Biodegradable polymers: A sustainable approach

The growing importance of biodegradable polymers is a testament to the increasing concern for environmental impact. These polymers offer an eco-friendly alternative to traditional plastics and are designed to decompose naturally, reducing the burden of plastic waste in the environment. Polylactic acid (PLA) is one

of the most well-known biodegradable polymers. PLA is derived from renewable resources such as corn starch and sugarcane. It is used in a variety of applications, including disposable cutlery, food packaging, and medical implants. PLA's biodegradability, combined with its versatility and processability, makes it an attractive choice for reducing plastic pollution while maintaining performance. Polyhydroxyalkanoates (PHAs) are another class of biodegradable polymers produced by microorganisms. These polymers exhibit similar properties to traditional plastics, offering a wide range of applications. PHAs are compostable and can be used in packaging, agriculture, and medical devices. Their potential to replace conventional plastics in various products underscores their role in mitigating the environmental impact of non-biodegradable materials<sup>[31]</sup>.

#### 4.3. Polymer electronics: The age of organic electronics

Conjugated polymers have revolutionized the field of organic electronics, opening doors to flexible and lightweight electronic devices, such as organic photovoltaics, organic light-emitting diodes (OLEDs), and organic transistors. The unique properties of conjugated polymers, including their electrical conductivity, optical properties, and mechanical flexibility, make them indispensable in the realm of electronic technologies. Organic photovoltaics (OPVs), often referred to as solar cells, utilize conjugated polymers to convert sunlight into electrical energy. These lightweight, flexible solar cells are used in various applications, including portable chargers, solar backpacks, and building-integrated photovoltaics<sup>[32,33]</sup>. The advantages of OPVs include their lightweight nature, ease of integration into various surfaces, and the potential for low-cost production. OLEDs have transformed display technologies, leading to the development of flexible and energy-efficient screens. Conjugated polymers in OLEDs emit light when an electric current is applied, resulting in vibrant and energy-efficient displays. This technology is used in smartphones, TVs, and lighting applications, promising thinner, more energy-efficient devices. Organic transistors, another product of conjugated polymers, enable flexible and low-power electronic circuits. These transistors are used in applications such as wearable electronics, sensors, and medical devices. The mechanical flexibility of polymers allows for the creation of conformable, wearable technology that can monitor health, detect environmental changes, and improve our daily lives.

#### 4.4. Biomedical polymers: Enhancing healthcare

Polymers play a pivotal role in the field of medicine and healthcare, where they are used in drug delivery systems, tissue engineering, and medical devices. Their biocompatibility, tunable properties, and versatile forms make them invaluable in improving patient care. Drug delivery systems utilize polymers to transport and release drugs in a controlled manner. Biodegradable polymers like poly(lactic-co-glycolic acid) (PLGA) are commonly used for drug encapsulation, allowing for sustained release of medications over time<sup>[34]</sup>. This technology is employed in a wide range of therapeutic applications, from cancer treatments to hormonal contraception. Tissue engineering harnesses the regenerative properties of polymers to create artificial organs, tissues, and implants. Polymers such as polyethylene glycol (PEG) and polyurethane provide scaffolds that support cell growth and tissue regeneration. These engineered tissues hold promise in the fields of regenerative medicine and transplantation, offering new hope to patients in need of organ replacements. Medical devices benefit from the diverse properties of polymers, including their biocompatibility, transparency, and ease of sterilization. Polymeric materials are used in items such as catheters, surgical instruments, and prosthetics. Silicone rubber, for example, is commonly employed in medical applications due to its flexibility, durability, and hypoallergenic properties<sup>[35]</sup>.

#### 4.5. Polymers in textiles: The fabric of fashion

Synthetic and natural polymers are the backbone of the textile industry, providing the raw materials for an array of fabrics and fashion products. The diverse range of polymers used in textiles offers a wide spectrum of properties, from moisture-wicking and breathability to durability and stretchability. Polyester, a synthetic polymer, is a staple in the textile industry. Its attributes, including resistance to wrinkles, quick drying, and colorfastness, have made it a popular choice for clothing, home furnishings, and athletic wear. The versatility of polyester fabric, coupled with its cost-effectiveness, has allowed it to permeate the fashion world. Nylon, another synthetic polymer, is renowned for its strength and durability. It is used in the production of hosiery, sportswear, and outdoor gear, where resistance to wear and tear is essential. The smooth and flexible nature of nylon fabric ensures comfort and performance in active wear. Natural polymers like cotton and silk have been cherished in the textile industry for centuries. Cotton's breathability and softness make it ideal for casual clothing and undergarments. Silk, known for its luxurious feel and sheen, is used in high-end fashion products such as evening gowns, lingerie, and accessories. The enduring appeal of these natural polymers is a testament to their timeless qualities in the world of fashion. Polymers are omnipresent in our daily lives, with applications spanning from the packaging that safeguards our food to the fabrics that adorn our bodies, such as DNA<sup>[36]</sup>. These versatile materials have transformed industries, delivering solutions that enhance our quality of life while mitigating environmental impacts. The future promises further innovation as polymer science continues to evolve, offering new possibilities and addressing emerging challenges<sup>[37]</sup>.

