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Cationic Polymers and Their Applications

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1.1 Introduction

Cationic polymers have emerged as a versatile and potent class of antimicrobial agents, particularly in response to the escalating global threat of antimicrobial-resistant bacteria [1]. These macromolecules, characterized by their positively charged functional groups in their main chains and/or side chains, target the negatively charged bacterial cell membranes, causing disruption of cellular integrity and subsequent cell death [2]. Unlike traditional antibiotics that act by targeting specific biochemical pathways, cationic polymers exert their antimicrobial effects through direct physical interactions with bacterial cell membranes. This unique nonspecific mode of action significantly reduces the likelihood of resistance development, positioning cationic polymers as a promising alternative in developing the next-generation of antimicrobial materials [3].

The diversity of cationic polymers in their polymeric structure and composition, encompassing linear, branched, hyper-branched, dendrimer-like, and hybrid systems, has facilitated their adaptability for a wide range of applications [3]. These cationic materials have also demonstrated their remarkable efficacy in preventing and controlling microbial contamination, crossing different fields such as medical device coatings [4], wound dressings [5], environmental water treatment [6], and food packaging [7]. Moreover, customizable chemical structures and functional groups in cationic materials enable precise optimization of their antimicrobial activity, biocompatibility, and environmental sustainability [8, 9], making them invaluable in addressing current challenges in healthcare, industry, and environmental fields [10].

This chapter provides a comprehensive overview of cationic polymers as antimicrobial materials by utilizing insights from some representative research in this field. It begins by defining and classifying cationic polymers, highlighting their structural diversity and functional mechanisms (see Figure 1.1). The subsequent sections categorize the applications of the most studied cationic polymers in various fields according to the referenced previous studies. Each section delves into the specific contributions of cationic polymers

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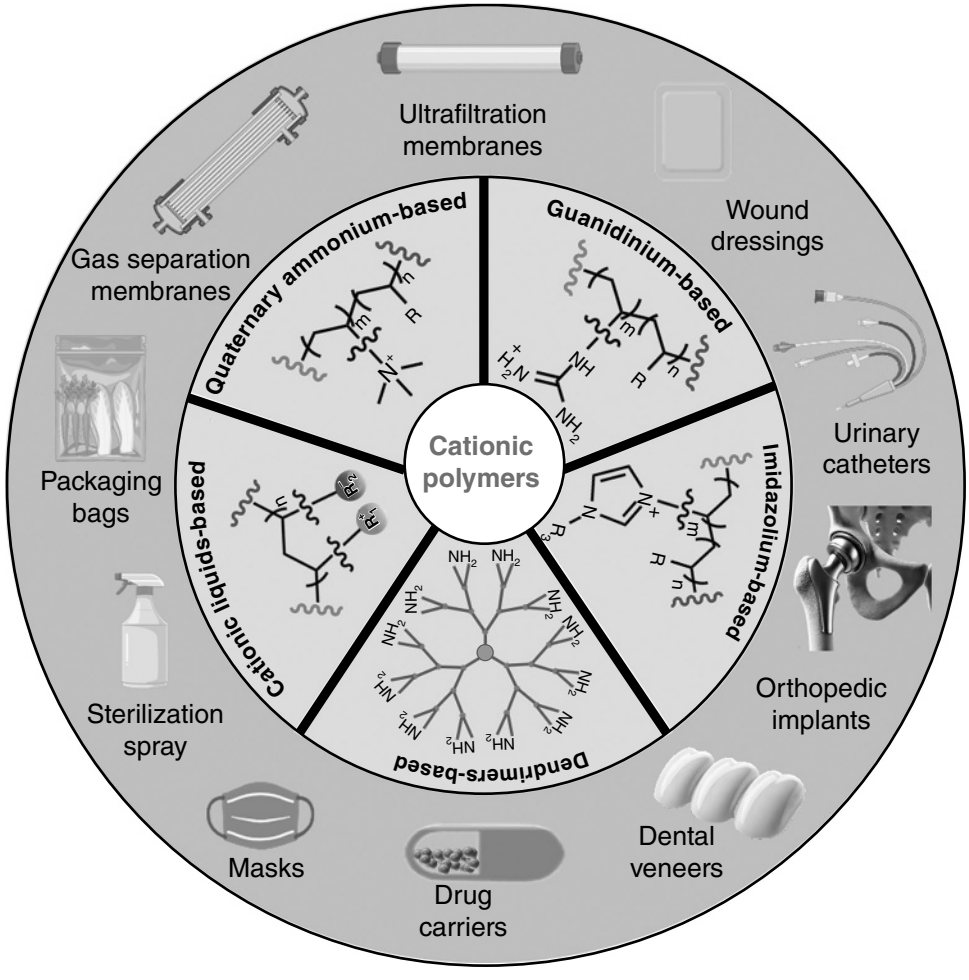

Figure 1.1 Overview of the categorization of cationic polymers and current applications in modern medicine, industry, and agriculture. Of note, R and R_3 can be adjusted according to the application scenario of the cationic polymers, which can be hydrophobic alkyl, hydrophilic polyethylene glycol, or other functional groups. In general, R_1 can be the quaternary ammonium salts, guanidine, imidazole, and other cationic groups. While R_2 can be halides, inorganic fluorides, perfluorinated sulfonamides, or other ionic groups. Source: Alexander/Adobe Stock Photos

from individual studies, concluding with a summary of the advantages, limitations, and future directions for each type of polymer. The chapter concludes with a broad perspective on the challenges and opportunities in this field, emphasizing the potential of cationic polymers to reshape global antimicrobial strategies.

1.2 Classification and Features of Cationic Polymers

Cationic polymers are of great significance for the development of novel antimicrobial agents, both to combat the growing trend of antimicrobial-resistant microorganisms, and to find materials useful for the prevention or treatment of bacterial infections with more

specific characteristics in different scenarios. In this section, due to the diversity of cationic polymers, an overview of the most common types of cationic polymers with antibacterial activity is presented, and some representative and recent examples from individual groups are also discussed to further clarify their action mechanisms and practical applications.

1.2.1 Quaternary Ammonium-based Polymers

Quaternary ammonium-based polymers, as applied materials in the field of antimicrobial polymers, are among the most extensively studied in the research community due to their broad-spectrum antimicrobial activity. These type of polymers are permanently positively charged independent of pH value due to their cationic quaternary ammonium moieties and thus can strongly interact with the negatively charged bacterial membranes [11]. This interaction is able to cause irreversible damage to the membrane structure of bacterial cells and subsequent cell death [12]. To our best knowledge, hitherto bacterial resistance to these polymers has not been reported and is generally considered highly unlikely to develop [13]. Hence, quaternary ammonium-based polymers have been utilized across a range of applications, including medical devices, water treatment, food packaging, and textiles.

1.2.1.1 Chemical Structure and Mechanism of Action

Quaternary ammonium-based polymers are relatively simple to prepare, either through the alkylation of polymers containing amine groups or through the polymerization of monomers with ammonium [14]. Although these polymers may differ in terms of polymerization degree or their monomer structure, some studies have focused on researching and summarizing the relationship between their chemical structure and antibacterial performance. First, the strongly positive charges allow cationic polymers themselves to bind onto the negatively charged bacterial cell membrane through electrostatic interaction, during which the density of the positive charge plays a critical role in determining the strength and efficiency of this binding (see Figure 1.2) [15]. Then, as another important parameter, the hydrophobic alkyl chains that are supported by ammonium nitrogen insert into the phospholipid bilayer *via* hydrophobic and electrostatic interaction. That disrupts the ordered arrangement of phospholipids and increases membrane instability and fluidity, leading to pore formation or even complete membrane disintegration, subsequent leakage of cellular components, and eventually bacterial cell death (see also Figure 1.2) [16]. Guided by this mechanism, various cationic polymers have been developed for efficiently preventing or controlling planktonic bacteria- and biofilm-related infections in different fields [17, 18].

1.2.1.2 Applications of Quaternary Ammonium-based Polymers

1.2.1.2.1 Medical Devices and Healthcare

Quaternary ammonium-based polymers have been widely used in medical device coatings to prevent biofilm formation and device-associated infections. Implantable devices, such as catheters and orthopedic implants, are highly susceptible to microbial adhesion, colonization, and subsequent biofilm formation after being implanted in the human body, leading to serious, life-threatening bacterial infections and complications. Quaternary ammonium-based polymers can be coated onto the surface of these implantable devices

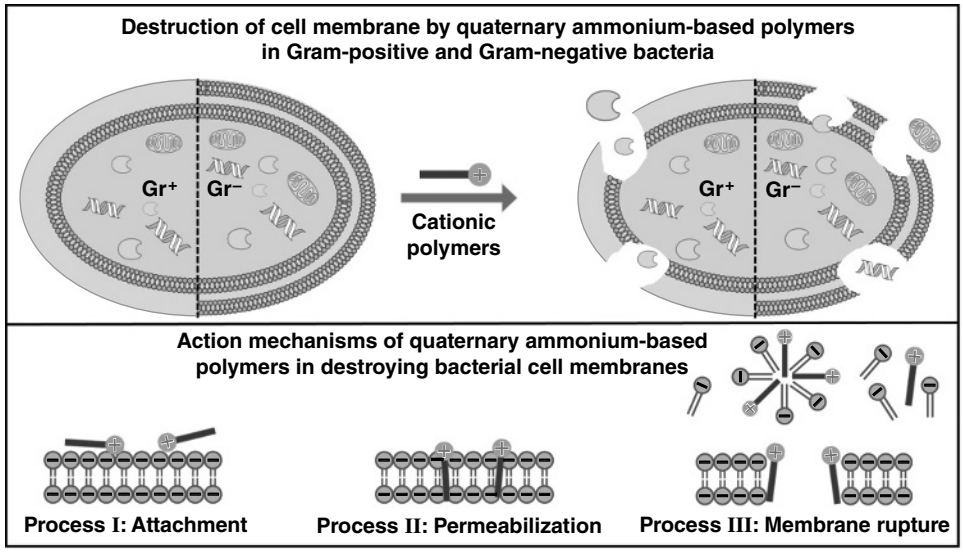

Figure 1.2 Destruction of the cell membrane by quaternary ammonium-based polymers in Gram-positive (Gr+) and Gram-negative (Gr−) bacteria. In detail, quaternary ammonium-based polymers disrupt bacterial cell membranes in a three-step process. First, the cationic polymers are electrostatically attracted to the negatively charged bacterial membrane. Then, the hydrophobic segments of the polymers insert and penetrate the lipid bilayer. Finally, these hydrophobic chains destabilize the bilayer through combined electrostatic and hydrophobic interactions, compromising the integrity of the bacterial membrane, cellular contents leakage, and ultimately bacterial cell death.

