

Method for Imparting Antibiotic Activity to the Surface of a Solid Substrate

Background of the Invention

5 Quaternary ammonium salts (quats) are well known for their antimicrobial activity and/or anti-septic activity. As a result, quaternary ammonium groups have been incorporated into various chemical structures. For example, U.S. Patent No. 6,251,967 to Perichaud, et al. disclose a method for making a non-cross-linked polymer from monomers containing a quaternary ammonium group.

10 There is also a great deal of interest in finding effective and efficient ways of attaching compounds containing quaternary ammonium groups onto solid substrates. U.S. Patent Application Publication No. 2005/0095266 to Perichaud et al. discloses a method for treating the surface of a solid substrate involving photopolymerization and covalent grafting of monomers containing
15 an antibiotic group to a solid substrate using photoprimers and grafting agents. The photopolymerization and covalent grafting occurs upon exposure of the solid substrate and a formulation containing the monomers to ultraviolet radiation.

20 However, the use of ultraviolet radiation has its limitations. For instance, ultraviolet radiation only penetrates a portion of a solid substrate, *e.g.*, a fabric, resulting in only the surface of the fabric being coated with the antibiotic polymer.

There remains a need for attaching an antibiotic polymer to a solid substrate so that the solid substrate will have layers of antimicrobial and/or antiseptic activity.

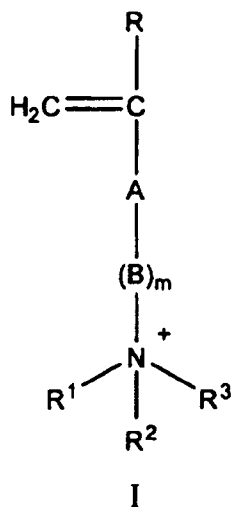
Summary of the Invention

The present invention relates to a method for imparting antibiotic activity to a surface of a solid substrate, comprising the steps of:

30 a) contacting the solid substrate with a composition comprising one or more antibiotic monomers Q_jX^{j-} wherein:

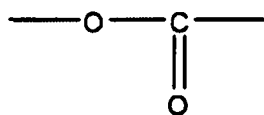
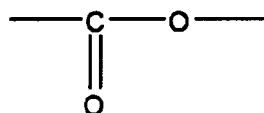
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Q represents a quaternary ammonium ion having formula (I):

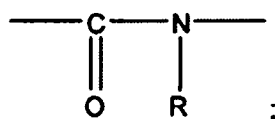


wherein:

A represents



or



R independently represents H or CH₃;

B represents a linear or branched C₁₋₅ alkanediyl chain; or an arylene or arylalkanediyl group;

m represents 0 or 1;

R¹ and R² independently represent a C₁₋₅ alkyl group;

R³ represents a C₈₋₂₀ alkyl group, an aryl group, or an arylalkyl group; and

X^{j-} represents an anion having valence j;

to form a solid substrate composition; and

b) exposing the solid substrate composition to conditions suitable for covalent grafting and thermal polymerization of the substrate.

For a better understanding of the present invention, together with other and further advantages, reference is made to the following detailed description, and its scope will be pointed out in the claims.

5 **Detailed Description**

The invention relates to a method for imparting antibiotic activity to a solid surface. Antibiotic activity includes any antimicrobial or antiseptic activity, *e.g.*, antibacterial activity, anti-fungal activity, and anti-yeast activity. Antibiotic activity includes activity that either stops or slows
10 the growth of, or kills, a microbe, *e.g.*, biocidal or biostatic activity.

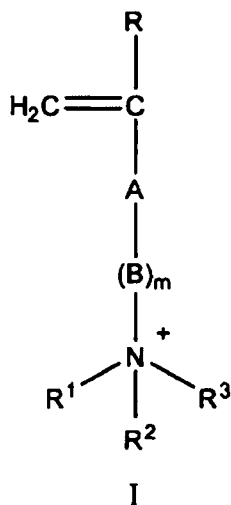
The solid substrate can be any solid, porous or non-porous material. Examples of solid substrates include, but are not limited to, non-woven or woven textiles made from synthetic or natural fibers or threads, cleaning wipes, plastic, medical gauze or bandages, water filtration
15 media, ceramic, glass, diatomaceous earth, sand, filter cartridges, diapers, medical or surgical masks, clothing, sponges, brushes, cellulose, wood, surfaces of pharmaceutical clean rooms, and bathroom surfaces such as walls, ceilings, floors, doors, flush handles, and toilet seats.

The method involves the steps of: a) contacting the solid substrate with a composition comprising one or more monomers Q_jX^{j-} wherein Q represents a quaternary ammonium ion having formula (I) to form a solid substrate composition and b) exposing the solid substrate composition to conditions suitable for covalent grafting and thermal polymerization of the substrate. Suitable conditions for covalent grafting and thermal polymerization include, but are not limited to, the use of an initiator and the pre-treating of the substrate either with a corona treatment or plasma discharge treatment. Corona treatments and plasma discharge treatments may
25 impart better grafting.

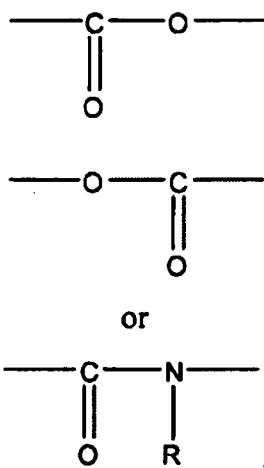
The solid substrate is contacted with the monomer composition by any means possible. Some examples of contacting the solid substrate with the monomer composition include introducing
30 the solid substrate into a solution of the monomer composition or spraying the monomer composition onto the solid substrate.