# 5. Energy storage application of all-organic polymer dielectrics

With the advancement of modern power systems and electronic devices, there is a growing emphasis on developing high-capacity and high-energy storage capacitors<sup>[37,38]</sup>. Dielectric capacitors, known for their quick charging and discharging capabilities, low weight, and density, are extensively employed in pulsed power applications within the electrical and electronic engineering domains. When compared to inorganic ceramic capacitors, polymer-based capacitors offer several benefits, including high breakdown strength, minimal dielectric loss, ease of manufacturing, and cost-effectiveness. Furthermore, they hold significant promise for applications in various fields, such as hybrid electric vehicles, microelectronic systems, wind-power generation, power transmission, microwave communications, as well as underground oil and gas exploration (as depicted in **Figure 4**)<sup>[39–44]</sup>.



Figure 4. Application fields of polymer-based capacitors.

The quest for high-energy storage density dielectrics has become a central focus of current research. Biaxially oriented polypropylene (BOPP) currently reigns as the most prevalent dielectric material, but its limited energy storage density (1–2 J/cm<sup>3</sup>) poses significant developmental challenges. Furthermore, temperature fluctuations adversely affect its energy storage density and efficiency<sup>[45]</sup>. In the early stages of this research, the primary emphasis was on enhancing the dielectric capacitors' dielectric constant (r) and breakdown strength (Eb). Yet, within polymers, achieving both high breakdown strength and robust polarization characteristics proves to be a challenging feat. Consequently, the main hurdles in the pursuit of new high-performance polymer dielectrics lie in addressing the strong interplay between breakdown strength and dielectric constant from a scientific viewpoint and considering service life from an engineering application perspective. With various research studies exploring capacitor energy storage strategies, three main methods

have emerged for enhancing energy storage density: first, the construction of filled composite dielectrics; second, the design of layered composite dielectrics; and third, the synthesis of new polymers<sup>[46,47]</sup>.

Filled composite dielectrics involve the incorporation of diverse fillers, such as ceramics, metal oxides, and conductive materials, into the polymer matrix. This filling process bolsters interface polarization and heightens the dielectric constant of the composites. However, it also tends to diminish breakdown strength<sup>[48]</sup>. Notably, the size of the fillers plays a significant role, with nano-sized fillers being more common than microsized ones. Achieving a higher dielectric constant in the composites demands a substantial amount of inorganic filler, which introduces a challenge: high inorganic metal oxides can compromise the polymer's flexibility and processing properties<sup>[49]</sup>. Layered composite dielectrics encompass polymers arranged in a sandwich or multilayer structure. By leveraging distinct properties within each layer, high dielectric constant layers are stacked with high breakdown strength layers. While the multilayer approach can mitigate carrier migration and enhance insulation, it doesn't significantly bolster polarization performance<sup>[50]</sup>. Drawing from the information presented above, this article offers a comprehensive review and summary of all-organic composite materials. Polymer-based dielectrics are categorized as linear or nonlinear, each with unique advantages and potential, in terms of three structural approaches: filling, blending, and multilayering. Finally, the article delves into the future development prospects and challenges associated with all-organic composite materials.

## 6. Linear polymer dielectrics

Linear polymers fall into two categories: polar and nonpolar. Among polar polymers are poly(methyl methacrylate) (PMMA), polyetherimide (PEI), polythiourea (PTU), and polysulfone (PSF). On the other hand, nonpolar polymers include polypropylene (PP) and polystyrene (PS). Several polymers, such as polycarbonate (PC), poly(phenylene sulfide) (PPS), poly(ethylene 2,6-naphthalate) (PEN), and poly(ethylene terephthalate) (PET), have found successful application as dielectrics in commercial capacitors<sup>[51–57]</sup>.

## 6.1. Linear polymer filling and blending

Traditional methods involve the incorporation of inorganic fillers like ceramic particles into the polymer matrix, resulting in a two-phase composite material consisting of inorganic particles and polymers. This approach aims to enhance the energy storage properties of polymer-based dielectrics<sup>[57]</sup>. However, it often leads to low breakdown strength and significant dielectric loss<sup>[58,59]</sup>. The lack of compatibility between the inorganic filler and the polymer matrix, along with the bonding characteristics of the organic-inorganic interface, significantly influences the composites' service life. Moreover, achieving a higher dielectric constant necessitates a greater filler content, which, in turn, reduces the polymer's flexibility and compromises its processing performance<sup>[60,61]</sup>.

An alternative approach involves introducing suitable organic polymers and organic polymer semiconductors as organic fillers into linear polymer matrices. This method can raise the dielectric constant and fine-tune the material's energy storage characteristics. This section explores the filling and blending techniques for the aforementioned linear polymers.