to provide durable antimicrobial activity. For example, the benzyl quaternary ammonium salt containing polycarbonates was coated onto the pristine silicone substrate of the urinary catheter, yielding 5 log-units and 3 log-units killing planktonic Gram-positive *Staphylococcus aureus* (*S. aureus*) and Gram-negative *Escherichia coli* (*E. coli*), respectively. Moreover, the antibacterial and antifouling activities of this coating remained unchanged after being incubated with *S. aureus* suspension over 14 days [19]. In addition to this, advanced hydrogels incorporating quaternary ammonium groups were also developed as the antibacterial coating of orthopedic implants, which not only led to a higher than 1 log-unit reduction of two Gram-positive bacterial strains *in vitro* but also almost fully eradicated the infection from the femoral fracture of intramedullary nail fixation in rats within 42 days [20].

1.2.1.2.2 Water Treatment

In the field of environmental applications, quaternary ammonium-functionalized membranes are highly effective in removing microbial contaminants from drinking water and industrial effluents. Studies have shown epoxy propyl dimethyl dodecyl ammonium chloride-grafted cellulose acetate (CA) membrane (QCA-X) presented an improved filtration capacity and antifouling performance compared with CA membranes in the process of water treatment. Meanwhile, this QCA-X membrane showed excellent antibacterial performance, and the sterilization efficacy against

S. aureus and *E. coli* were both more than 2 log-units even after four repeated antibacterial cycles, highlighting their potential for large-scale water purification systems [21]. Additionally, hybrid membranes combining quaternary ammonium polymers with TiO_2 nanoparticles can further enhance pathogen removal efficacy. That can be maintained close to 100% killing efficacy against *S. aureus* and *E. coli* and completely inhibited bacterial adhesion and biofilm formation within 7 days, exhibiting great potential to be applied in water treatment [22].

1.2.1.2.3 Food Packaging and Textiles

Quaternary ammonium-based polymers can also be employed in food packaging and textiles due to their broad antibacterial property. As food packaging materials, quaternary ammonium-based polymers can inhibit the growth of spoilage organisms, extend food shelf life, and thus reduce food waste [14, 15]. By incorporating quaternary ammonium salt-modified chitosan into poly(vinyl alcohol) film, the obtained composite films yielded more than 2 log-units killing against planktonic *S. aureus* and *E. coli* and significantly extended the storage time of strawberries [23]. In textiles, these polymers have been integrated into fibers to produce antimicrobial fabrics for face masks, hospital bedding, and uniforms. For instance, the nanofibrous filter was fabricated by grafting a layer of poly(2-(dimethyldecyl ammonium) ethyl methacrylate) onto the surface of the metal–organic framework. The composite filter demonstrated a comparable PM filtration efficiency (>95%) to the commercial N95 respirators and was capable of efficiently killing both *Staphylococcus epidermidis* (*S. epidermidis*) and *E. coli* airborne bacteria. Importantly, these textiles retained their antimicrobial efficacy after multiple wash cycles, offering a durable solution for infection control in healthcare settings [24].

1.2.1.3 Recent Advances and Innovations of Quaternary Ammonium-based Polymers

Recent studies have focused on developing biodegradable quaternary ammonium-based polymers to address their environmental concerns. Traditional quaternary ammonium-based polymers are highly effective against Gram-positive and Gram-negative bacterial strains but generally nondegradable, posing a potential pollution risk to a natural ecosystem. Quaternary ammonium-based polymers with enzymatically or acidly degradable linkages have been developed, which allow them to be degraded under different conditions and thus reduce environmental persistence while maintaining their antimicrobial activity. For instance, an acid-cleavable silaketal linkage was introduced of the backbones on quaternary ammonium polymer as a kind of pesticide, enabling control of hydrolysis over the time range of 10 minutes to 3 months according to the conditions of use. Moreover, the pesticide demonstrated outstanding bactericidal and insecticidal properties but became harmless to humans and other organisms after hydrolysis [25].

Another innovative direction is the combination of quaternary ammonium polymers with photodynamic therapy (PDT) agents, creating a dual-action antimicrobial system. Quaternary ammonium-based polymers disrupt bacterial cell membranes through electrostatic interactions and physical damage. PDT agents, after being activated by specific wavelengths of light, produce reactive oxygen species (ROS) that not only damage cell membranes but also oxidize intracellular components like proteins and DNA. This complementary mechanism produces a synergistic antimicrobial effect, significantly enhancing

antimicrobial efficacy but without causing bacterial drug resistance. Additionally, the PDT agents allows to be activated precisely and locally by the specific light, making this combination particularly effective for wound infection and skin surface disinfection [26].

Sustainable development is also a key factor to consider when using ammonium-based polymers in any field. Chitosan, a natural and renewable polysaccharide, has attracted more and more attention due to its low cost, biocompatibility, and biodegradability. By chemically modifying chitosan with quaternary ammonium groups, the quaternized polysaccharides not only present the broad-spectrum antibacterial property but also maintain their original excellent performance, such as film forming, biocompatibility, and biodegradation. Hence, quaternized chitosan has been widely applied as wound dressings due to their hemostatic and antibacterial ability, ion exchange membrane for fuel cells due to their high ion conductivity, and so on [27].

1.2.1.4 Advantages and Limitations of Quaternary Ammonium-based Polymers

The rapid development and wide-ranging applications of quaternary ammonium-based polymers are primarily attributed to their two major advantages. First, cationic quaternary ammonium moieties on the backbone or side main of these polymers provide a permanent positive charge, imparting them with long-term and broad-spectrum antimicrobial activity against Gram-positive and Gram-negative bacterial strains, fungi, and some viruses [11, 28]. The contact-killing mechanism composes the second merit of quaternary ammonium-based polymers. Quaternary ammonium-based polymers interact with the negatively charged microbial cell membranes through electrostatic and physical interaction and then disrupt the structural integrity of the cell membrane, significantly reducing the risk of bacterial drug resistance compared to conventional antibiotics [11].

However, adverse effects may occur when concentrations used of these polymers reach a certain level, including severe and chronic toxicity to susceptible organisms, animals, and humans. The cytotoxic effects of these polymers arise primarily from their strong interactions with cell membranes, which makes them effective antimicrobial agents but also poses risks to mammalian cells. It has been reported that a high dose of quaternary ammonium-based polymer can induce dysfunction in mitochondria, leading to cell death and a predisposition toward asthma in healthcare workers [29]. A possible way to solve this problem is through tailoring the structure–activity relationship of these polymers to improve their selectivity and minimize cytotoxicity to normal tissue cells. Meanwhile, they should also be used strictly within the safe dosage, especially in clinical practice.

1.2.2 Guanidinium-based Polymers

Guanidinium-based polymers represent a versatile class of antimicrobial materials, distinguished by their guanidinium functional groups. These polymers exhibit strong antibacterial activity, primarily due to the guanidine groups that carry a positive charge under physiological conditions. That enables strong electrostatic interactions with negatively charged bacterial cell membranes, leading to membrane disruption and bacterial cell death [30, 31].

In addition, guanidine-functionalized polymers have shown the capability to dissociate the formed biofilms, which are microbial communities embedded in a self-produced

extracellular polymeric substance (EPS) matrix, adhering to surfaces or interfaces such as medical devices, implants, and wounds. The polymers can penetrate into the depth of the biofilm matrix, destabilize or degrade key components of the EPS, such as polysaccharides and extracellular DNA, and then kill the exposed bacteria inside the biofilm [32].

1.2.2.1 Chemical Structure and Mechanism of Action

Guanidinium-based polymers are characterized by the presence of guanidinium functional groups within their polymeric structure. Guanidine groups are highly basic, with a pKa value of approximately 12.5. This means they retain a positive charge across a broad range of pH levels. Under acidic (pH<7.0) or neutral (pH 7.0) conditions, guanidine is fully or largely protonated and carries strong positive charges, making it effective for bacteria- or biofilm-related infection [33, 34]. Guanidine-based polymers present a dual antibacterial mechanism, primarily driven by their strong cationic nature and hydrogen-bonding capability. These polymers can interact electrostatically with the negatively charged bacterial cell membrane. Meanwhile, due to its planar structure and multiple hydrogen donors, guanidinium groups can also form strong multiple ionic hydrogen bonds with negatively charged or polar moieties in bacterial cell membranes. That leads to severe membrane disruption and subsequently the leakage of intracellular contents, and ultimately bacterial cell death [35, 36]. Additionally, guanidinium-based polymers can also penetrate and accumulate into the biofilms by interacting with the negatively charged EPS of the biofilm. That disrupts the structural integrity of the EPS, making the biofilm matrix more permeable, less stable, or even completely destabilized (see Figure 1.3). This dual mechanism underpins the high efficacy of guanidinium-based polymers against both planktonic bacteria and bacteria in a biofilm mode of growth [37–39].

