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Antimicrobial polymer

From Wikipedia, the free encyclopedia
(Redirected from Antimicrobial polymers)

Antimicrobial polymers, also known as polymeric biocides, is a class of polymers with antimicrobial activity, or the ability to inhibit the growth of microorganisms such as bacteria, fungi or protozoans. These polymers have been engineered to mimic antimicrobial peptides which are used by the immune systems of living things to kill bacteria. Typically, antimicrobial polymers are produced by attaching or inserting an active antimicrobial agent onto a polymer backbone via an alkyl or acetyl linker. Antimicrobial polymers may enhance the efficiency and selectivity of currently used antimicrobial agents, while decreasing associated environmental hazards because antimicrobial polymers are generally nonvolatile and chemically stable. This makes this material a prime candidate for use in areas of medicine as a means to fight infection, in the food industry to prevent bacterial contamination, and in water sanitation to inhibit the growth of microorganisms in drinking water.[1]

Contents [hide]

Process [edit]

Antimicrobial agents kill bacteria through different methods depending on the type of bacteria. Most antiseptics and disinfectants kill bacteria immediately on contact by causing the bacterial cell to burst, or by depleting the bacteria's source of food preventing bacterial reproduction, also known as bacterial conjugation.[2] Antimicrobial polymers commonly kill bacteria through this first method, which is accomplished through a series of steps, shown in Figure 1.[1] First, the polymer must adsorb onto the bacterial cell wall. Most bacterial surfaces are negatively charged, therefore the adsorption of polymeric cations has proved to be more effective than adsorption of polymeric anions. The antimicrobial agent must then diffuse through the cell wall and adsorb onto the cytoplasmic membrane. Small molecule antimicrobial agents excel at the diffusion step due to their low molecular weight, while adsorption is better achieved by antimicrobial polymers.

The disruption of the cytoplasmic membrane and subsequent leakage of cytoplasmic constituents leads to the death of the cell. Comparison of small molecule antimicrobial agents and antimicrobial polymers are shown in the following table:[1]

Step	Small Molecule Antimicrobial Agents	Antimicrobial polymers
(1) Initial adsorption	Weak	Strong
(2) Diffusion past the cell wall	Strong	Weak
(3) Binding into the membrane	Weak	Strong
(4) Disruption and disintegration of the membrane	Weak	Strong

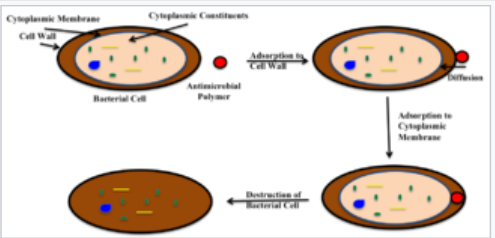


Figure 1: A schematic of how an antimicrobial polymer kills a bacterial cell

Factors that Affect Antimicrobial Activity [edit]

Molecular Weight [edit]

The molecular weight of the polymer is perhaps one of the most important properties to consider when determining antimicrobial properties because antimicrobial activity is markedly dependent on the molecular weight. It has been determined that optimal activity is achieved when polymers have a molecular weight in the range of $1.4x10^4$ Da to $9.4x10^4$ Da. Weights larger than this range show a decrease in activity. This dependence on weight can be attributed to the sequence of steps necessary for biocidal action. Extremely large molecular weight polymers will have trouble diffusing through the bacterial cell wall and cytoplasm. Thus much effort has been directed towards controlling the molecular weight of the polymer.[3]

Counter Ion [edit]

Most bacterial cell walls are negatively charged, therefore most antimicrobial polymers must be positively charged to facilitate the adsorption process. The structure of the counter ion, or the ion associated with the polymer to balance charge, also affects the antimicrobial activity. Counter anions that form a strong ion-pair with the polymer impede the antimicrobial activity because the counter ion will prevent the polymer from interacting with the bacteria. However, ions that form a loose ion-pair or readily dissociate from the polymer, exhibit a positive influence on the activity because it allows the polymer to interact freely with the bacteria.[4][5]

Spacer Length/Alkyl Chain Length [edit]

The spacer length or alkyl chain length refers to the length of the carbon chain that composes the polymer backbone. The length of this chain has been investigated to see if it affects the antimicrobial activity of the polymer. Results have generally shown that longer alkyl chains have resulted in higher activity. There are two primary explanations for this effect. Firstly, longer chains have more active sites available for adsorption with the bacteria cell wall and cytoplasmic membrane. Secondly, longer chains aggregate differently than shorter chains, which again may provide a better means for adsorption. However, shorter chain lengths diffuse more easily.[4][5]