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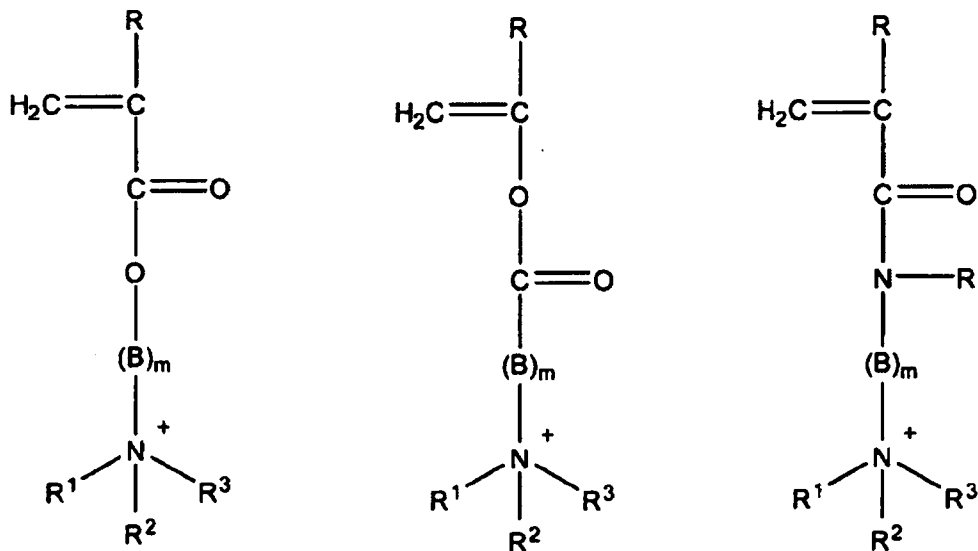
The quaternary ammonium ion of formula (I) is shown below:



In formula (I) A represents:



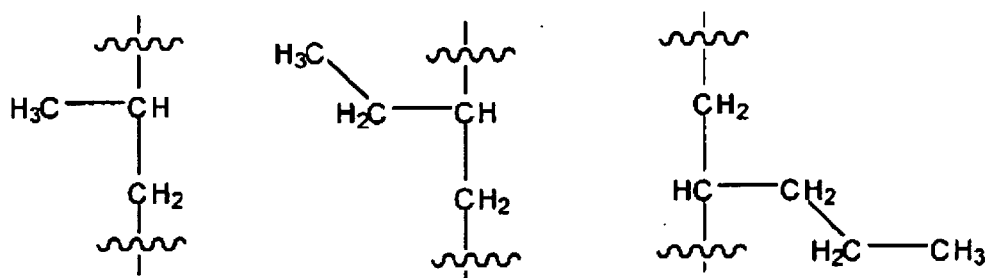
In the three possible structures for A shown above, the left side of the structure as shown is attached to the vinyl group ($\text{H}_2\text{C}=\text{CR}-$) and the right side of the structure as shown is attached to B. Therefore, the three possibilities for A in formula (I) are shown below:



In formula (I), R independently represents H or CH₃.

In $-(B)_m-$, m represents 0 or 1. B represents a linear or branched C₁₋₅ alkanediyl chain; or an arylene or arylenealkanediyl group. A linear C₁₋₅ alkanediyl chain may be represented as $-(CH_2)_n-$, where $n = 1$ to 5. Therefore, an alkanediyl chain is bonded independently at each end to another chemical moiety, *e.g.*, to a group, or to an atom. In a preferred embodiment, m is 1 and B represents at least a linear C₂ alkanediyl chain so that at least two carbon atoms separate A from the nitrogen of the ammonium ion.

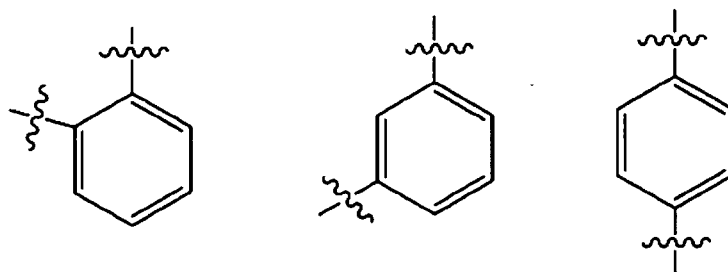
Examples of branched C₁₋₅ alkanediyl chains are shown below:



When m is 0, group A is directly connected to the nitrogen of the quaternary ammonium group. Preferably, the letter m is 1.

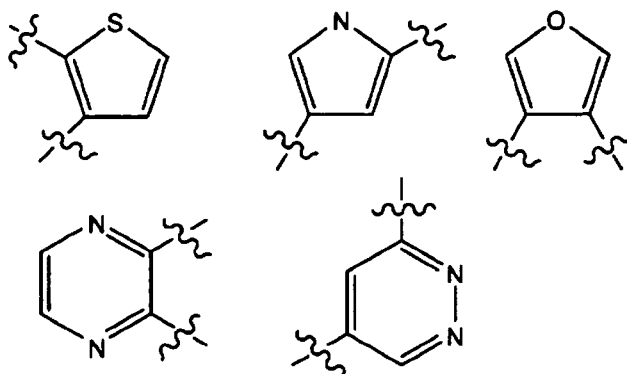
Arylenyl groups are aromatic groups bonded independently to two chemical moieties, *e.g.*, to a group, or to an atom, and may be represented as $-Ar-$ wherein Ar is a phenylene or heterocycloarylenyl group.