1.2.2.2 Applications of Guanidinium-based Polymers

1.2.2.2.1 Wound Care and Medical Devices

Guanidinium-functionalized hydrogels have shown remarkable potential in wound care applications. For example, poly(hexamethylene guanidine) hydrochloride was first modified with methacrylic anhydride, which was further polymerized with acrylamide initiated by ultraviolet irradiation to prepare guanidinium-based hydrogels in aqueous medium. The hydrogels demonstrated strong antimicrobial activity against *S. aureus* and *E. coli*, yielding a close to 2 log-units reduction against both bacterial strains. Furthermore, due to the chemical bonding of the cationic guanidine segment in the hydrogel backbone, these hydrogels can maintain their antimicrobial activity even after soaking in water for 1 month and washing with water many times [40]. In medical devices, a series of guanidinium-based polymers with different side chain lengths and conformations were synthesized and subsequently grafted to the surface of poly(dimethylsiloxane) substrate. These modified substrates can reduce more than 1 log-unit of both *S. aureus* and *E. coli*, and effectively inhibit the formation of the biofilm as well as present good biocompatibility, significantly lowering the incidence of device-associated infections in clinical settings [41].

1.2.2.2.2 In Dental Applications

In dental care, guanidinium-based polymers have shown great potential for eradicating oral bacteria-related infections. The guanidine was covalently conjugated onto polyurethanes

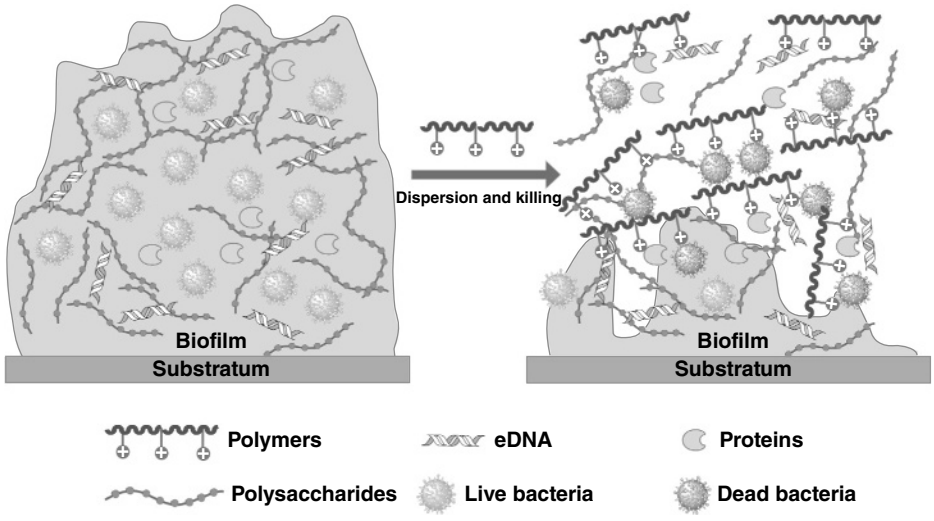

Figure 1.3 Overview of the interaction of guanidinium-based polymers with biofilm structures, including dispersion of biofilm and subsequent microbial clearance. Bacterial biofilms are complex, three-dimensional communities of microorganisms that are embedded in a self-produced EPS matrix. This matrix is primarily composed of extracellular DNA (eDNA), proteins, and polysaccharides, which provide protection to the bacteria against the immune system and antimicrobial agents. Highly positively charged guanidine-based polymers can interact with the negatively charged components of the EPS matrix, including eDNA, proteins, and polysaccharides through electrostatic, hydrogen bonds, and ionic interactions. These interactions lead to the destabilization and partial degradation of the EPS structure, exposing bacteria inside the biofilm to the external environment. Then, the positively charged guanidinium-based polymers interact with the negatively charged bacterial cell membranes, leading to membrane disruption and cell death.

through a click reaction. These guanidine-functionalized polyurethanes exhibited strong contact-killing antibacterial activity against both Gram-negative and Gram-positive bacteria. Noteworthily, these polymers can yield a more than 3 log-units reduction against *S. aureus* that is the one of the main bacteria in oral infection, as well as effectively inhibited the formation of oral bacterial biofilm. Moreover, the covalent conjugation of guanidine onto polyurethanes allowed long-term antimicrobial activity and made them a valuable tool in preventive dentistry disease [42].

1.2.2.2.3 Agricultural Films and Coatings

Guanidinium-based polymers have been widely used in agricultural applications; these materials inhibited the growth of plant pathogens such as *Fusarium oxysporum* (*F. oxysporum*) and *Xanthomonas campestris*, improving crop yield and quality. For example, guanidinium chloride was grafted onto the surface of hydroxyapatite-modified Fe_2O_3 magnetic nanoparticles, and their antifungal capacity against *F. oxysporum* which primarily causes vascular wilt diseases in a wide range of crops, was determined and analyzed. According to the experimental result, the product demonstrated excellent eradicating efficacy against *F. oxysporum* by a very low dosage, presenting the potential of being the alternative antifungal drug to increase the resistance of a wide variety of crop plants. Additionally,

guanidinium-functionalized sprays provided prolonged protection against bacterial and fungal infections in post-harvest storage [43].

1.2.2.3 Recent Advances and Innovations

Guanidinium-based polymers have garnered significant attention in recent years due to their wide applications across diverse fields. Recent innovations have focused on designing polymers with optimized chain lengths, balanced ratios of hydrophilic and hydrophobic segments, and tailored charge densities to maximize their antimicrobial efficacy and minimize cytotoxicity to human cells. In the field of drug delivery, guanidinium-based polymers have also demonstrated their ability to form stable complexes with nucleic acids through strong electrostatic interactions for effective gene delivery. Their high transfection efficiency, together with relatively low cytotoxicity, makes them considerable and attractive alternatives to traditional viral vectors or traditional cationic polymers such as polyethyleneimine. Meanwhile, researchers have also developed stimuli-responsive guanidinium-based polymers as the drug carriers that release drugs or genetic material in response to environmental changes such as pH [44], temperature [45, 46], or redox potential [31]. These innovations improve therapeutic efficacy and reduce their side effects on normal tissue cells.

Applications of guanidinium-based polymers in the environmental field have also made rapid progress. Due to their strong binding affinity with anionic pollutants such as phosphates, sulfates, and organic dyes, these polymers are being developed as highly efficient adsorbents for water purification [47–52]. Another innovation involves the integration of guanidinium-based polymers with photothermal therapy (PTT) agents, creating multifunctional materials for eradicating bacterial infection and promoting tissue regeneration. The combined system not only effectively eliminates bacteria by direct interaction with guanidinium groups, but also promotes wound healing by enhancing blood circulation and tissue repair processes through localized heating effects of PTT agents under specific light irradiation [53, 54].

1.2.2.4 Advantages and Limitations

Guanidinium-based polymers have drawn increasing interest for their diverse applications due to their unique molecular structures and highly effective antibacterial properties. Guanidinium groups have a high positive charge density, allowing these polymers to interact with and disrupt negatively charged bacterial membranes effectively. This mechanism makes them highly efficient against a broad spectrum of microorganisms, including multidrug-resistant strains, and thus applies in various fields such as biomedicine and environmental engineering [55, 56].

However, there also are some limitations that need to be addressed to broaden their practical applications and achieve clinical translation. For example, in biomedical applications, guanidinium-based polymers can be effective as antimicrobial agents and delivery systems, but can also exhibit potential toxicity toward mammalian cells at higher concentrations, causing unintended side effects, such as inflammation and excessive immune responses [57, 58]. In addition, the introduction of guanidinium groups often requires complex and multi-step chemical processes, which can be costly and time-consuming. Lastly, the long-term environmental impact of degradation products from guanidinium-based

polymers remains poorly understood. If not properly designed, these polymers may persist in the environment and potentially contribute to environmental pollution [59]. Thus, efforts to enhance their selectivity and simplify manufacturing processes are crucial for expanding their applications.

1.2.3 Imidazolium-based Polymers

Imidazolium-based polymers are a class of cationic materials characterized by the presence of imidazolium functional groups. The group is a five-membered ring containing a nitrogen atom with a positive charge, which confers a unique combination of hydrophobic and cationic properties. This unique combination enables imidazolium-based polymers to interact effectively with hydrophobic substances as well as negatively charged entities like bacterial membranes, anionic contaminants, and some greenhouse gases, making them highly effective in a wide range of applications, including medical, environmental, and industrial applications (see Figure 1.4) [60].

1.2.3.1 Chemical Structure and Mechanism of Action

Imidazolium-based polymers are prepared by direct polymerization of imidazolium-containing monomers and post-polymerization modification [61, 62]. The imidazolium group, containing an aromatic heterocyclic ring with a positive charge, interacts strongly with negatively charged bacterial membranes. This interaction destabilizes the lipid bilayer, causing membrane disruption and eventual cell death. Additionally, the hydrophobic nature of the imidazolium group facilitates deeper penetration into the lipid bilayer, enhancing its antimicrobial efficacy. Meanwhile, imidazolium-based polymers can also induce oxidative stress in microbial cells by disrupting intracellular components like DNA and proteins, further contributing to their bactericidal activity [63, 64].