Disadvantages [edit]

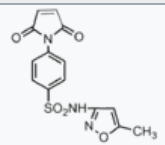
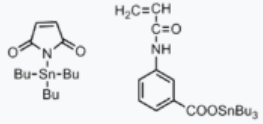
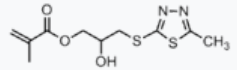
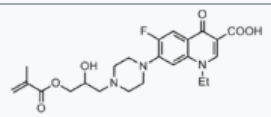
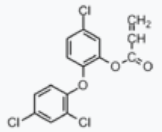
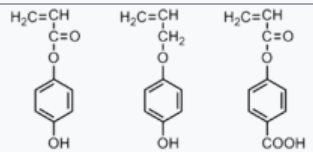
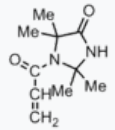
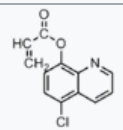
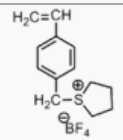
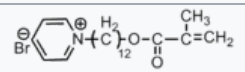
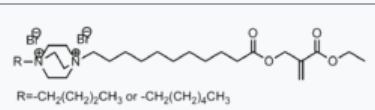
A major disadvantage of antimicrobial polymers is that macromolecules are very large and thus may not act as fast as small molecule agents. Biocidal polymers that require contact times on the order of hours to provide substantial reductions in pathogens, really have no practical value. Seconds, or minutes at most, should be the contact time goal for a real application. Furthermore, if the structural modification to the polymer caused by biocidal functionalization adversely affects the intended use, the polymer will be of no practical value. For example, if a fiber that must be exposed to aqueous bleach to render it antimicrobial (an N-halamine polymer) is weakened by that exposure, or its dye is bleached, it will have limited use.[1]

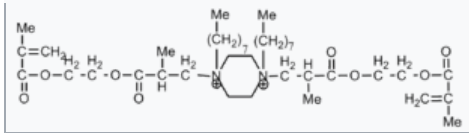
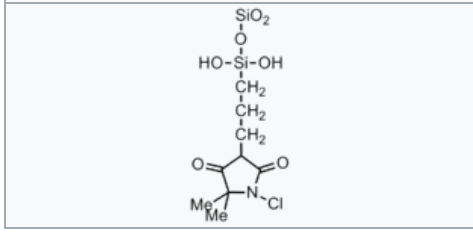
Synthetic Methods [edit]

Synthesis from Antimicrobial Monomers [edit]

This synthetic method involves covalently linking antimicrobial agents that contain functional groups with high antimicrobial activity, such as hydroxyl, carboxyl, or amino groups to a variety of polymerizable derivatives, or monomers before polymerization. The antimicrobial activity of the active agent may be either reduced or enhanced by polymerization. This depends on how the agent kills bacteria, either by depleting the bacterial food supply or through bacterial membrane disruption and the kind of monomer used. Differences have been reported when homo-polymers are compared to copolymers.[1] Examples of antimicrobial polymers synthesized from antimicrobial monomers are included in Table 2:

Table 2: Polymers Synthesized from Antimicrobial Monomers and their Antimicrobial Properties

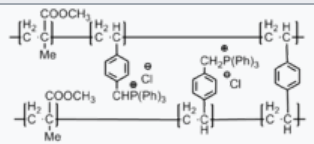
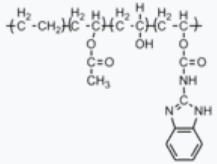
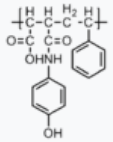
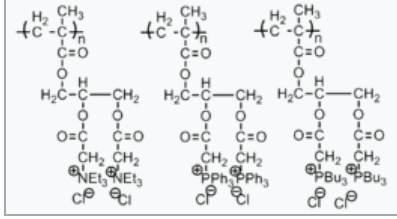
Monomer	Inhibited Microbial Species	Antimicrobial Mechanism	Comparison of Polymers with Monomer
	**Fungus**: C. albicans; A. niger	Slow release of 4-amino-N-(5-methyl-3-isoxazoly)benzenesulfonamide	The homopolymer is more effective than the monomer at all concentrations.[6]
	**Bacteria**:Gram-positive; Gram-negative	Tin moiety on the polymer surface interacts with the cell wall.	Copolymerization of antimicrobial monomer and styrene decreases the potency of the monomer.[7]
	**Bacteria**:S. aureus; P. aeruginosa; E. coli;	The presence of benzimidazole derivatives inhibit cytochrome P-450 monooxygenase	The homopolymer is more effective than the monomer.[8]
	**Bacteria**:Gram-positive; Gram-negative	Release of norfloxacin which inhibits bacterial DNA gyrase and cell growth.[9]	----
	**Bacteria**:Pseudomonas aeruginosa;Staphylococcus	Active agent is 2,4,4'-trichloro-2'-hydroxydiphenyl-ether	The homopolymer and copolymers with methyl methacrylate, styrene are all less effective than the monomer.[10]
	**Bacteria**:S. aureus; P. aeruginosa;	Active agent is phenol group.	Polymerization significantly decreases the anitimicriobial activity of the monomers.[11]
	**Bacteria**:E-coli	Direct transfer of oxidative halogen from polymer to the cell wall of the organism.[12]	----
	**Bacteria**:E. coli;S. aureus; S. typhimurium	Release of 8-hydroxyquinoline moieties	The homopolymer and the copolymers with acrylamide are both less effective than the monomer.[13]
	**Bacteria**:Gram-positive bacteria	Active agent is Sulfonium salt	The homopolymer is more effective than the corresponding model compound (p-ethylbenzyl tetramethylene sulforium tetrafluoroborate).[14]
	**Bacteria**: Oral streptococci	Direct cationic binding to cell wall, which leads to the disruption of the cell wall and cell death.[15]	----
	**Bacteria**: S. aureus; E-coli	Cationic biocides targets the cytoplasmic membranes; Similarities of the polymer pendent groups and the lipid layer enhances diffusion into the cell wall	The monomers are not active, while homopolymers show moderate activities in concerntration from 1 mg/mL to 3.9 mg/mL.[16]