## 6.1.1. Polar polymer filling and blending

Polyimide (PI) is an aromatic ring polymer containing imide groups and finds widespread application in industries requiring insulation, flame resistance, sound absorption, and coatings<sup>[62]</sup>. It boasts a dielectric constant of approximately 3–3.5, a dielectric loss of around  $10^{-3}$ , and a dielectric strength of up to 200 MV/m. For instance, Kapton PI exhibits an energy storage (Ue) of 0.44 J/cm<sup>3</sup> and an efficiency ( $\eta$ ) of 76% at 220 MV/m. Additionally, PI offers high-temperature energy storage performance due to its elevated glass transition temperature<sup>[63–65]</sup>.

#### 6.1.2. Filling and blending with nonpolar polymers

Polypropylene (PP) is a hydrocarbon-based polymer that serves as the foundation for commercial dielectrics, notably in the form of biaxially oriented polypropylene film (BOPP). PP is classified as a nonpolar polymer. At room temperature, it exhibits an impressive breakdown strength of 700 MV/m, with a maximum operating temperature of 105 °C. Its dielectric properties, including a dielectric constant of approximately 2.25 and a loss of about 0.01% at 1 kHz, are noteworthy<sup>[66,67]</sup>. However, it's important to note that temperature variations influence discharge energy density and energy storage efficiency. For instance, raising the temperature from room temperature to 100 °C results in a decrease in energy storage (Ue) from 2.43 J/cm<sup>3</sup> to 2 J/cm<sup>3</sup> and a drop in efficiency (η) from 99.3% to 80.5%<sup>[68]</sup>.

Generally, there are two strategies to enhance the energy storage density of polypropylene-based polymers. One approach involves introducing polar groups into the molecular structure of PP. The other method entails incorporating conductive fillers or nano-fillers into the PP-based nanocomposite during the filling process. Elevating the dielectric constant of PP leads to increased material energy density, which is of paramount importance for engineering applications. Yuan et al.<sup>[69]</sup> successfully augmented the  $\epsilon r$  of PP by modifying it and synthesizing a copolymer enriched with flexible hydroxyls (–OH 4.2 mol% content) and polar groups (–NH<sub>2</sub>). Their results demonstrated that this synthesis approach doubled the dielectric constant of modified PP compared to BOPP, maintained a linear and reversible polarization curve, and ultimately achieved a final energy storage density exceeding 7 J/cm<sup>3</sup> at 600 MV/m.

Furthermore, Deng and Chen, among others, grafted maleic anhydride onto polypropylene (MA-g-PP) to create hybrid dielectrics in combination with pure PP films. FTIR spectra of pure PP and PP/MA-g-PP confirmed the presence of polar groups in the composite film, illustrating the success of the grafting reaction (**Figure 5**). As the volume percentage of MA-g-PP increased, the dielectric constant rose, albeit at the expense of breakdown strength. The addition of the maleic anhydride group to the composite material enhanced dipole group polarization, resulting in relatively low dielectric loss. A composition of 10 vol% MA-g-PP/PP achieved a peak energy density of 1.96 J/cm<sup>3</sup> with a maximum efficiency of 96%<sup>[70]</sup>.



**Figure 5.** Types of porous organic polymer frameworks and their coupling chemistries. Porous polymers from left to right: covalent organic frameworks (COFs), hypercrosslinked polymers (HCPs), covalent triazine frameworks (CTFs), porous aromatic frameworks (PAFs), and conjugated microporous polymers (CMPs). Note that these classifications can overlap somewhat; for example, some COFs are also conjugated, and not all COFs reported are particularly crystalline.

Li et al.<sup>[37]</sup> established a binary PP composite by grafting PP with maleic anhydride. This composite displayed a breakdown strength of 308.2 MV/m in the DC circuit, a dielectric constant of 2.56, a loss of 0.4%, and an energy storage density of 1.076 J/cm<sup>3</sup>. High electric fields triggered the accumulation of space charges and impurity ions near the electrode, leading to ion transitions and polarization, resulting in increased dielectric loss. Optimizing the intermolecular interactions<sup>[38,39]</sup> of PP plays a pivotal role in boosting the energy storage

density of these composites, given the close association between the activation energy of ion jumps and the activation energy of molecular chain motion<sup>[71]</sup>.