The arylene groups may be bonded to two chemical moieties at any two positions of the aromatic ring. For example, possible phenylene groups are shown below:

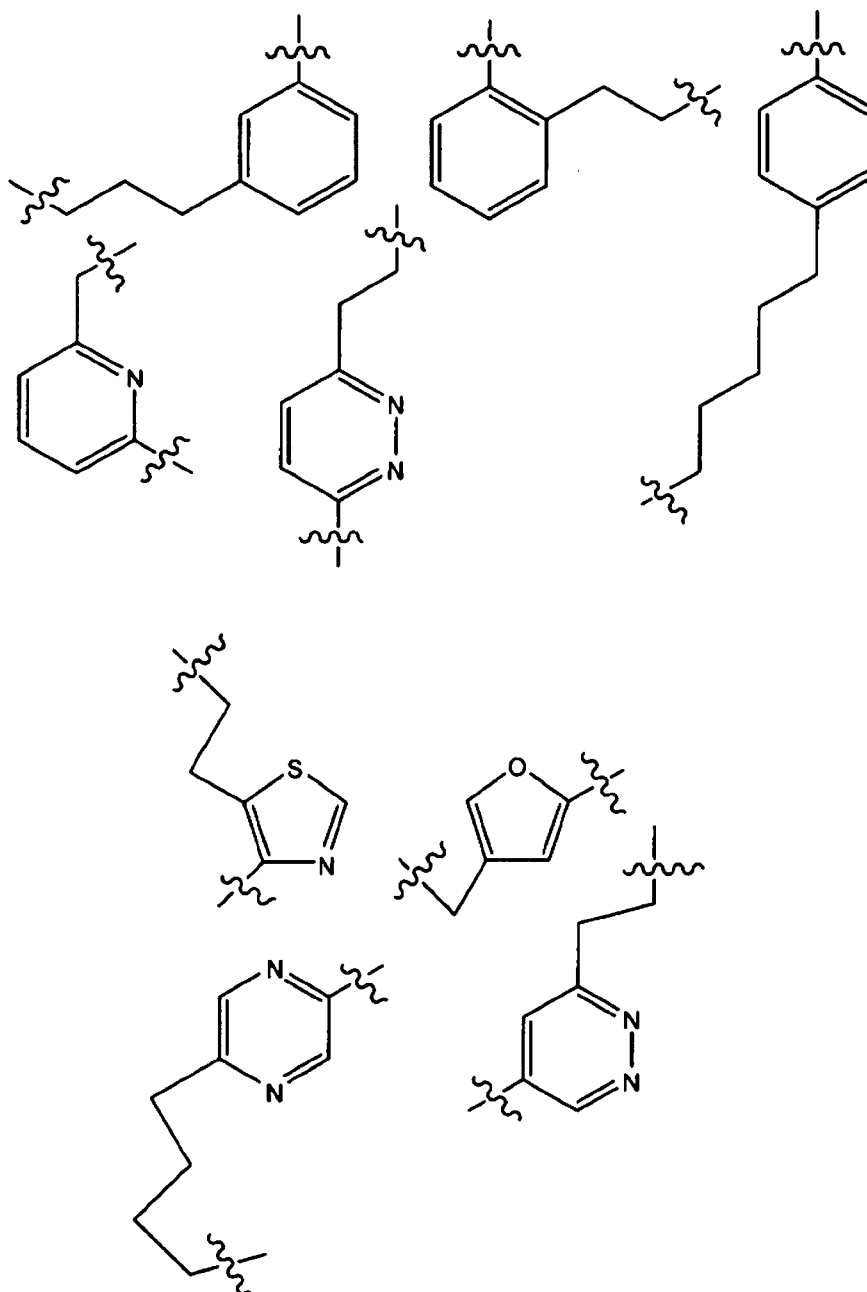


Heterocyclic arylene groups contain rings with 5 to 6 ring members having one to three heteroatoms selected from $-O-$, $-S-$, $=N-$, or $-NR^4-$, wherein R^4 represents hydrogen, methyl, or ethyl. Examples of heterocyclic arylene groups include thiophenylene, furylene, pyrrolylene, pyrazinylene, pyrimidinylene, imidazolylene, oxazolylene, and pyrimidinylene. For example, possible heterocyclic arylene groups are shown below:

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Arylenylalkanediyl groups contain any of the arylene groups described above bonded to any of the alkanediyl groups described above, and may be in either direction, *e.g.*, $-\text{Ar}-(\text{CH}_2)_n-$ or $-(\text{CH}_2)_n-\text{Ar}-$. Examples of arylenealkanedyl groups are shown below:



R^1 and R^2 independently represent a saturated and linear or branched C_{1-5} alkyl group. Examples of C_{1-5} alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert*-butyl, and pentyl.

- 5 R^3 represents a C_{8-20} hydrocarbyl group, an aryl group, a hydrocarbylaryl group, or an aryl-hydrocarbyl group. The hydrocarbyl groups may be saturated (alkyl) or unsaturated (alkenyl). Examples of saturated C_{8-20} alkyl groups include octyl, decyl, dodecyl, tridecyl, and icosanyl. Examples of unsaturated C_{8-20} alkenyl groups include 5-octenyl, oleyl, linoleyl, linolenyl, and elaidolinolenyl.