	**Bacteria**: S. aureus; E. coli	Membrane disruption[17]	----
	**Bacteria**: Staphylococcus;E. coli	Immobilization of high concentrations of chlorine to enable rapid biocidal activities and the liberation of very low amounts of corrosive free chlorine into water[18]	----

Synthesis by Adding Antimicrobial Agents to Preformed Polymers [edit]

This synthetic method involves first synthesizing the polymer, followed by modification with an active species. The following kinds of monomers are usually used to form the backbone of homopolymers or copolymers: vinylbenzyl chloride, methyl methacrylate, 2-chloroethyl vinyl ether, vinyl alcohol, maleic anhydride. The polymers are then activated by anchoring antimicrobial species, such as phosphonium salts, ammonium salts, or phenol groups via quaternization, substitution of chloride, or hydrolysis of anhydride.[1] Examples of polymers synthesized from this method are provided in Table 3:

Table 3: Antimicrobial Polymers Synthesized from Preformed Polymers and Antimicrobial Properties

Polymer	Inhibited Microbial Species	Antimicrobial Mechanism
	**Fungus**: Candida albicans; Aspergillus flavus; **Bacteria**: S. aureus; E. coli; B. subtilis; Fusarium oxysporum	Active group: Phosphonium groups.[6]
	**Fungus**: Aspergillus fumigatus; Penicillium pinophilum	The release of m- 2-benzimidazolecarbamoyl moiety.[19]
	**Bacteria**: E. coli; S. aureus	Active groups: phenolic hydroxyl group.[20]
	Bacteria: E. coli; S. aureus	Active group: Quaternary ammonium group.[21]
	**Fungus**: Trichophyton rubrum; **Bacteria**: Gram-negative bacteria	Active groups: Phosphonium and quaternary ammonium groups.[22]

Synthesis by Adding Antimicrobial Agents to Naturally Occurring Polymers [edit]

Chitin is the second-most abundant biopolymer in nature. The deacetylated product of chitin—chitosan has been found to have antimicrobial activity without toxicity to humans. This synthetic technique involves making chitosan derivatives to obtain better antimicrobial activity. Currently, work has involved the introduction of alkyl groups to the amine groups to make quaternized N-alkyl chitosan derivatives, introduction of extra quaternary ammonium grafts to the chitosan, and modification with phenolic hydroxyl moieties. An example is shown in Figure 2.[23]

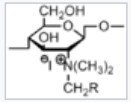


Figure 2. Quaternized N-alklyl Chitosan

Synthesis by insertion of antimicrobial agents into polymer backbone [edit]

This method involves using chemical reactions to incorporate antimicrobial agents into the polymeric backbones. Polymers with biologically active groups, such as polyamides, polyesters, and polyurethanes are desirable as they may be hydrolyzed to active drugs and small innocuous molecules. For example, a series of polyketones have been synthesized and studied, which show an inhibitory effect on the growth of B. subtilis and P. fluorescens as well as fungi, A. niger and T. viride. There are also studies which incorporate antibiotics into the backbone of the polymer, as shown in Figure 3.[24]