# 7. Microporous polymers

Zeolites represent a class of inorganic porous frameworks that have become ubiquitous in society, boasting a substantial global market with a wide range of applications, from detergent production to the removal of radioactive particles from nuclear waste. Another class of inorganic-containing porous materials is hybrid metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs). MOFs are extended crystalline structures constructed from metal ions or clusters that form directional bonds with organic ligands, creating voids within the framework and thus imparting porosity. While zeolites and MOFs both incorporate metals, there exists a diverse category of purely organic porous materials. In porous MOFs, metal ions coordinated to typically aromatic organic linkers provide rigidity and directionality to the structure. Similarly, porous organic materials tend to be rigid and exhibit somewhat directional bonding to maintain the integrity of the porous framework, which is achieved through careful selection of the molecular building blocks. It's important to note that not all porous materials need to manifest as extended networks. For example, porous organic cages (POCs) represent discrete porous molecules, where the molecular cage is initially synthesized and then assembled in the solid state in a separate step. POCs are a unique class of solutionprocessable molecular materials, characterized by their intrinsic cavities interconnected to create porosity, which can be tailored by modifying the solid-state packing of the cage molecules. Polymers of intrinsic microporosity (PIMs) are a rare example of one-dimensional polymers featuring porosity, achieved through inefficient packing of the twisted polymer backbone. The past two decades have witnessed the introduction of a wide array of porous organic polymer networks, including crystalline covalent organic frameworks (COFs), various amorphous networks like hypercrosslinked polymers (HCPs), covalent triazine frameworks (CTFs), porous aromatic frameworks (PAFs), and conjugated microporous polymers (CMPs) (Figure 5). Each subclass of these materials typically favors specific network formation reactions. While these materials differ structurally, they share common characteristics such as high porosity, lightweight elements, and robust, covalently bonded 2- or 3-D structures. CMPs were initially groundbreaking among porous materials due to their extended  $\pi$ -conjugation throughout the porous 3D network. On the other hand, PAFs, closely related to CMPs and synthesized using similar coupling chemistries, lack extended  $\pi$ -conjugation because they are linked by tetrahedral tetraphenylmethane nodes. Another term used to describe PAFs is porous polymer networks (PPNs), as they essentially represent the same materials. Element-organic frameworks (EOFs), silanecontaining analogues of PAFs, are formed using organo-metallic coupling routes. CTFs could also be considered a CMP subclass since they are microporous and exhibit extended  $\pi$ -conjugation, although they were developed separately with different formation chemistry. In 2007, the synthesis of microporous poly(aryleneethynylene) networks was reported, marking the inception of what would become known as CMPs. Since their discovery, CMP chemistry has seen significant contributions from scientists worldwide, resulting in substantial growth in publications over the past decade. Just over a decade after their discovery, it is now appropriate to reassess the significance of CMPs. In this review, we present an up-to-date overview of CMPs, commencing with a historical look at their origins and a selection of key advances. We provide a comprehensive survey of the diverse synthesis routes available for CMPs, a feature that positions them as a pivotal platform for the development of new organic porous materials. We delve into the functional design of CMPs, offering access to a range of potential applications, with a particular focus on the utilization of optoelectronic properties for photoredox catalysis, light emission, energy storage, biological applications, and photocatalytic H2 generation. Finally, we provide an outlook on the future of CMP research.

# 8. Chemical reactions involving polymerization

Various synthetic methods have been employed to produce organic polymers, and their selection can significantly impact the properties of the resulting materials. The initial CMPs were prepared using Sonogashira-Hagihara cross-couplings, facilitating the introduction of lightweight alkyne struts. Another commonly used approach is the Suzuki-Miyaura coupling, which allows the linkage of aryl groups with advantages such as broad functional group compatibility and mild reaction conditions, although sensitivity to oxygen can lead to homocoupling. The Yamamoto coupling, based on coupling aryl halides with at least three reactive sites, is employed for its simplicity and high surface area generation, but its sensitivity to water may limit scale-up<sup>[40]</sup>. The Heck coupling forms C-C bonds by coupling an unsaturated halide with a primary alkene using a Pd catalyst and base, while cyclotrimerization reactions produce aromatic 6-membered rings from three alkyne monomers, and phenazine ring fusion yields ladder-type polymers. Other methods encompass Schiffbase condensations, heterocycle linkages, alkyne metathesis, oxidative coupling, Buchwald-Hartwig amination, electropolymerization, and hypercrosslinking of linear conjugated polymers, with each offering unique benefits and considerations. The choice of synthesis parameters, including coupling chemistry, monomer choice, and solvent selection, significantly influences CMP properties, allowing tunability and the creation of diverse CMP materials. Additionally, unconventional synthesis methods such as microwaveassisted synthesis, mechanochemistry, and composite synthesis on surfaces, offer efficient, solvent-free, and substrate-enhanced alternatives for CMP production, expanding the scope of possible materials and applications in the field. Like MOFs, the versatility of CMPs in terms of customization is nearly boundless. Researchers have a wide array of options to fine-tune the pore structure, morphology, and optoelectronic properties by altering monomer geometry or introducing various heteroatoms or metals. Additionally, postsynthetic modifications can be made to CMPs. Various reactive coupling groups have been harnessed for CMP synthesis, including halogens, boronic acids, alkynes, alkenes, nitriles, amines, aldehydes, and activated phenol-substituted aromatic monomers, with more potential options anticipated to emerge in the future. The most prevalent reaction methods used for CMP synthesis are summarized in Figure 6.

Figure 6. Reaction schemes for the synthesis of CMPs. (a) Sonogashira-Hagihara, (b) Suzuki-Miyaura, (c) Yamamoto, (d) Heck, (e) cyclotrimerization, (f) phenazine ring fusion, (g) Schiff-base, (h) heterocycle linkages, (i) alkyne metathesis, (j) oxidative coupling, (k) BuchwaldHartwig, (l) electropolymerization, and (m) hypercrosslinking linear polymers.