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Aryl groups may be carbocyclic or heterocyclic. A carbocyclic aryl group is phenyl. Heterocyclic aryl (heteroaryl) groups contain rings with 5 to 6 ring members having one to three heteroatoms selected from $-O-$, $-S-$, $=N-$, or $-NR^4-$, wherein R^4 represents hydrogen, methyl, or ethyl. Examples of heterocyclic aryl groups include thiophenyl, furyl, pyrrolyl,

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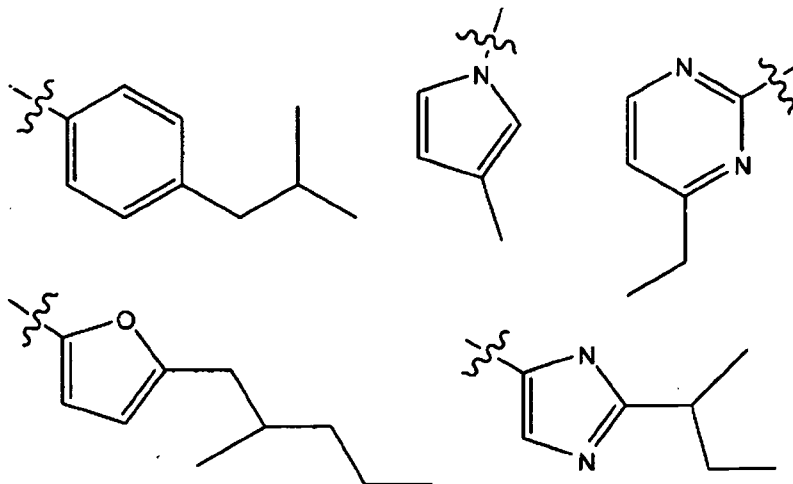
pyrazinyl, pyrimidinyl, imidazolyl, oxazolyl, and pyrimidinyl.

Hydrocarbylaryl and aryhydrocarbyl groups contain an aryl or arylenyl group bonded to a saturated, branched or linear C_{1-5} alkyl chain or group. Examples of aryhydrocarbyl groups are shown below:

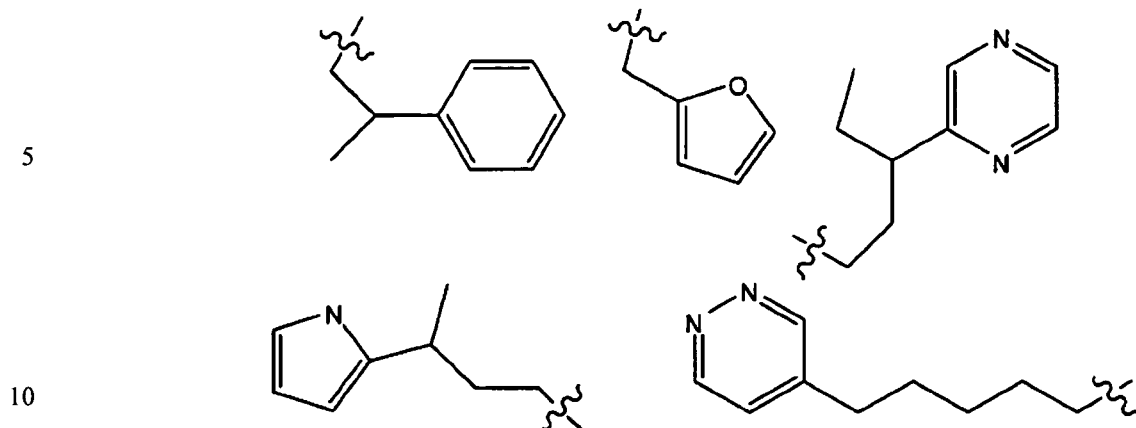
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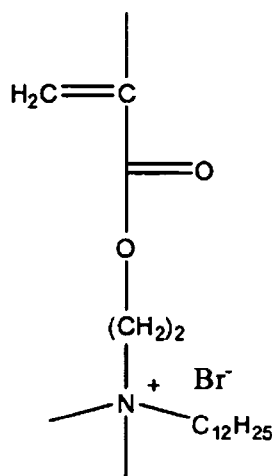


Examples of hydrocarbaryl groups are shown below:



X represents an anion having valence j . Examples of anions include halogenides, sulfate, phosphate, nitrate, cyanide, or organic anions such as *p*-toluenesulfonate (tosylate), salicylate, benzoate, acetate, or undecylenate. The letter j may represent, for example, 1, 2, or 3.

In a preferred embodiment, the monomer Q_jX^{j-} is:



In another preferred embodiment, m in formula I is 1.

In still another preferred embodiment, B in formula I is a linear C_2 alkanediyl chain.

The solid substrate composition is exposed to conditions suitable for covalent grafting and thermal polymerization of the substrate. Such conditions are well known to a person having ordinary skill in the art. For example, a convenient minimum temperature for thermal polymerization is at least about 60 °C, more preferably at least about 80 °C. A convenient maximum temperature for thermal polymerization is at most about 150 °C, more preferably at most about 130 °C. Furthermore, the solid substrate composition may be exposed to conditions

suitable for covalent grafting and thermal polymerization for a least about 5 minutes and at most about 30 minutes.

The anion X^{j-} is preferably a halide, *i.e.*, Cl^- , Br^- , F^- , or I^- , wherein j is 1.

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The solid substrate composition may further comprise i) one or more monomers or oligomers selected from the group consisting of acrylate, epoxide, and vinyl ether monomers or oligomers suitable for copolymerization with the antibiotic monomer; and ii) one or more radical initiators suitable for thermal polymerization.

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An oligomer is comprised of two or more monomers. The maximum number of monomers contemplated for the oligomers of the invention is eight.