1.2.3.2 Applications of Imidazolium-based Polymers

1.2.3.2.1 Medical Applications

Imidazolium-based polymers have been extensively used in medical settings due to their potent antimicrobial properties and compatibility with other functional materials. For instance, hydrogels incorporating imidazolium-functionalized nanoparticles demonstrated enhanced wound healing in preclinical models. Imidazolium-based polymer microspheres were prepared through emulsion polymerization. Subsequently, these microspheres were integrated into a gelatin methacryloyl-polyethylene glycol hydrogel. The composite hydrogels can yield close to 2 log-unit reduction of both *S. aureus* and *E. coli*, and maintain a minimal cytotoxicity and hemolysis activity. Moreover, the hydrogels can also facilitate the migration of human skin fibroblasts and human umbilical vein endothelial cells and promote osteogenic differentiation, suggesting the potential applications of these hydrogels in wound infection and bone repair [65]. In dental care, the imidazolium-containing resin was incorporated into a methacrylate-based scaffold using a simplified condensation reaction to prevent the fouling of oral pathogens like *Streptococcus mutans* (*S. mutans*). Only 2% inclusion of imidazolium moiety can result in superior bioactivity with minimal cytotoxicity without compromising the mechanical integrity of the restorative material. Moreover, it can effectively inhibit the adhesion, colonization, and subsequent formation of *S. mutans*

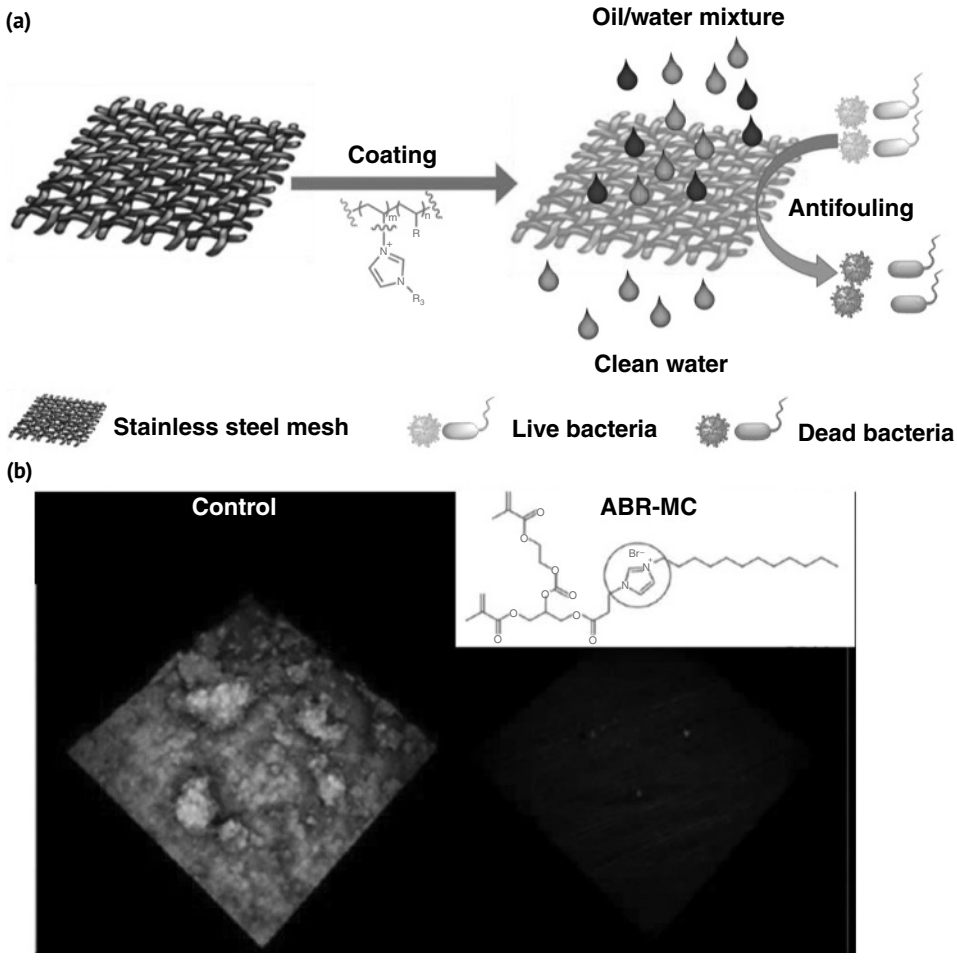

Figure 1.4 Applications of imidazolium-based polymer in different fields. (a) Stainless-steel mesh coated with imidazolium-based polymers has high water flux and oil separation efficiency as well as superb antibacterial and anti-biofouling activity against both Gram-positive and Gram-negative bacteria. (b) A low dose of imidazolium-based resin presents a strong ability to prevent the formation of biofilm. *Source:* Reproduced with permission of the American Chemical Society [66].

biofilms over a period of 67 hours, which may serve as a platform for long-term protection against plaque formation and associated diseases [66].

In advanced drug delivery systems, imidazolium-functionalized polymers have been employed as carriers for delivering antibiotics and other therapeutic agents. These systems have been engineered into smart nanocarriers capable of precisely targeting infection sites, followed by responding to the different microenvironments of infectious sites, enabling controlled drug release on demand. These smart delivering systems significantly enhance the delivery efficacy of drugs to infection sites, reduce systemic toxicity, and improve treatment efficacy [64, 67]. Additionally, imidazolium-based coatings on medical implants, such as orthopedic devices and vascular grafts, effectively prevented

biofilm formation, significantly reducing the risk of device-associated infections in clinical settings [68–70].

1.2.3.2.2 Environmental and Industrial Applications

In environmental applications, imidazolium-based polymers have shown promise in water and wastewater treatment (see Figure 1.4a). For example, highly stable imidazolium-based ionic porous organic polymers were prepared by the condensation reaction between imidazole with Tris-(4-bromomethyl-phenyl)-[1,3,5]triazine. The as-made polymers were characterized by nitrogen-rich triazine core and imidazole derivatives, bearing exchangeable bromide anions inside the porous networks. The polymers showed highly selective and efficient capture of toxic and hazardous CrO_4^- (170 mg g^{-1}) and ReO_4^- (515.5 mg g^{-1}) anions from wastewater. In addition, this showed reusability up to three cycles for the oxo-anions, advocating as potential candidates for real-time utilization in such oxo-anion sequestration applications. These polymers have also been used as antifouling coatings for oil/water separation in the industrial field. Besides, poly-imidazolium-based hydrogel-coated stainless steel mesh with super-hydrophilicity and underwater super-oleophobicity was constructed *via* cross-linking chitosan with a poly-imidazolium chain. The as-prepared 3D hydrogel network demonstrated outstanding stability and endurance under harsh conditions such as acidic, alkaline, and salty environments. Moreover, they presented high water flux and oil separation efficiency (>99.5%) as well as superb antibacterial efficacy (99.999%) and anti-biofouling activity against both Gram-positive and Gram-negative bacteria [71].

1.2.3.2.3 Food Packaging

Imidazolium-based polymers have been integrated into food packaging materials to inhibit microbial growth and subsequent biofilm formation (see Figure 1.4b) and thus extend the shelf life of perishable products. Films incorporating these polymers effectively prevented the proliferation of foodborne pathogens, including *Salmonella enterica* and *Listeria monocytogenes*, ensuring food safety during transportation and storage. Their compatibility with other antimicrobial agents, such as essential oils and nanoparticles, has further enhanced their utility in smart packaging solutions [69].

1.2.3.3 Recent Advances and Innovations

Recent studies have focused on improving the biodegradability and sustainability of imidazolium-based polymers. For instance, biodegradable imidazolium-functionalized polymers have demonstrated comparable antimicrobial efficacy and minimal side effects. Herein, a series of main-chain imidazolium oligomers with degradable linkers, such as carbonate, hemiaminal, ester, or urea functional, were synthesized through chemical modification. The new imidazolium materials not only retain excellent antimicrobial properties, leading to more than 2 log-units reduction against planktonic *E. coli* at low concentrations within 2 minutes but also the oligomers are self-degradable under different environmental conditions and thus produce a better biocompatibility and less cytotoxicity toward normal tissue cells [72]. In addition, imidazolium-based hydrogels have been designed to release antimicrobial agents in response to specific stimulation, such as pH or temperature changes, enabling more precise infection control. For example,

1-methyl-3-hexadecylimidazolium salicylate-based stimuli-responsive ionic hydrogel was prepared as a local drug administration system of the poorly water-soluble drug DOX. DOX could be effectively encapsulated into the cores of cylindrical micelles formed by the amphiphilic hydrogel in water and released from the ionic hydrogel formulation in a well-controlled and sustained manner at 37 °C and pH 5. This controlled release method reduced their side effects toward mammalian cells and enhanced their therapeutic efficacy [73].

1.2.3.4 Advantages and Limitations

Imidazolium-based polymers have been applied in a wide range of fields. That must be attributed to their following advantages. First, the presence of imidazolium groups in these polymers imparts strong antimicrobial activity by interacting with negatively charged bacterial membranes. Additionally, these polymers exhibit excellent ionic conductivity, which has facilitated their use in energy storage devices, sensors, and fuel cells [74].

The structural tunability of imidazolium-based polymers is another advantage, which ultimately stems from the inherent advantages of polymers. It is known well that polymers can achieve multiple functions by introducing co-polymerizable units or chemical modification in side chains. Thus, imidazolium-based polymers can be tailored to incorporate various functional groups to apply in different scenarios [61].

However, there are still limitations to be addressed for imidazolium-based polymers. Environmental concerns arise from their nonbiodegradable nature, leading to potential long-term accumulation in ecosystems. Meanwhile, their strong positive charges can also lead to cytotoxicity toward mammalian cells, limiting their direct application in certain biomedical fields [75]. Additionally, the preparation of these polymers often requires complex procedures and expensive precursors, leading to a high cost of synthesis and limiting their large-scale production [76]. Ongoing research aims to address these issues by developing biodegradable variants and optimizing their molecular structures for improved selectivity and safety.

1.2.4 Poly(ionic liquid)s

Poly(ionic liquid)s (PILs), also named polymerized ionic liquids, are polyelectrolytes that consist of a polymeric backbone and an ionic liquid (IL) species in monomer repeating units. PILs combine the unique properties of ionic liquids such as thermal stability, high charge density, high ionic conductivity, and wide electrochemical stability with properties of macromolecular architectures. This unique combination endows PILs with novel properties and functionalities that have aroused considerable attention in a multitude of fields from researchers. So far, due to their broad-spectrum antimicrobial activity, PILs have demonstrated a huge application potential in biomedical engineering, industrial processing, and marine systems [77]. Of note, PILs are typically divided into three sub-classes: polycation type, polyanion type, and amphoter type, among which the polycationic type is generally the one with significant antimicrobial activity [78]. Thus, in this section, we will mainly discuss polycationic types and their mechanism of action and applications in different fields.