# 9. Nonlinear polymer dielectrics

In practical applications, ferroelectric polymers are the most commonly used nonlinear polymers. Despite their high dielectric constant, their limited breakdown strength and energy storage efficiency render them unsuitable for use in capacitor dielectrics<sup>[72]</sup>. This limitation primarily arises from the interaction of large domains and closely linked dipoles within ferroelectric polymers. This interaction alters the dipole orientation and causes polarization hysteresis, leading to substantial dielectric loss and a reduction in both discharge energy density and charge-discharge efficiency.

## 9.1. Nonlinear polymer combination

Poly(vinylidene fluoride) (PVDF) is a frequently employed nonlinear polymer, used in both binary and ternary forms. For example, poly(vinylidenefluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)) is a ferroelectric material known for its high dielectric constant (50), a high  $\beta$  phase, and a low breakdown strength (Eb). However, its low breakdown strength disqualifies it from electrical insulation applications<sup>[73–75]</sup>.

Methods for blending polymers have been proposed to balance or optimize their properties. Regulating the interaction between the molecular segments at the two-phase interface enhances the mechanical and dielectric properties while also improving breakdown characteristics. The direct mixing of ferroelectric polymers and their derivatives allows for precise control of internal composition, crystallization behavior, and interface-related issues<sup>[76,77]</sup>.

One of the simplest approaches involves blending PVDF with the binary copolymer poly(vinylidenefluoride-trifluoroethylene) (P(VDF-TrFE)). Meng et al. found that blending PVDF with a small quantity of P(VDF-TrFE) increased the  $\beta$ -phase content and preferred orientation of PVDF. Consequently, the dielectric constant of the composite material after blending increased by 80% compared to PVDF and 30% compared to P(VDF-TrFE). Additionally, the residual polarization strength (Pr) was enhanced. By suppressing the Curie transition, this approach expanded the operating temperature range, providing improved high-temperature stability for dielectrics<sup>[78,79]</sup>. As shown in **Figure 7a**, Mao et al.<sup>[80]</sup> created blend composite membranes by combining poly(vinylidene fluoride) with poly(vinylidenefluoride-trifluoroethylene-chlorofluoroethylene) (PVDF/P(VDF-TrFE-CFE)) and adjusted the PVDF ratio to enhance the dielectric constant ( $\epsilon$ r) and breakdown strength (Eb) of the membranes. Incorporating terpolymer into PVDF improved compatibility between the two polymers, increasing recombination and interfacial polarization effects in dielectrics. Ultimately, at 480 MV/m, the discharge energy density reached 13.63 J/cm<sup>3</sup> (**Figure 7b**)<sup>[80]</sup>.



Figure 7. (a) Schematic diagram of PTC/PVDF preparation process and a photograph of the PVDF blended with 20 wt% PTC; (b) Contrast curve of discharge energy density, electric field intensity and dielectric constant.

#### 9.2. Nonlinear polymer incorporation

In the initial stages of research and development, the prevailing method involved filling nonlinear polymers. These fillers could take the form of zero-dimensional particles (0D), with oxides and perovskite structure compounds being the most commonly used. One-dimensional fibers (1D) and common fibrous

perovskite structures were filled using techniques like electrospinning, hydrothermal processes, and template methods. Two-dimensional flake fillers (2D) consisted of nanoflakes, such as BN and MoS<sub>2</sub>, and were prepared through methods like peeling, chemical vapor deposition (CVD), and molten salt techniques.

However, the size and characteristics of these fillers, along with microstructural factors such as particle, fiber, and flake dispersion, void defects, and cavity defects, all have a bearing on the breakdown performance and mechanical properties of the composite material. Consequently, these factors place constraints on the overall manufacturing process. Consequently, industrialization and large-scale production have been predominantly limited to nonlinear polymers filled with 0D fillers. Presently, researchers are directing their attention toward organic conductive filler/polymer composite dielectrics. Organic conductive fillers offer two notable advantages: a wider range for adjusting conductivity and a more robust interaction with the matrix<sup>[81]</sup>.

#### 9.3. Multilayered structures in nonlinear polymers

The fundamental idea behind incorporating spherical (0D), fibrous (1D), and plate-like (2D) fillers into the polymer matrix to create high-k materials is to increase the interfacial area. However, an increase in the dielectric constant typically leads to a reduction in breakdown strength, thus compromising the dielectric flexibility characteristics inherent in polymer-based dielectrics<sup>[82,83]</sup>. To address this challenge, nonlinear polymers, which were previously discussed, have been blended and filled to produce all-organic composites, aiming to strike a harmonious balance between insulation and flexibility. Recent research has unveiled a solution in the form of multilayer structures that can effectively address the interplay between breakdown strength and dielectric properties in composite materials. These layered structures enhance dielectric energy loss within an electric field through the benefits of layer-by-layer assembly and cooperative layering effects. Moreover, they progressively reduce the migration rate of impurity ions across different layers, allowing for greater combinations of various polymers.