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Acrylate, epoxide, and vinyl ether monomers or oligomers suitable for copolymerization with the antibiotic monomer are well-known in the art. For example, U.S. Patent Application Publication No. 2005/0095266 to Perichaud et al. discloses examples of suitable acrylate, epoxide, and vinyl ether monomers and oligomers in paragraphs 137–152. Preferred acrylate monomers include 1,6-hexanediol diacrylate and bisphenol A ethoxydiacrylate.

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Radical initiators suitable for thermal polymerization are well-known in the art. Examples of suitable radical initiators include peroxy compounds such as *tert*-amyl peroxybenzoate; 4,4'-azobis(4-cyanovaleric acid); 2,2'-azobisisobutyronitrile; benzoyl peroxide; 2,2-bis(*tert*-butylperoxy)butane; 1,1-bis(*tert*-butylperoxy)cyclohexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne; bis(1-(*tert*-butylperoxy)-methylethyl)benzene; 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane; *tert*-butyl hydroperoxide; *tert*-butyl peracetate; *tert*-butyl peroxide; *tert*-butyl peroxybenzoate; *tert*-butylperoxy isopropyl carbonate; cumene hydroperoxide; cyclohexanone peroxide; dicumyl peroxide; lauroyl peroxide; 2,4-pentanedione peroxide; peracetic acid; and potassium persulfate.

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30 Most preferably, the radical initiator is benzoyl peroxide.

The solid substrate composition may further comprise iii) one or more grafting agents. Grafting agents are well-known in the art. For example, grafting agents are described in U.S. Patent Application Publication No. 2005/0095266 to Perichaud et al. in paragraphs 99–132.

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According to a preferred embodiment, the solid substrate composition is pretreated with a corona treatment or plasma discharge treatment in order to impart better grafting.

In a preferred embodiment the solid substrate is porous.

According to another preferred embodiment the solid substrate is a non-woven or woven textile.

5 Preferred examples of non-woven textiles are cleaning wipes.

According to another preferred embodiment the solid substrate comprises a plastic material. Examples of plastic materials are polyolefines such as polyethylene or polypropylene, polyesters such as polyethylene terephthalate, polyacrylates, polystyrene, polyamides, or
10 copolymers thereof.

According to still another preferred embodiment the solid substrate is a medical gauze or bandage.

15 In another preferred embodiment the solid substrate is a water filtration medium, for example for potable or industrial water.

Preferred water filtration media comprise materials such as plastics, ceramics, glass, diatomaceous earth, sand, or combinations thereof.

20 Another preferred application in water filtration media is in filter cartridges.

Diapers are another preferred type of solid substrates.

25 Still another preferred application of the solid substrates treated according to the invention comprises medical or surgical masks and respirators.

Surfaces used in pharmaceutical clean rooms are another preferred field of use of the solid substrates treated according to the present invention.

30 Still another preferred application of the solid substrates treated according to the present invention are surfaces used in bathrooms.

Examples of such surfaces in bathrooms are walls, ceilings, floors, doors, toilet seats, and flush
35 handles.

The compounds Q_jX^{j-} can be synthesized by methods well known in the art. For example, U.S. Patent No. 6,251,967 to Perichaud et al., discusses the synthesis of quaternary ammonium salts at cols. 5–10.

5 In this specification, groups of various parameters containing multiple members are described. Within a group of parameters, each member may be combined with any one or more of the other members to make additional sub-groups. For example, if the members of a group are a, b, c, d, and e, additional sub-groups specifically contemplated include any two, three, or four of the members, *e.g.*, a and c; a, d, and e; b, c, d, and e; etc.

10 In some cases, the members of a first group of parameters, *e.g.*, a, b, c, d, and e, may be combined with the members of a second group of parameters, *e.g.*, A, B, C, D, and E. Any member of the first group or of a sub-group thereof may be combined with any member of the second group or of a sub-group thereof to form additional groups, *i.e.*, b with C; a and c with B, D, and
15 E, etc.

For example, in the present invention, groups of various parameters are defined (*e.g.* Q, A, R, B, R^1 , R^2 , R^3 , and X). Each group contains multiple members. For example, R^3 represents a C_{8-20} alkyl group, an aryl group, or an arylalkyl group. Each member may be combined with each
20 other member to form additional sub-groups, *e.g.*, C_{8-20} alkyl group and aryl group, aryl group and arylalkyl group, and C_{8-20} alkyl group and arylalkyl group.

The instant invention further contemplates embodiments in which each element listed under one group may be combined with each and every element listed under any other group. For example,
25 R^1 and R^2 are identified above as independently representing a C_{1-5} alkyl group. R^3 is identified above as independently representing a C_{8-20} alkyl group, an aryl group, or an arylalkyl group. Each element of R^1 and R^2 (a C_{1-5} alkyl group) can be combined with each and every element of R^3 (a C_{8-20} alkyl group, an aryl group, or an arylalkyl group). For example, in one embodiment, R^1 may be a propyl group; R^2 may be a pentyl group; and R^3 may be an aryl group.
30 Alternatively, R^1 may be a methyl group; R^2 may be an ethyl group; and R^3 may be an arylalkyl group. Similarly, a third group is B, in which the elements are defined as a linear or branched C_{1-5} alkanediyl chain; or an arylene or arylalkanediyl group. Each of the above embodiments may be combined with each and every element of B. For example, in the embodiment wherein R^1 is a butyl group; R^2 is a methyl group; R^3 is an octyl group; and B may be an arylene group
35 (or any other chemical moiety within the element of B).

