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].

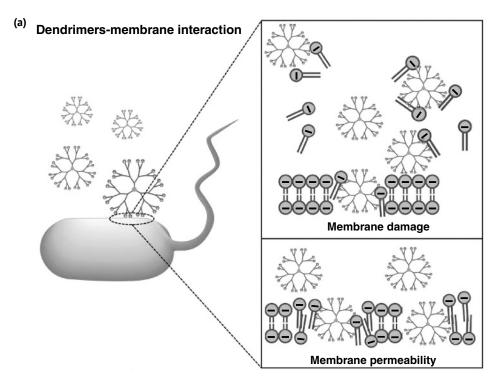


Figure 1.6 Illustration of dendritic polymer interactions with bacterial biofilms and their role in drug delivery. (a) The interaction of dendrimers with bacterial cells, which generally includes damage of bacterial cell membrane and membrane permeability by dendrimers. *Source:* Reproduced with permission 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 amideconjugated 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].

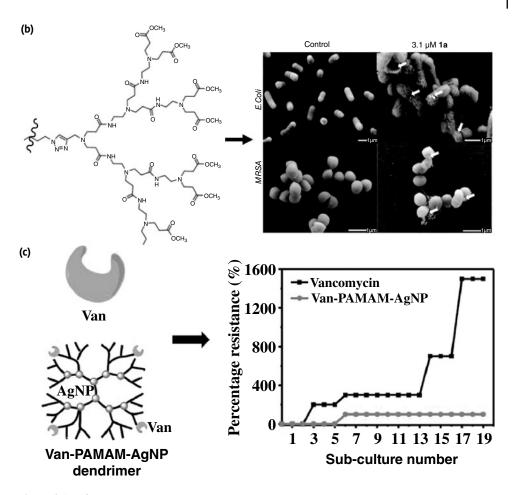


Figure 1.6 (Cont'd)

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 $1.42 \, \mathrm{g} \, \mathrm{Cu}^2/\mathrm{m}^2 \, [112]$.

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.

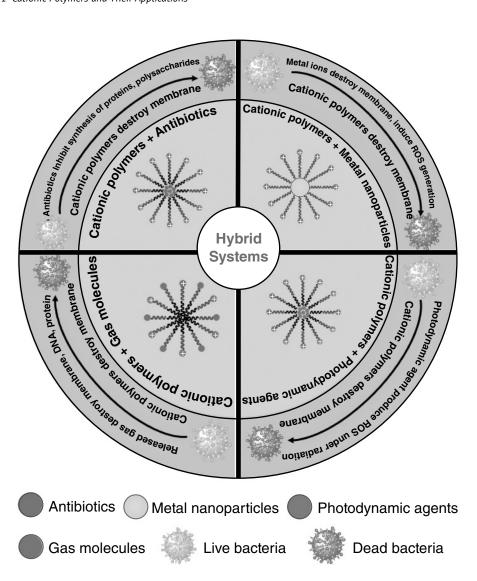


Figure 1.7 Illustration of hybrid systems combining cationic polymers and other methods for killing bacteria.

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.Al₃O₄) 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 carbonbased 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.

Summary and Outlook 1.3

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 ecofriendly 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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