1.2.4.1 Chemical Structure and Mechanism of Action

Poly(cationic liquid)s (PCLs) are typically synthesized by polymerization of cationic liquid (CL) monomers that are composed of cationic centers such as imidazolium, pyridinium, or quaternary ammonium and a counter anions. The backbone provides the macromolecular framework and can vary in flexibility, rigidity, or functionality by adjusting the monomer component. While the cationic moieties incorporated into the backbone impart an inherent positive charge to PCLs. Thus, PCLs often act as membrane disruptors by electrostatically interacting with the negatively charged bacterial membranes. This interaction disrupts the membrane structure, leading to leakage of cellular contents and eventual bacterial cell death (see Figure 1.5a). Also, due to this mechanism of action, PCLs are effective against a wide range of bacteria, bacteria in their biofilm mode of growth, including Gram-positive and Gram-negative species, and even multidrug-resistant strains (see Figure 1.5b) [78].

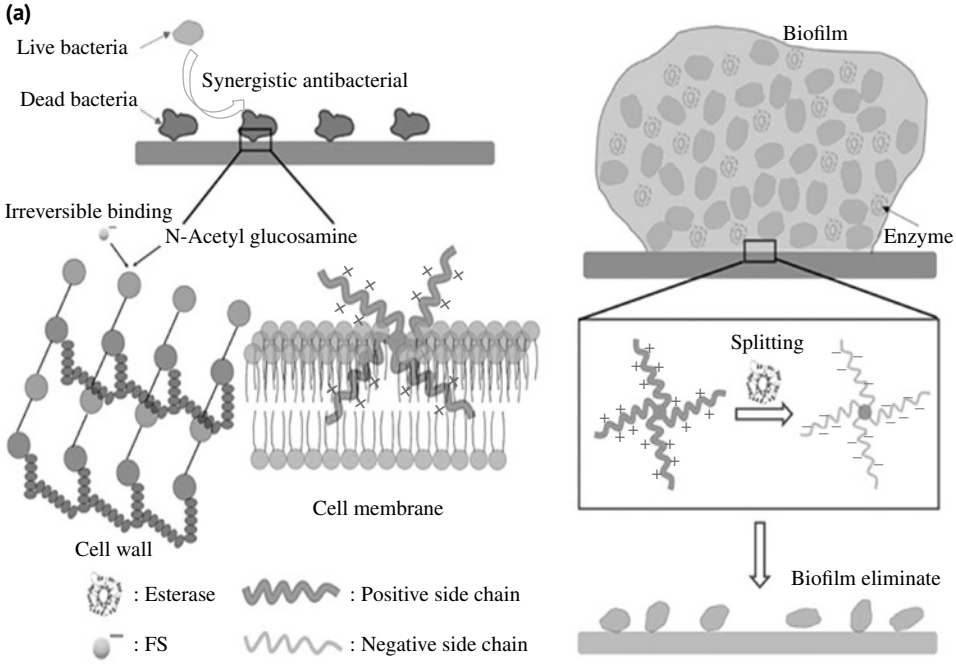

Figure 1.5 Schematic representation of PCL-coated membranes used in industrial water treatment, highlighting antimicrobial and antifouling properties. (a) The mechanism of poly(cationic liquid)s-based coating for killing bacteria and preventing biofilm formation. *Source:* Reproduced with permission of the American Chemical Society [99]. For the detailed description, see Figure 1.2. (b) Imidazolium-type PCLs could effectively inhibit biofilm growth. *Source:* Reproduced with permission of the American Chemical Society [100]. (c) Polyethersulfone grafted ionic liquid porous membrane was prepared and revealed extremely improved water flux, antifouling, and antibacterial properties in comparison to the neat polyethersulfone porous membranes. *Source:* Reproduced with permission of the Elsevier [101].

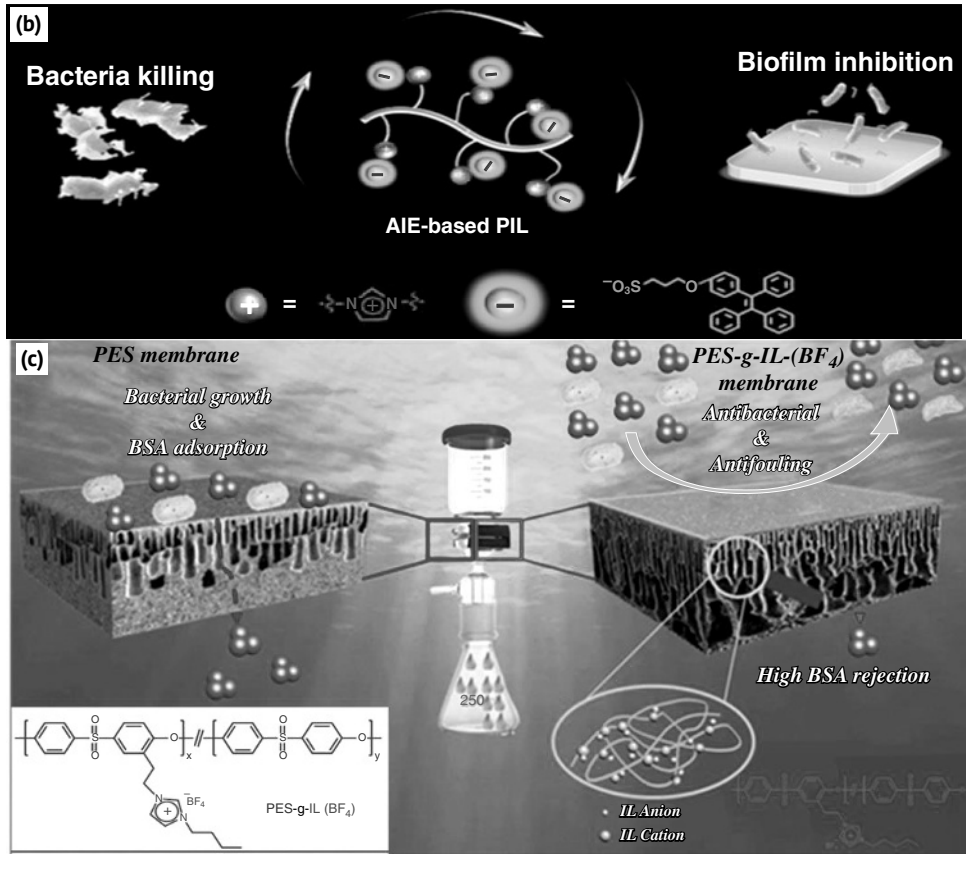

Figure 1.5 (Cont'd)

1.2.4.2 Applications of Poly(ionic liquid)s

1.2.4.2.1 Medical Applications

PCLs-based materials have been extensively explored as coatings for medical implants, catheters, and wound dressings. Recently, imidazolium-type PCLs have presented a broad spectrum of antibacterial activities. In detail, imidazolium-based PCLs membranes were synthesized through *in situ* photo-crosslinking polymerization followed by anion-exchange with L-tryptophan (Trp). The resultant membranes can lead to more than 2 log-units reduction against both *S. aureus* and *E. coli* and present low cytotoxicity and good blood compatibility. Furthermore, the PCLs-Trp membranes could be easily recycled without a significant decrease in antimicrobial activity [79]. In particular, PCL-functionalized hydrogels have shown dual functionality in wound care, providing sustained antimicrobial activity as well as anti-inflammatory activities. For example, Poly(1-ethyl-3-vinylimidazolium furan-2-carboxylate) (PCLs) were synthesized and then mixed with montmorillonite clay and 2-furfurylamine-modified hyaluronic acid and chemically crosslinked with four-arm maleimide-polyethylene glycol to form degradable semi-inter penetrate network hydrogels

(semi-IPN). The synthesized semi-IPN hydrogels exhibited high antibacterial activities, yielding almost 2 log-units reduction against *E. coli* and *S. aureus*. Furthermore, the semi-IPN hydrogel could be quickly degraded, and the released PCLs from the degraded hydrogels exhibited high anti-inflammatory activities [80].

1.2.4.2.2 Water and Wastewater Treatment

In environmental contexts, PCLs have been widely used in filtration membranes for water and wastewater treatment (see Figure 1.5c). A polyvinylidene fluoride copolymer-based ultrafiltration membrane was fabricated through copolymerizing with polycationic liquids *via* atom transfer radical polymerization for removing antibiotic-resistant bacteria from water and wastewater. The as-prepared membrane exhibited effective bactericidal properties against wild-type bacteria and opportunistic pathogens, showcasing an inactivation efficiency exceeding 2 log-units [81]. These membranes also maintained antimicrobial efficacy in high-salinity environments, making them suitable for desalination plants and industrial wastewater systems [82, 83].

1.2.4.2.3 Marine and Industrial Applications

PCLs-functionalized coatings have been employed in antifouling applications, particularly in marine environments where microalgae can adhere to the surface of ships and subsequently compromise the performance of ships and underwater equipment. These coatings prevented microalgae colonization while exhibiting high durability against mechanical and chemical stresses [84]. For instance, the poly(glycidyl methacrylate) (PGMA) brushes were grafted onto crosslinked polystyrene nanospheres through subsurface-initiated atom transfer radical polymerization. Subsequently, the imidazolium-based PCLs were bound onto PGMA brushes through a ring-opening reaction between the epoxide groups of PGMA and the amine groups of PCLs. The as-obtained IL-functionalized polystyrene nanospheres can be mixed effectively with the self-polishing resin to acquire a novel self-polishing nanocomposite coating. The complex coating not only presented good antibacterial activity against *E. coli* and *S. aureus* but also a substantial antifouling property against microalgae, yielding eradicating efficacy of 83 and 85% against *Porphyridium* and *Dunaliella*, respectively. That must be attributed to the strong positive charged imidazole groups of PCLs, imparting self-polishing nanocomposite coating good potential in overcoming the issue of marine biofouling [85]. Additionally, PCLs have been developed as ion-gel membranes for CO_2/light gas separations. The solid composite gas separation membrane was composed of free CLs and PCLs that were prepared through the photo-polymerization of a simple imidazolium-based styrene monomer. The obtained complex membrane yielded a CO_2 permeability increase of about 400% with a 33% improvement to CO_2/N_2 selectivity relative to the analogous membrane lacking any free ion pairs [86, 87].