With each group, it is specifically contemplated that anyone of more members can be excluded. For example, if radical initiators are defined as *tert*-amyl peroxybenzoate; 4,4-azobis(4-cyano-

valeric acid); 2,2'-azobisisobutyronitrile; benzoyl peroxide; 2,2-bis(*tert*-butylperoxy)butane; 1,1-bis(*tert*-butylperoxy)cyclohexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne; bis(1-(*tert*-butylperoxy)-methylethyl)benzene; 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane; *tert*-butyl hydroperoxide; *tert*-butyl per-
 5 acetate; *tert*-butyl peroxide; *tert*-butyl peroxybenzoate; *tert*-butylperoxy isopropyl carbonate; cumene hydroperoxide; cyclohexanone peroxide; dicumyl peroxide; lauroyl peroxide; 2,4-pentanedione peroxide; peracetic acid; and potassium persulfate; it is also contemplated that radical initiators are defined as *tert*-amyl peroxybenzoate; *tert*-butyl hydroperoxide; and lauroyl peroxide.

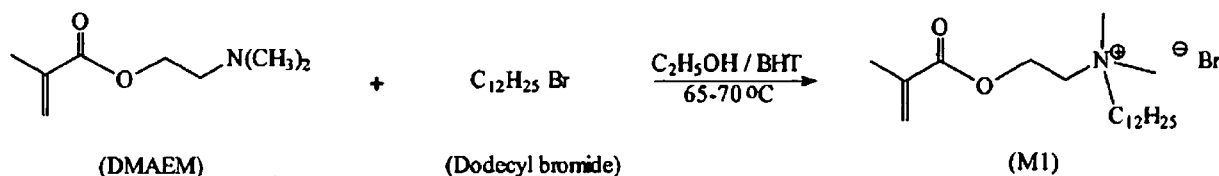
The compounds of this invention are limited to those that are chemically feasible and stable. Therefore, a combination of substituents or variables in the compounds described above is permissible only if such a combination results in a stable or chemically feasible compound. A stable compound or chemically feasible compound is one in which the chemical structure is not
 15 substantially altered when kept at a temperature of 40 °C or less, in the absence of moisture or other chemically reactive conditions, for at least a week.

A list following the word "comprising" is inclusive or open-ended, *i.e.*, the list may or may not include additional unrecited elements. A list following the words "consisting of" is exclusive or closed ended, *i.e.*, the list excludes any element not specified in the list.

Examples

Example 1

The synthesis of the antimicrobial monomer M1 is as follows:



A 1% aqueous solution of the monomer M1 was made by dissolving 5 g of monomer M1 into 494.25 g of deionized water. In a separate beaker, a mixture containing 9.9 g of 1,6-hexanediol diacrylate and 0.1 g of benzoyl peroxide was sonicated for 10 minutes in order to dissolve the
 35 benzoyl peroxide. Once the benzoyl peroxide was dissolved, 0.75 g of this mixture was added to the 1% monomer M1 solution and mixed (using a magnetic stir bar). The solution was hazy at this point. While continuing to mix, a plastic pipette was used to extract some of the liquid.

The liquid in the pipette was then transferred to a dry wipe substrate. The amount added was such as to deliver a 3% concentration of monomer M1 to the wipe substrate. For example, a dry wipe weighs approximately 2 g. By adding 6 g of the monomer M1 solution to the wipe, 3% by weight of monomer M1 was added to the wipe.

5

Once the liquid was added to the wipe substrate, it had to be heated to at least 80 °C and dried completely. An oven set at 80 °C was used to dry the substrate.

10 The prepared samples were then evaluated using the American Association of Textile Chemists and Colorists test method AATCC 100-2004. A mixed bacteria culture was used.

Bacterial Counts (CFU/gram)

<u>Sample #</u>	<u>Test Samples</u>	<u>Day 0</u>	<u>24 Hrs</u>	<u>Day 7</u>
1	Monomer M1 on Wipes	4.7×10^6	1.0×10^3	<100
2	Untreated Control Wipes	5.1×10^6	1.3×10^7	1.5×10^8

15 Bacterial Inoculum: 7.0×10^6

Example 2

20 The antimicrobial monomer M1-C12 can then be converted into a polymer either via UV curing or thermal techniques. The antimicrobial activity of the monomer is maintained even after polymerization. M1-C12 is only one of many monomers that can be made having antimicrobial properties. See Appendix A for list of other examples of monomers that can be used.

25 The polymerization and grafting of the monomers can be achieved either through UV or thermal techniques. For this application (applied to either medical gauze or bandages), the preferred technique is by thermal polymerization and grafting. This is because it is desirable to have the polymer grafted throughout the substrate. UV techniques would only produce grafted polymer on the surface of the substrate. UV techniques are more desirable for solid surfaces where a coating of the surface is only needed.

30

In the study described below, benzoyl peroxide was used as the initiator for polymerizing and grafting the monomer to the medical gauze or bandage. Benzoyl peroxide is not soluble in Monomer M1-C12, so 1,6-hexanediol diacrylate (Miramer M200) was used as a co-monomer to solubilize the benzyl peroxide. A 1% benzyl peroxide in 1,6-hexanediol diacrylate was made.

The Monomer M1-C12 (0.8 g) was dissolved in deionized water (199.1 g). To this mixture, 0.1 g of the 1% benzoyl peroxide in 1,6-hexanediol diacrylate was added.