As illustrated in **Figure 8a**, Jiang et al.<sup>[84]</sup> proposed an electrospinning technique for crafting multilayered P(VDF-HFP)/P(VDF-TrFE-CFE) (Co/Ter polymer) nanocomposites with distinct topological structures and phase compositions, comprising 4, 8, and 16 layers. Phase-field simulations demonstrated a significant reduction in local electric fields between the Co/Ter polymer layers, thereby lowering the leakage current density and conduction loss (**Figure 8b**). Remarkably, this approach achieved a high energy density of 20 J/cm<sup>3</sup> at 600 MV/m (**Figure 8c**).



**Figure 8.** (a) Schematic diagram of multilayer structure, pure copolymer and pure terpolymer; (b) Comparison chart of discharge energy density and efficiency; (c) Schematic diagram of breakdown path evolution with time by phase-field simulation. Reprinted with permission from<sup>[84]</sup>. Copyright (2018), Elsevier.

# **10. Linear/nonlinear polymer dielectrics**

Ferroelectric polymers are commonly used nonlinear polymers, but their low breakdown strength and energy storage efficiency make them unsuitable for capacitor dielectrics. To develop high-performance capacitor dielectrics, a mixture of linear and nonlinear polymers can be used. Linear/nonlinear polymer blending can significantly improve the dielectric properties of composite materials, and the combination of two different types of polymers can also enhance energy storage performances. Studies have shown that combining PMMA, PVDF, and their derivatives can increase the dielectric constant, convert PVDF from a nonpolar  $\alpha$  phase to a polarity  $\beta$  phase, and increase energy density. The space charge behavior of the two polymers also reveals that the blend system's amorphous region is composed of amorphous PVDF and miscible PMMA/PVDF, increasing charge transport capacity. The crystallinity of the composite material decreases as the PMMA content increases due to its dilution effect and good compatibility with PVDF.

The blending of PMMA and other PVDF copolymers has shown promising results in improving energy storage characteristics and reducing dielectric loss. The Flory-Huggins model was used to investigate Gibbs energy, miscibility, and phase composition of binary mixtures. The  $\gamma$  phase formed when PMMA reacts with P(VDF-HFP) was found to be stable and improved by hydrogen bonds, van der Waals forces, and molecular chains on the interface. The blending of PMMA and P(VDF-TrFE-CFE) improved breakdown strength and energy storage density. Research has focused on controlling filler content, achieving a high dielectric constant at a low filler content, minimizing pores and defects, and optimizing the structure and properties of composites. All-organic composite structures offer lower preparation costs, softer machinery, easier processing, and a relatively simple process. PVDF was added to improve the dielectric constant via low-temperature chemical imidization of PI, resulting in interfacial polarization<sup>[85]</sup>.

Linear/nonlinear polymer filling can enhance energy storage characteristics of composite dielectrics by adding molecular semiconductors. Zhang et al.<sup>[86]</sup> created all-organic composites by adding organic polymer semiconductor [6,6]-phenyl C61 butyrate acid methyl ester (PCBM) as a filler to a PMMA/PVDF blend matrix. This method minimized structural defects and improved the composite dielectric's polarization and breakdown strength. Electrospinning technology combines combinatorial-electrospinning and hot-pressing to fabricate all-organic dielectrics based on P(VDF-TrFE-CFE) with a ferroconcrete-like structure. The combination of electrospinning and hot-pressing technology optimizes the energy density and breakdown strength of composite materials, allowing for the investigation of the relationship between structure and properties.

Linear/nonlinear polymer blending and filling presents two challenges: understanding the mechanism underlying interface polarization effect and addressing interfacial corrosion during the preparation process. Researchers have evaluated the linear/nonlinear multilayer composite structure, which has advantages in increasing micro-interfaces, enhancing interface polarization, and increasing breakdown strength. The double-layer structure is the simplest structure in the multilayer structure, and studies have shown that the electrodes' relative position directly affects the breakdown strength of the composite dielectrics. The electrode-dielectric interface's effect on breakdown strength has also been investigated. The sandwich structure, a highly efficient, low dissipation, long service life, and extremely stable multilayer structure, can be designed when linear and nonlinear polymers are combined, allowing for the design of all structured sandwich dielectrics. The composite dielectric maintains good dielectric/energy storage characteristics due to the synergy between interfaces and the control of interlayer thickness in the multilayer structure.

Linear and nonlinear polymer dielectrics are fundamental components in various electrical and electronic applications, playing a pivotal role in modern technology. These dielectric materials are integral for their ability to store and manage electrical energy efficiently, making them crucial in devices like capacitors and as insulators in the electrical and electronics industries.

#### **10.1. Linear polymer dielectrics**

Linear polymer dielectrics are characterized by their predictable and linear response to applied electric fields. They are commonly used in many electrical and electronic engineering applications due to their stable and well-understood properties. Linear polymers possess several desirable attributes, such as rapid charging and discharging capabilities, low density, lightweight structure, and affordability. These properties make them particularly suitable for applications in pulsed power devices. Notable examples of linear polymers include polyethylene, polypropylene, and polystyrene. These materials exhibit high breakdown strength, low dielectric loss, ease of processing and production, and cost-effectiveness. The advantages of linear polymers have led to their extensive application in various domains, including hybrid electric vehicles, microelectronic systems, wind-power generation, power transmission, microwave communications, and underground oil and gas exploration<sup>[87]</sup>.