1.2.4.2.4 Food Packaging

PCL-based materials have also been integrated into food packaging to ensure food safety and extend shelf life. For instance, the ionogel films were prepared by incorporating the bioactive ionic liquid, i.e. choline salicylate, to enhance antimicrobial and antioxidant performance. The ionic liquid/gelatin-based films can reduce higher than 2 log-units of *Bacillus subtilis* compared to the films without ionic liquid. The ionic liquid-incorporated films also demonstrated the ability to enhance the shelf life of *Malus pumila* by preventing

their air oxidation. Moreover, the films displayed exceptional ultraviolet shielding and antioxidant properties with high mechanical strength [88].

1.2.4.3 Recent Advances and Innovations

PCLs, combining the unique properties of cationic liquids with the versatility of polymeric materials, have made remarkable advancements in different fields. These materials possess inherent cationic charges, which are critical for their antimicrobial properties. Recent innovations have focused on enhancing the antimicrobial efficiency of PCLs to further expand their applications. For instance, researchers have tailored the molecular structures of PCLs to improve their biocompatibility and selectivity to ensure effective antibacterial activity and minimize toxicity to mammalian cells. That can be attributed to the development of advanced polymerization techniques, such as atom transfer radical polymerization, enabling precise control over molecular weight and architecture in PCLs, and then ensuring their antimicrobial performance. Meanwhile, researchers have synthesized PCLs from renewable feedstocks, reducing their environmental footprint while maintaining high antimicrobial activity [89]. Responsive PCL systems, designed to release antimicrobial agents under specific pH or temperature conditions, have been developed for precision-targeted applications [90]. Additionally, hybrid materials combining PCLs with nanoparticles or photodynamic therapy agents have shown synergistic effects, achieving both antimicrobial action and pollutant degradation in environmental systems [91, 92].

1.2.4.4 Advantages and Limitations

PCLs have gained significant attention due to their unique combination of properties derived from ionic liquids and polymeric systems. Their thermal and chemical stability enhances their performance under extreme conditions, enabling their application in harsh environments. The ability to precisely design and modify both the ionic moieties and the polymer backbone allows the development of tailored PCLs with specific functionalities, ensuring an effective killing efficacy against a wide range of pathogens, including drug-resistant strains. Moreover, PCLs can be fabricated into versatile forms such as membranes, films, or gels, providing adaptability for a wide range of practical applications [93–95]. However, the synthesis of ionic liquid monomers and their subsequent polymerization processes can be complicated, costly, and time-consuming, limiting their large-scale production [96]. Additionally, toxicity concerns associated with certain cationic groups, such as imidazolium or phosphonium, also restrict their use, particularly in sensitive fields like biomedicine [97, 98]. Therefore, research on cost-effective production methods and the development of bio-safe PCLs remains a critical area of focus for researchers from different fields.

1.2.5 Positively Charged Dendritic Polymers

Dendritic polymers, including dendrimers and hyperbranched polymers, represent a unique class of macromolecules with highly branched, tree-like architectures. Also, they typically are characterized by their well-defined molecular weights, high degree of branching, and abundant functional end groups on the surface. If the surface groups are protonated amines or other cationic moieties, the dendritic polymer will carry positive charges. Positively charged dendritic polymers are often used in lots of applications like antimicrobial coatings, drug delivery, and wound healing [102–104].

1.2.5.1 Chemical Structure and Mechanism of Action

Positively charged dendritic polymers, such as poly(amidoamine) dendrimers functionalized with amine or quaternary ammonium groups, have been widely studied for their potent antimicrobial properties. These polymers exhibit a highly branched structure with a high density of positively charged at their surface, which plays a critical role in their interaction with bacterial cells. First, the cationic groups on the polymer surface are attracted to the anionic components of the bacterial membrane, such as phospholipids and lipopolysaccharides. This interaction disrupts the membrane's integrity, leading to increased permeability and eventual leakage of intracellular contents. Meanwhile, the dense, multivalent nature of dendritic polymers enhances their binding affinity to bacterial cells compared to linear or less branched polymers. That allows the polymers to interact simultaneously with multiple sites on the bacterial membrane, further amplifying their antimicrobial efficiency (see Figures 1.6a, b). Moreover, the structure of dendritic polymers can be easily tuned by modifying their generation or surface functionalities, allowing for the optimization of their antimicrobial properties [105, 106].

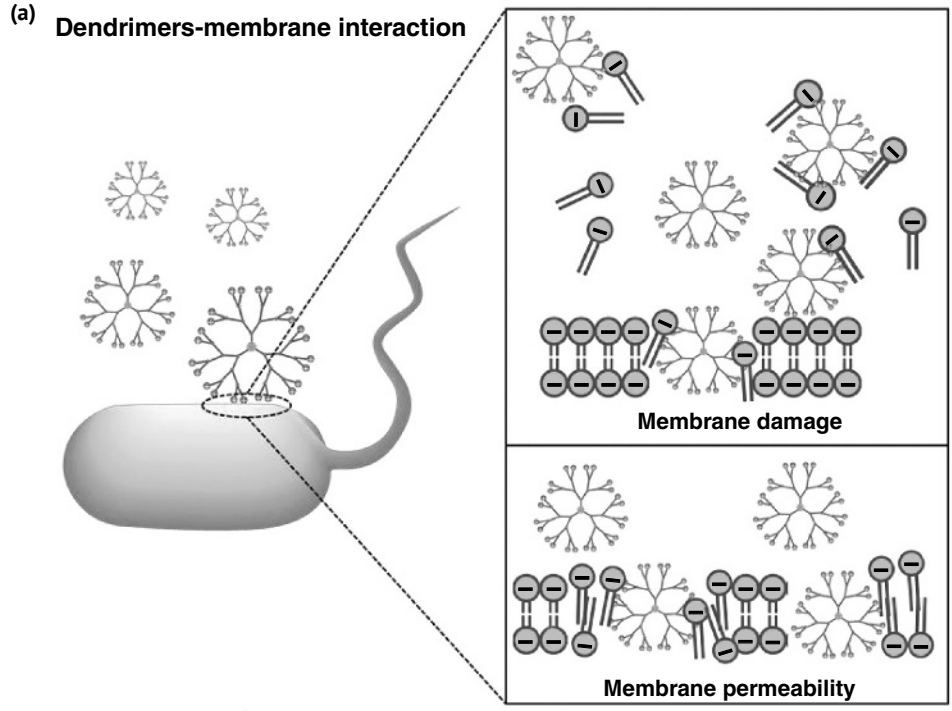

Figure 1.6 Illustration of dendritic polymer interactions with bacterial biofilms and their role in drug delivery. (a) The interaction of dendrimers with bacterial cells, which generally includes damage of bacterial cell membrane and membrane permeability by dendrimers. *Source:* Reproduced with permission of Elsevier [121]. (b) Dendritic systems presented a high efficacy against multidrug-resistant bacteria. *Source:* Reproduced with permission of the Royal Society of Chemistry [122]. (c) Heterofunctionalized poly-(amido-amine) dendrimers, as the drug carriers, with amide-conjugated vancomycin and incorporated Ag nanoparticles, showed a significant reduction in colony-forming units of a vancomycin-resistant *S. aureus* strain, while not inducing resistance in a vancomycin-susceptible strain. *Source:* Reproduced with permission of the Elsevier [110].

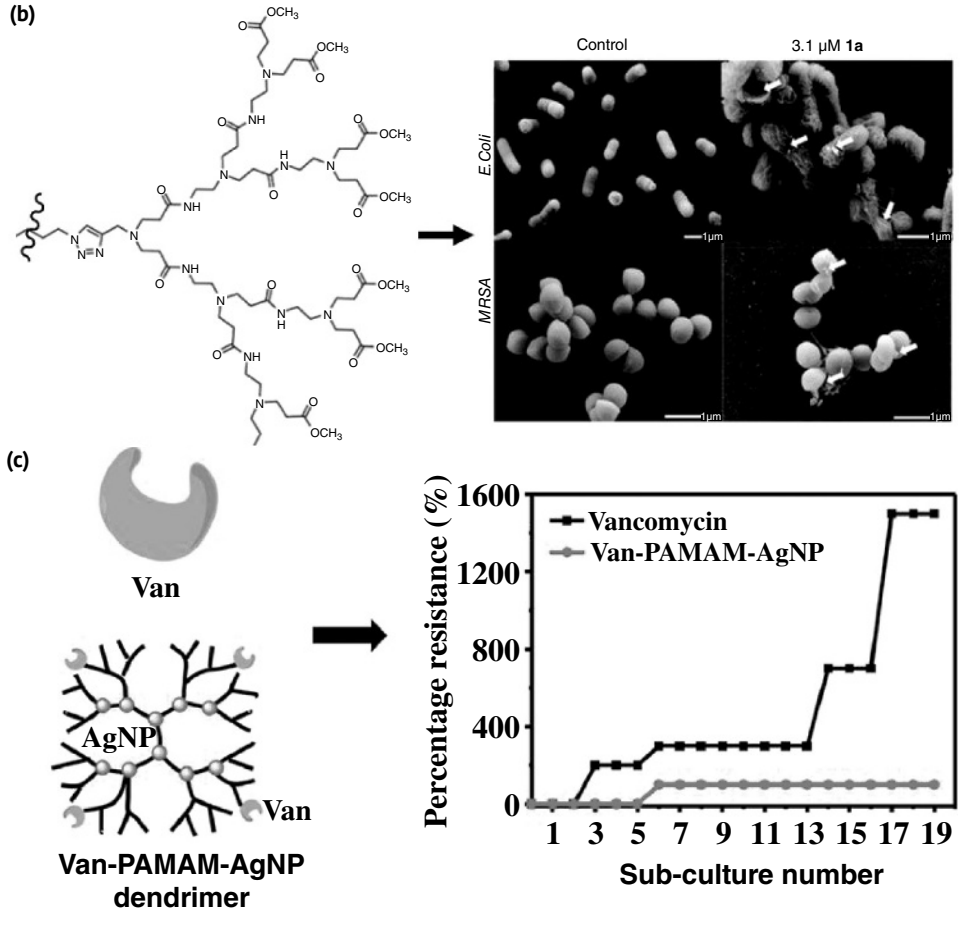

Figure 1.6 (Cont'd)