A total of 2.5 g of the above described mixture was absorbed onto a piece of medical gauze (Johnson & Johnson's FirstAid® brand) weighing 0.9 g. The gauze was then dried in a microwave oven for 5 minutes in order to dry off the excess moisture and bring the temperature of the gauze to above 80 °C in order to initiate the polymerization reaction. A total of three samples were prepared using the same procedure. Samples of bandages (Johnson & Johnson's Band-Aid® brand) were prepared by absorbing 1.5 g of the above described mixture onto a piece of bandage weighing 0.6 g. The bandage was then dried in a microwave oven for 5 minutes in order to dry off the excess moisture and bring the temperature of the gauze to above 80 °C in order to initiate the polymerization reaction. A total of three samples were prepared using the same procedure.

Test method AATCC 100 was used to evaluate the antimicrobial properties of the treated medical gauze and bandages. The table below summarizes the performance against *S. aureus*.

Organism Counts (CFU)

<u>Sample Reduction</u>	<u>Time = 0</u>	<u>Time = 24 Hours</u>	<u>Log Reduction</u>	<u>%</u>
Untreated Gauze	3.0×10^7	3.0×10^8	NA	NA
Treated Gauze	2.7×10^7	7.8×10^3	4.59	99.997
Untreated Band-Aid®	3.0×10^7	3.0×10^8	NA	NA
Treated Band-Aid®	3.0×10^7	<100	6.48	99.999

Example 3

The antimicrobial monomer M1-C12 can then be converted into a polymer either via UV curing or thermal techniques. The antimicrobial activity of the monomer is maintained even after polymerization. M1-C12 is only one of many monomers that can be made having antimicrobial properties. See Appendix A for list of other examples of monomers that can be used.

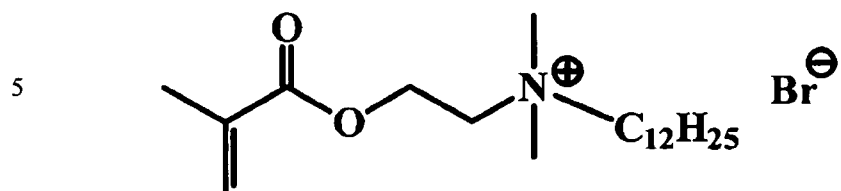
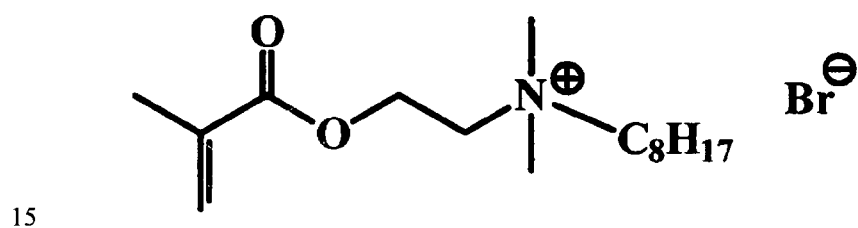
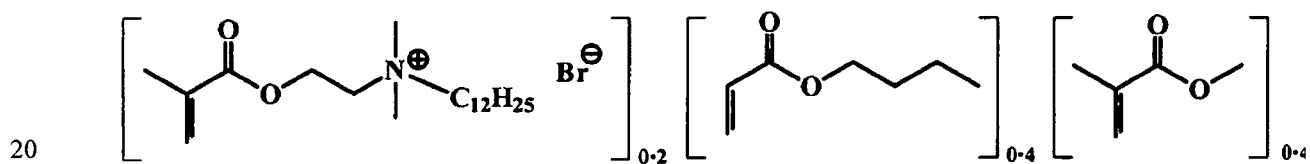
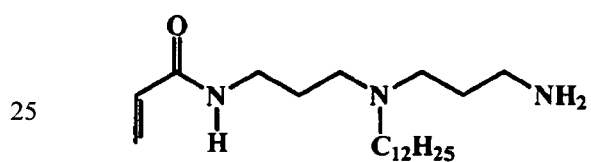
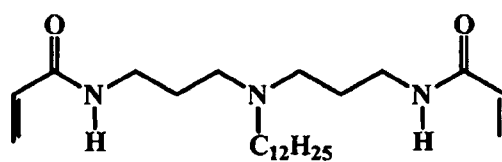
The polymerization and grafting of the monomers can be achieved either through UV or thermal techniques.

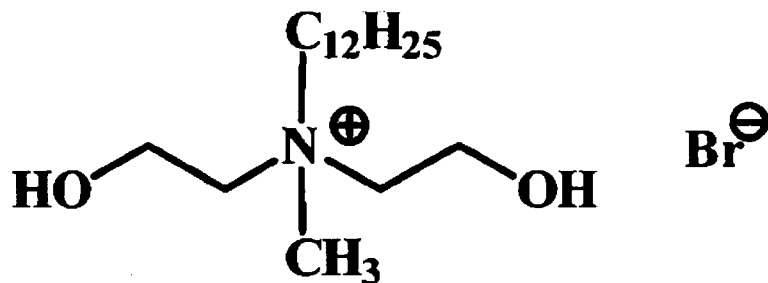
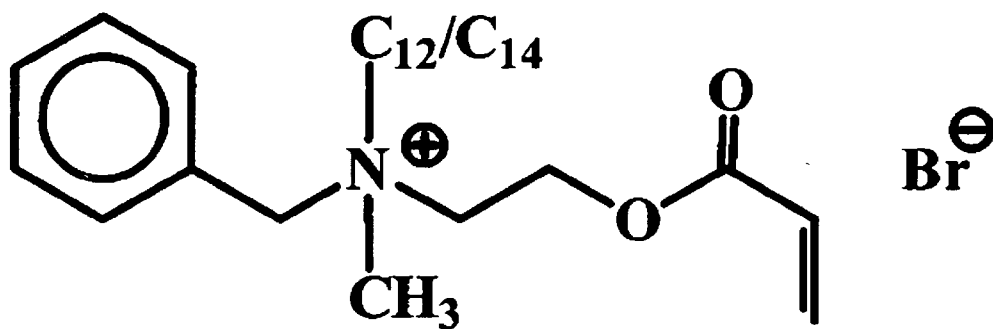
In the method described below, benzoyl peroxide was used as the initiator for polymerizing and grafting the monomer to sand. Benzoyl peroxide is not soluble in Monomer M1-C12, so 1,6-hexanediol diacrylate (Miramer M200) was used as a co-monomer to solubilize the benzoyl peroxide. A 1% benzoyl peroxide solution in 1,6-hexanediol diacrylate was made. The