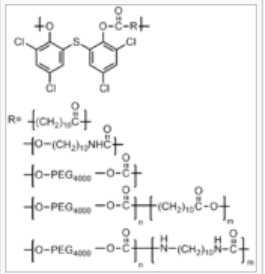


Figure 3. Incorporation of Bithionol into the Polymer Backbone

Requirements of an antimicrobial polymer [edit]

In order for an antimicrobial polymer to be a viable option for large-scale distribution and use there are several basic requirements that must be first fulfilled:

- The synthesis of the polymer should be easy and relatively inexpensive. To be produced on an industrial scale the synthetic route should ideally utilize techniques that have already been well developed.
- The polymer should have a long shelf life, or be stable over long periods of time. It should be able to be stored at the temperature for which it is intended for use.
- If the polymer is to be used for the disinfection of water, then it should be insoluble in water to prevent toxicity issues (as is the case with some current small molecule antimicrobial agents).
- The polymer should not decompose during use, or emit toxic residues.
- The polymer should not be toxic or irritating to those during handling.
- Antimicrobial activity should be able to be regenerated upon loss of activity.
- Antimicrobial polymers should be biocidal to a broad range of pathogenic microorganisms in brief times of contact.[1]

Applications [edit]

Water treatment [edit]

Polymeric disinfectants are ideal for applications in hand-held water filters, surface coatings, and fibrous disinfectants, because they can be fabricated by various techniques and can be made insoluble in water. The design of insoluble contact disinfectants that can inactivate, kill, or remove target microorganisms by mere contact without releasing any reactive agents to the bulk phase being disinfected is desired. Chlorine or water-soluble disinfectants have problems with the residual toxicity, even if minimal amounts of the substance used.[25] Toxic residues can become concentrated in food, water, and in the environment. In addition, because free chlorine ions and other related chemicals can react with organic substances in water to yield trihalomethane analogues that are suspected of being carcinogenic, their use should be avoided. These drawbacks can be solved by the removal of microorganisms from water with insoluble substances.[26][27]

Food applications [edit]

Antimicrobial substances that are incorporated into packaging materials can control microbial contamination by reducing the growth rate and the maximum growth population. This is done by extending the lagphase of the target microorganism or by inactivating the microorganisms on contact.[28] One of these applications is to extend the shelf life of food and promote safety by reducing the rate of growth of microorganisms when the package is in contact with the surfaces of solid foods, for example, meat, cheese, etc. Second, antimicrobial packaging materials greatly reduce the potential for recontamination of processed products and simplify the treatment of materials to eliminate product contamination. For example, self-sterilizing packaging might eliminate the need for peroxide treatment in aseptic packaging. Antimicrobial polymers can also be used to cover surfaces of food processing equipment as self-sanitizer. Examples include filter gaskets, conveyors, gloves, garments, and other personal hygiene equipment.

Some polymers are inherently antimicrobial and have been used in films and coatings. Cationic polymers such as chitosan promote cell adhesion.[29] This is because charged amines interact with negative charges on the cell membrane, and can cause leakage of intracellular constituents. Chitosan has been used as a coating and appears to protect fresh vegetables and fruits from

fungal degradation. Although the antimicrobial effect is attributed to antifungal properties of chitosan, it may be possible that the chitosan acts as a barrier between the nutrients contained in the produce and microorganisms.[30]

Medicine and healthcare [edit]

Antimicrobial polymers are powerful candidates for controlled delivery systems and implants in dental restorative materials because of their high activities. This can be ascribed to their characteristic nature of carrying a high local charge density of active groups in the vicinity of the polymer chains. For example, electrospun fibers containing tetracycline hydrochloride based on poly(ethylene-co-vinyl acetate), poly(lactic acid), and blending were prepared to use as an antimicrobial wound dressing.[31][32] Cellulose derivatives are commonly used in cosmetics as skin and hair conditioners. Quaternary ammonium cellulose derivatives are of particular interest as conditioners in hair and skin products.

Future work in this field [edit]

The field of antimicrobial polymers has progressed steadily, but slowly over the past years, and appears to be on the verge of rapid expansion. This is evidenced by a broad variety of new classes of compounds that have been prepared and studied in the past few years. Modification of polymers and fibrous surfaces, and changing the porosity, wettability, and other characteristics of the polymeric substrates, should produce implants and biomedical devices with greater resistance to microbial adhesion and biofilm formation. A number of polymers have been developed that can be incorporated into cellulose and other materials, which should provide significant advances in many fields such as food packaging, textiles, wound dressing, coating of catheter tubes, and necessarily sterile surfaces. The greater need for materials that fight infection will give incentive for discovery and use of antimicrobial polymers.[1]

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