## 10.2. Nonlinear polymer dielectrics

Nonlinear polymer dielectrics, on the other hand, are characterized by their complex and non-linear response to electric fields. Although they offer a high dielectric constant, nonlinear polymers often come with a trade-off. They tend to have lower breakdown strength and energy storage efficiency, making them unsuitable for some capacitor applications. This limitation is primarily attributed to the interaction between large domains and highly coupled dipoles within these materials. Such interactions can lead to changes in the direction of dipoles, resulting in polarization hysteresis, high dielectric loss, and decreased discharge energy density and charge-discharge efficiency. Poly(vinylidene fluoride) (PVDF) is a commonly used nonlinear polymer, with variants such as poly(vinylidenefluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE) being known for their high dielectric constants. However, their low breakdown strength has limited their use in electrical insulation<sup>[88]</sup>.

#### 10.3. Blending and multilayer structures

Researchers have addressed the limitations of both linear and nonlinear polymers by blending and creating composite materials. This approach aims to achieve a balance between dielectric flexibility and insulation. For instance, blending PVDF with other polymers like poly(vinylidenefluoride-trifluoroethylene) has demonstrated the ability to enhance dielectric properties and high-temperature stability. Moreover, recent advancements in the field have explored the use of multilayered structures in dielectric properties in composite materials. The layered structure improves dielectric energy loss through layer-by-layer stacking and the cooperation of the layering effect. It also reduces the migration rate of impurity ions between layers, enabling the combination of various polymers for superior performance. In a recent study, multilayered P(VDF-HFP)/P(VDF-TrFE-CFE) nanocomposites demonstrated promising results. These materials showed a significant reduction in leakage current density and conduction loss, resulting in a high energy density of 600 MV/m<sup>[87,88]</sup>.

## **11. Challenges and future directions**

Despite the progress in the field of linear and nonlinear polymer dielectrics, several challenges remain. Balancing the dielectric constant and breakdown strength while maintaining other desirable properties is an ongoing challenge. Achieving high energy density without compromising other performance factors is a critical area of research.

The future of polymer dielectrics lies in addressing these challenges and exploring new possibilities. There is a growing demand for advanced dielectric materials in emerging industries such as renewable energy, electric vehicles, and high-frequency communication systems. Researchers are increasingly focused on enhancing the properties of polymer dielectrics to meet the evolving needs of these industries. Linear and nonlinear polymer dielectrics are integral components in the world of electrical and electronic engineering. They find applications in a wide range of technologies, from power generation and transmission to modern communication systems. By blending different types of polymers and exploring innovative structures, researchers are continually advancing the capabilities of polymer dielectrics, paving the way for future breakthroughs in the field.

# 12. Emerging trends and future prospects in polymer science

Polymer science, a field that is continually evolving, has witnessed numerous breakthroughs and innovative trends that promise to shape the future of materials and technologies. Recent advancements in polymer science encompass a spectrum of disciplines, including stimuli-responsive polymers, smart materials, and sustainable polymer production. These emerging trends not only expand the boundaries of polymer science but also hold great promise for addressing current and future challenges in diverse fields.

# 13. Stimuli-responsive polymers: A new frontier

Stimuli-responsive polymers, also known as smart polymers or intelligent materials, have become a focal point in polymer science due to their adaptability in response to environmental cues. These polymers can change their properties, such as shape, size, or solubility, in reaction to various external stimuli, including temperature, pH, light, and electric fields. One notable subcategory of stimuli-responsive polymers is shapememory polymers (SMPs). SMPs have the remarkable ability to "remember" a specific shape and, when triggered by an external stimulus, return to that shape from a deformed state. This property has found applications in medical devices, aerospace, and engineering. For instance, in the medical field, SMPs have been used in minimally invasive surgical instruments that change shape upon heating, facilitating complex procedures with smaller incisions. Another class of stimuli-responsive polymers is hydrogels that respond to changes in pH. These pH-sensitive hydrogels are particularly valuable in drug delivery systems, as they can release drugs when the pH changes within the body. This precision in drug release reduces side effects and enhances the therapeutic effect. Furthermore, pH-sensitive hydrogels are employed in the development of selfhealing materials, where they can autonomously repair damage when triggered by pH changes, contributing to the durability of materials in various applications. Stimuli-responsive polymers are also paving the way for innovative applications in fields such as biotechnology and environmental science. The ability to design polymers that respond to specific biomolecules or pollutants opens doors to advanced diagnostics and environmental remediation methods. The continuous exploration of these intelligent materials promises solutions to complex challenges in the areas of healthcare, energy, and environmental sustainability<sup>[89]</sup>.