1.2.5.2 Applications

1.2.5.2.1 Medical Applications

Hyperbranched and dendritic polymers have found extensive use in medical devices and wound care. It is worth mentioning that the adhesion of pathogenic bacteria and the formation of biofilm on the implant are the most common causes of failure of medical devices. Thus, different types of amphiphilic dendrimers have been developed due to their superior antibacterial and antifouling activity. For example, a hierarchical surface integrating both a geminized cationic amphiphilic antibacterial upper layer and a zwitterionic antifouling sublayer has been developed. The hierarchical surface can eradicate almost all *S. aureus* and *E. coli* bacterial cells within 30 minutes. Moreover, this novel hierarchical surface holds great potential for the prevention of protein adhesion and biofilm formation on the surfaces, displaying a certain antifouling capacity, making the hierarchical platform a great potential candidate material for future applications in the field of implantable medical devices [107]. In wound healing, dendritic polymers functionalized

hydrogel can provide both infection control and tissue repair, accelerating the healing process in chronic wound models. Cationic dendritic hydrogels were fabricated by chemically cross-linking trans-1,4-cyclohexanediamine with 1,3-dibromo-2-propanol using a condensation reaction. The prepared hydrogel possessed an inherent antibacterial ability that can kill effectively *S. aureus* and *E. coli*. Furthermore, *in vivo* experiments confirmed that the hydrogel can quickly stop bleeding, efficiently eradicate the bacterial infection, promote the conversion of macrophages from the pro-inflammatory M1 phenotype to the anti-inflammatory M2 phenotype, and accelerate collagen deposition and blood vessel formation, thereby promote rapid wound healing [108]. Additionally, hyperbranched polysaccharide derivatives have been employed in advanced wound dressings, where they demonstrated broad-spectrum antimicrobial activity and biocompatibility [109].

1.2.5.2.2 Drug Delivery Systems

The unique architecture of hyperbranched and dendritic polymers has been leveraged in drug delivery applications to enhance the solubility and stability of antimicrobial agents. First, the dendritic structure in dendritic polymers provides a large number of terminal functional groups on the polymer surface, which can be chemically modified to bind antimicrobial agents. Also, dendritic polymers have a well-defined, globular structure with internal cavities, which can encapsulate hydrophobic or hydrophilic drugs inside these cavities, protect them from enzymic degradation, and enhance their stability during transport. For example, heterofunctionalized, poly-(amido-amine) dendrimers were prepared as the delivery systems, to which vancomycin was covalently conjugated and Ag nanoparticles were physically loaded (see Figure 1.6c). The dual conjugation of vancomycin and Ag nanoparticles in PAMAM dendrimers showed a 6–7 log reduction in colony-forming units of a vancomycin-resistant *S. aureus*, while not inducing resistance in a vancomycin-susceptible strain. Moreover, that can also significantly faster and more effectively promote healing of a superficial wound infected with vancomycin-resistant *S. aureus* than traditional antibiotics [110]. Thus, hyperbranched polymeric micelles loaded with antibiotics can improve drug encapsulation efficiency and target delivery to infection sites, reducing systemic toxicity and improving therapeutic outcomes [111].

1.2.5.2.3 Environmental Applications

In water treatment, hyperbranched polymers functionalized with cationic groups have been incorporated into filtration membranes because of their high water permeability and low operation pressure, as a result, reducing the operation cost and energy consumption. For example, poly(tetrafluoroethylene) (PTFE) membrane has been grafted with hyper-branched poly(amidoamine) for the removal of Cu(II) cations from aqueous media. The experiment showed that relatively at low operation pressure (25 kPa), the water flux through the grafted PTFE membrane was higher than the PTFE membrane before modification due to the increase in its hydrophilicity. The grafted membrane was able to adsorb 1.42 g Cu^2/m^2 [112].

1.2.5.3 Recent Advances and Innovations

Dendritic polymers have emerged as a versatile class of macromolecules with significant advancements in recent years. Dendritic polymers play an increasing role in drug delivery

systems. Researchers have developed dendrimers and hyperbranched polymers with stimuli-responsive properties, enabling controlled drug release triggered by pH, temperature, or enzymatic activity [113, 114]. For instance, dendritic polymers with acid-sensitive linkages have been designed to release chemotherapeutic agents selectively in acidic tumor microenvironments, minimizing systemic toxicity and enhancing therapeutic efficacy [114]. Additionally, surface functionalization with targeting ligands, such as antibodies or peptides has been used to improve the ability of these polymers to selectively deliver drugs to specific tissue sites [115].

In addition, energy storage and conversion have also benefited from the development of dendritic polymers. Their high surface area and ability to host functional groups make them ideal for use in batteries, fuel cells, and supercapacitors [116, 117]. For example, dendritic polymers have been employed as ion-conducting membranes or as supports for metal catalysts, which enhance the performance and stability of energy systems. Furthermore, their customizable structure enables the fine-tuning of conductivity and mechanical properties, addressing critical challenges in energy-related applications [118].

1.2.5.4 Advantages and Limitations

The primary advantage of dendritic polymers lies in their highly branched structure, which provides a large surface area with numerous terminal groups. These functional groups enable extensive chemical modification, allowing for tailored interactions with specific targets. That is particularly important in applications such as drug delivery, where functional groups can be used to conjugate therapeutic agents, targeting ligands, or stimuli-responsive moieties. Meanwhile, the interior cavities of dendritic polymers can provide spaces for encapsulating small molecules, including drugs, dyes, or catalysts. This encapsulation protects sensitive molecules from degradation, broadening the utility of dendritic polymers in drug delivery, imaging, and catalysis [119, 120].

However, some points also limit their further application in different fields. The synthesis of dendritic polymers often involves multiple iterative steps, including protection, activation, and deprotection reactions, which make the process time-consuming and may limit their large-scale production. Moreover, a potential cytotoxicity associated with dendritic polymers, especially those with cationic functional groups, raises concerns about their practicality for applications in the biomedical field. Surface modification of dendrimers with biocompatible molecules or groups such as PEG, has been employed to mitigate this issue, but they add complexity to the production process and increase production costs [120]. Thus, simplifying production methods and improving cost-effectiveness are critical for their broader adoption.

1.2.6 Hybrid Systems

Hybrid systems represent an innovative approach in the field of cationic polymers, which combines the inherent antimicrobial properties of cationic polymers with the unique functionalities of other materials, such as nanoparticles, natural extracts, and photodynamic agents [110, 123, 124]. By integrating multiple components, hybrid systems can achieve enhanced and broad-spectrum antimicrobial efficacy (see Figure 1.7). Thus, these systems have gained significant application in medical, environmental, and industrial sectors.

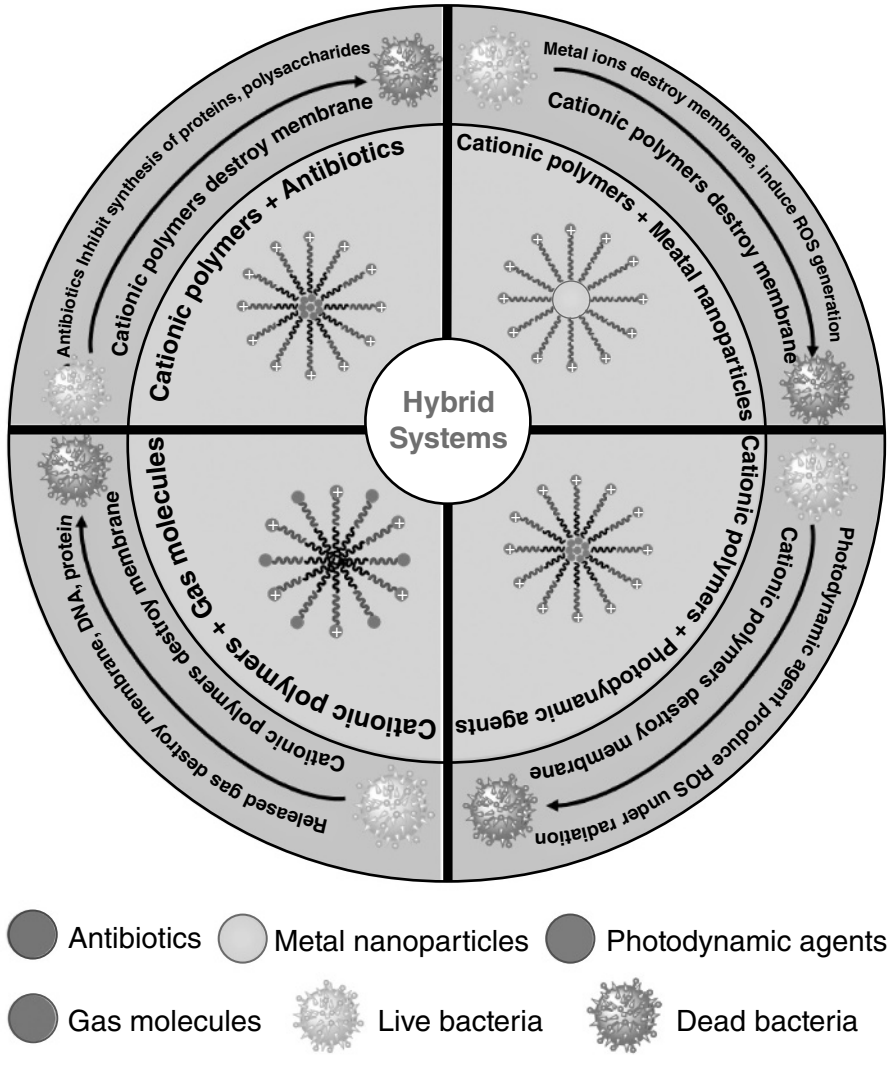

Figure 1.7 Illustration of hybrid systems combining cationic polymers and other methods for killing bacteria.

1.2.6.1 Chemical Structure and Mechanism of Action

Hybrid systems, integrating cationic polymers with additional components, can harness the advantages of each component and generate synergistic effects. For instance, when hybrid systems consist of cationic polymers with nanoparticles such as silver, gold, or zinc oxide nanoparticles, these nanoparticles can produce antimicrobial activity by releasing metal ions that disrupt bacterial metabolic pathways, while cationic polymers target and destroy bacterial membranes through electrostatic interactions [125, 126]. This dual action achieves synergistic antimicrobial efficiency and significantly reduces the development of

resistant bacteria. Similarly, the incorporation of natural extracts into hybrid systems, such as essential oils, also provides complementary antimicrobial mechanisms. The essential oils can eradicate bacteria by inhibiting enzymatic pathways and disrupting membranes. On the other hand, cationic polymers can destroy bacterial membranes through electrostatic and hydrophobic interactions. As a result, these combined actions result in enhanced efficacy and reduced microbial resistance [127].

1.2.6.2 Applications of Hybrid Systems

1.2.6.2.1 Medical Applications

Hybrid systems incorporating cationic polymers and other systems have shown great promise in preventing biofilm formation and treating infections associated with medical devices. For example, cationic poly-(amido-amine) dendrimers were applied to physically load Ag nanoparticles to eradicate the infection resulting from vancomycin-resistant *S. aureus*. The hybrid systems showed a 6–7 log-units reduction of both *S. aureus* and *E. coli* while not inducing resistance in a vancomycin-susceptible strain. Moreover, that can also significantly faster and more effectively promote the healing of a superficial wound infected with vancomycin-resistant *S. aureus* than traditional antibiotics, presenting a great potential to be a coating for catheters and orthopedic implants [110]. In wound care, a hybrid system combining cationic polymers with photodynamic therapy agents provided dual-mode action, eradicating bacterial infection and preventing the formation of biofilms. For example, the photosensitizer Ce6-loaded polyethyleneimine-based micelle was constructed by a cationic dendritic polymer and physically loaded with photosensitizer Ce6. Cationic polymers can promote the interaction between photosensitizer and negatively charged bacteria, resulting in enhanced targeting of photosensitizer and lethality of photodynamic therapy, and remain active for a longer duration to prevent bacterial re-growth when removing the light. The hybrid system can reduce 4 log-units of Gram-negative *E. coli* with visible light irradiation for 5 minutes, which was usually insensitive to photosensitizers. Moreover, the cationic polymer and photodynamic combination also exerted significant inhibitory and ablative effects on fungi and biofilms [128].

1.2.6.2.2 Environmental Applications

Hybrid systems have been extensively employed in water treatment and environmental remediation. Graphene oxide-cationic polymer composites demonstrated high efficacy in removing bacterial contaminants and organic pollutants from wastewater, making them suitable for large-scale water purification systems [79]. For example, a kind of magnetic graphene oxide/cationic hydrogel hybrid system was synthesized for an organic dye acid red 88 (AR88) removal. Given the numerous cationic functional groups within its backbone, the hybrid system can adsorb component anionic AR88 uptake through electrostatic attraction. As a result, the cationic hybrid system exhibited an AR88 adsorption capacity of more than 1140.2 mg g^{-1} in a strongly alkaline solution (pH > 10), which indicated that the hybrid system was a reusable adsorbent for the fast and highly efficient removal of AR88 from wastewater [129]. In industrial pipelines, hybrid coatings combining cationic polymers have been developed to maintain the pipeline body against corrosion and degradation by harsh environments. Acrylic-polyurethane hybrid coatings were prepared by mixing metal oxide pigment acrylic emulsion (AC) with polyurethane (PU) polymer using the traditional physical blend method. Subsequently, the modified acrylic emulsion (AC-PU) was then

enriched with a novel mixed metal pigment of ($CoO.ZnO.Al_3O_4$) based on bauxite ore as a natural source of alumina. The results showed that the coating formulated with AC mixed with 15% polyurethane in the presence of the prepared pigment offered higher corrosion protection toward pipelines compared to the other formulations and the parent polymers [130].

1.2.6.2.3 Food Packaging

Hybrid systems have found applications in food packaging, where they inhibit the growth of foodborne pathogens and extend the shelf life of perishable goods. For example, cationic polymer films embedded with essential oils effectively reduce microbial contamination and preserve freshness during transportation and storage. Here, essential oil (LEO) was encapsulated with cationic chitosan (CS) to prepare a sustained-release natural essential oil nanocapsule. Subsequently, the as-prepared essential oil nanocapsules were added into grass carp collagen (GCC) as the film-forming matrix to prepare edible films. Edible GCC/CS-LEO films exhibited excellent morphology, oxygen permeability (OP), and superior antibacterial properties due to the presence of essential oil and CS. Importantly, GCC/CS-LEO film can be applied as chilled pork packaging with great preservative and antioxidant efficacy for 21 days [131].

1.2.6.3 Recent Advances and Innovations

Hybrid systems that combine cationic polymers with other materials represent a burgeoning area of research, which further enhances their functionality and broadens the application range. Herein, this section explores recent advances in the development and innovation of these hybrid systems.

One of the innovation directions is the integration of cationic polymers with metal nanoparticles, such as silver, gold, and zinc oxide nanoparticles. These hybrid systems not only can interact with bacterial membranes through the electrostatic interactions of cationic polymers, but also the metal ions released from the hybrid systems can yield a synergistic antibacterial effect [110].

Another significant advancement is the combination of cationic polymers with carbon-based nanomaterials, such as graphene oxide (GO) and carbon nanotubes (CNTs). These materials provide unique properties such as high surface area, electrical conductivity, and mechanical strength. For example, GO incorporated in hybrid systems physically disrupts bacterial membranes due to its sharp edges and high surface area, while cationic polymers disrupt bacterial membranes through electrostatic interactions with negatively charged microbial surfaces. The dual antibacterial mechanism ensures synergistic and effective eradication efficacy of bacterial infection [132].

In addition, the combination of photodynamic and/or photothermal agents with cationic polymers achieves controllable treatment against microbial infections by switching radiation sources between on and off state, improving treatment efficiency, and also minimizing toxic side effects on normal tissues [124, 132].

1.2.6.4 Advantages and Limitations

Hybrid systems excel in achieving multifunctional antimicrobial action, combining the strengths of cationic polymers with complementary components. Their versatility allows for tailored solutions across diverse applications. However, this combination is also

a double-edged sword to some extent. From the perspective of clinical application, the combination of cationic polymers and other materials improves the antibacterial activity, but they also make the system more complicated, including material preparation, and purification, and thus may lead to a high cost. At the same time, when these hybrid systems are used in clinical practice, the components in this system may interact with the complex tissue environment and lead to unpredictable negative results. Thus, up to what extent this will affect clinical translation of the use of hybrid systems as a new, non-antibiotic-based infection control strategy remains to be seen.

1.3 Summary and Outlook

Cationic polymers have established themselves as versatile and powerful antimicrobial materials, addressing a wide range of challenges across medical, environmental, and industrial domains. Their ability to interact with negatively charged microbial membranes through electrostatic interactions and additional mechanisms such as oxidative stress and membrane disruption has made them an essential component in the fight against antimicrobial resistance. This chapter has explored their various classifications, applications, and advancements, with insights drawn from 132 key studies. Meanwhile, several key areas require continued research and development to fully harness the potential of cationic polymers.

1.3.1 Sustainability and Biodegradability

Developing biodegradable cationic polymers from renewable feedstocks not only aligns their use with global sustainability goals but also addresses the growing need for eco-friendly alternatives in various industries. That is particularly critical for applications in environmental systems, such as water treatment and soil remediation, as well as in consumer products like packaging and personal care items, where minimizing long-term ecological impacts is essential. By ensuring these materials degrade harmlessly after use, we can reduce environmental pollution, conserve resources, and contribute to a circular economy, making them a sustainable solution for modern challenges.

1.3.2 Targeted and Responsive Systems

Advances in stimuli-responsive materials can enhance the precision and efficiency of antimicrobial actions. These systems, capable of releasing antimicrobial agents in response to specific environmental triggers, will be instrumental in reducing off-target effects, enhancing therapy efficacy, and improving safety profiles.

1.3.3 Interdisciplinary Integration

The integration of cationic polymers with emerging technologies such as nanotechnology, artificial intelligence, and 3D printing can accelerate the development of next-generation materials. These interdisciplinary approaches will enable the design of more sophisticated and customizable antimicrobial solutions.

1.3.4 Scalability and Cost Reduction

Simplifying the synthesis and manufacturing processes of cationic polymers is essential for their commercial success. Collaborations between academia and industry will play a critical role in achieving cost-effective production at scale.

1.3.5 Expanding Applications

The versatility of cationic polymers can be further explored in emerging areas such as antimicrobial coatings for wearable electronics, self-sterilizing surfaces in public spaces, and advanced filtration systems for pandemics.

In conclusion, cationic polymers offer a promising solution to the growing threat of antimicrobial resistance, with their ability to adapt to diverse applications and evolving microbial challenges. By addressing current limitations and exploring innovative functionalities, these materials have the potential to transform antimicrobial strategies across sectors, ensuring a safer and more sustainable future.

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