## 13.1. Smart materials: Beyond polymers

Smart materials encompass a broader spectrum of materials that exhibit responsive behaviors to external stimuli, not limited to polymers. Recent developments in smart materials have led to novel applications and solutions in various domains. In the realm of structural engineering and architecture, the integration of shape memory alloys (SMAs) alongside polymers has resulted in smart materials that can self-monitor and repair structural damage. SMAs, such as nitinol, can change shape when subjected to temperature changes, making them invaluable in constructing self-repairing buildings and bridges that adapt to environmental conditions. In the field of electronics, conductive polymers are playing a pivotal role. Conductive polymers like poly(3,4-ethylenedioxythiophene) (PEDOT) are being used in flexible and stretchable electronic devices, paving the way for wearable technology, bendable displays, and soft robotics. These materials offer the advantage of flexibility, making them an essential component of future electronics. Moreover, advancements in nanomaterials, including carbon nanotubes and graphene, have expanded the possibilities for smart materials.

These nanomaterials can be incorporated into polymers to enhance their electrical conductivity, mechanical strength, and other properties. This integration has potential applications in sensors, nanoelectronics, and advanced composite materials<sup>[90]</sup>.

#### 13.2. Sustainable polymer production: A greener future

Sustainability is a driving force in modern polymer science. The traditional reliance on petrochemicalbased polymers has led to environmental concerns, including plastic pollution and resource depletion. As a result, sustainable polymer production has become a focus of research and innovation. One approach to sustainable polymer production is the development of bioplastics. These polymers are derived from renewable sources, such as plant starch, algae, or agricultural waste. One notable example is polyhydroxyalkanoates (PHAs), which are biodegradable and produced by microorganisms. PHAs are considered a more environmentally friendly alternative to conventional plastics. In addition to bioplastics, recycling and upcycling of plastics have gained prominence. Researchers are exploring ways to convert waste plastics into valuable materials through processes like depolymerization and chemical recycling. This not only reduces the environmental impact of plastics but also offers economic incentives for the recycling industry. Furthermore, the development of bio-based monomers and green chemistry methods is contributing to sustainable polymer production. Bio-based monomers are derived from biomass and can be used to synthesize a variety of polymers, including polyesters and polyamides. Green chemistry principles aim to minimize the use of hazardous substances and energy in polymer synthesis, reducing the environmental footprint of the manufacturing process.

An exciting avenue in sustainable polymer production is the use of carbon capture and utilization (CCU) to convert carbon dioxide into polymers. Researchers are exploring ways to capture carbon emissions and convert them into valuable polymeric materials, offering a dual benefit of mitigating climate change and reducing the environmental impact of polymer production.

# 14. Challenges and future prospects

While these emerging trends in polymer science hold great promise, they also present challenges that require innovative solutions. The design of stimuli-responsive polymers necessitates a deep understanding of their behavior under various stimuli, which calls for advanced characterization techniques and computational modeling. Smart materials, including nanocomposites, must address issues related to stability, reliability, and scalability to reach their full potential in electronic devices and structural applications.

Sustainable polymer production faces the challenge of balancing cost-effectiveness with environmental benefits. The development of economically viable bioplastics and the establishment of efficient recycling infrastructures are critical for the widespread adoption of sustainable polymers. Furthermore, the implementation of carbon capture and utilization technologies requires significant investment and regulatory support to become a viable solution on a global scale. In conclusion, the emerging trends in polymer science are revolutionizing materials and technologies in unprecedented ways. Stimuli-responsive polymers and smart materials are reshaping industries such as healthcare, electronics, and construction, while sustainable polymer production offers a path to reduce the environmental impact of plastics. The challenges that accompany these trends underscore the need for interdisciplinary collaboration and continuous innovation. The future of polymer science promises sustainable, intelligent, and environmentally responsible materials that will contribute to a more technologically advanced and ecologically conscious society.

# **15. Conclusion**

This comprehensive review of the history, evolution, and future prospects of organic polymers underscores the transformative impact of these materials on our world. The journey began with the utilization of natural polymers such as rubber and silk, setting the stage for a revolution in materials science and engineering. The development of synthetic polymers, from Bakelite and nylon to polyethylene and polypropylene, reshaped industries and modern life. The theoretical foundations established by Hermann Staudinger paved the way for a deeper understanding of polymer science. The post-war era witnessed an explosive growth in polymer development with the advent of versatile materials like PVC, neoprene, and silicone polymers. The emergence of high-performance polymers, exemplified by Kevlar and carbon-based materials, revolutionized industries ranging from textiles to aerospace. These remarkable advancements have expanded the boundaries of what is possible in fields as diverse as electronics, medicine, and environmental protection. Looking ahead, the future of organic polymers is characterized by innovation, sustainability, and environmental responsibility. As the world grapples with the challenges of pollution and climate change, polymers are at the forefront of green initiatives, with biodegradable materials and recycling methods offering promising solutions. The remarkable adaptability and versatility of polymers continue to inspire researchers and engineers to develop novel materials and applications. In an age where organic polymers are irreplaceable in our daily lives, from packaging and textiles to advanced medical devices and renewable energy solutions, understanding their rich history and future potential is of paramount importance. This review article provides a valuable resource for researchers, students, and anyone interested in the fascinating journey of organic polymers, and it highlights the continued role they will play in shaping the technological landscape and addressing global challenges. Organic polymers have come a long way, and the journey is far from over.

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# **Conflict of interest**

The author declares no conflict of interest.

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