Monomer M1-C12 (0.8 g) was dissolved in deionized water (199.1 g). To this mixture, 0.1 g of the 1% benzoyl peroxide solution in 1,6-hexanediol diacrylate was added.

5 A total of 20 g of the above described mixture was absorbed onto 50 g of sand (KolorScape White Play Sand). The sand was then dried in a microwave oven for 5 minutes in order to dry off the excess moisture and bring the temperature of the sand to above 80 °C in order to initiate the polymerization reaction. A total of two samples were prepared using the same procedure.

10 Since the antimicrobial polymer is cationic in nature, it will stain a blue color when exposed to a solution of bromophenol blue solution. The above described treated sand sample turned blue when exposed to a bromophenol blue solution and the blue color would not rinse off the sand when washed with water. Whereas an untreated sand sample did not retain a blue color after washing with water. This experiment demonstrates that the antimicrobial polymer is grafted onto the sand particles.

Appendix A**M1-C12****M1-C8****M1 COPO4****M-L12 (Lonzabac 12 based)****Mx****My**

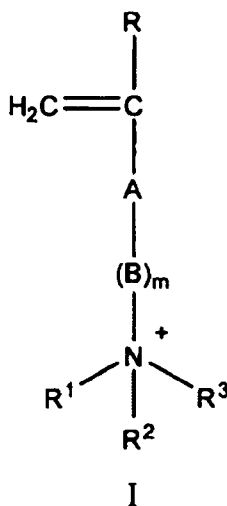
Appendix A (Continued)M-B26 (Bardap 26 based)M4 (ADBAC based)

Claims

1. A method for imparting antibiotic activity to a surface of a solid substrate, comprising the steps of:

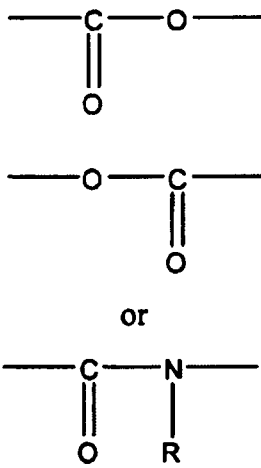
a) contacting the solid substrate with a composition comprising one or more antibiotic monomers Q_jX^{j-} wherein:

Q represents a quaternary ammonium ion having formula (I):



wherein:

A represents



R independently represents H or CH₃;

B represents a linear or branched C₁₋₅ alkanediyl chain; or an arylene or arylalkanediyl group;

m represents 0 or 1; R¹ and R² independently represent a C₁₋₅ alkyl group; R³

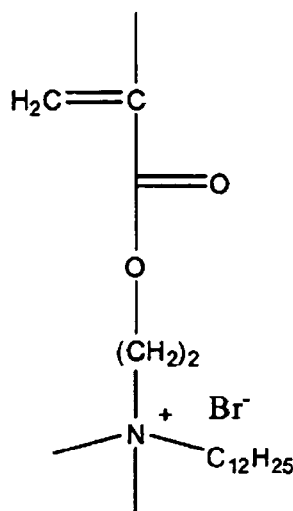
represents a C₈₋₂₀ alkyl group, an aryl group, or an arylalkyl group; and

X^{j-} represents an anion having valence j;

to form a solid substrate composition; and

- b) exposing the solid substrate composition to conditions suitable for covalent grafting and thermal polymerization of the substrate.

2. The method of claim 1, wherein the monomer comprises:



3. The method of claim 1, wherein m is 1.

4. The method of claim 3, wherein B is a linear C₂ alkanediyl chain.

5. The method of any of claims 1 to 4, wherein the conditions in step b) comprise a minimum temperature of 60 °C and a maximum temperature of 150 °C.

6. The method of any of claims 1 to 5, wherein the conditions in step b) comprise a minimum temperature of 80 °C and a maximum temperature of 130 °C.

7. The method of any of claims 1 to 6, wherein the solid substrate composition in step b) is exposed to the conditions for at least 5 minutes.

8. The method of any of claims 1 to 7, wherein the solid substrate composition in step b) is exposed to the conditions for at most 30 minutes.

9. The method of any of claims 1 to 8, wherein X^{j-} is a halide.

10. The method according of any of claims 1 to 9, wherein the solid substrate composition further comprises:
- i) one or more monomers or oligomers selected from the group consisting of acrylate, epoxide, and vinyl ether monomers or oligomers suitable for copolymerization with the antibiotic monomer; and
 - ii) one or more radical initiators suitable for thermal polymerization.
11. The method of claim 10, wherein the one or more monomers or oligomers are selected from the group consisting of 1,6-hexanediol diacrylate or bis-phenol A ethoxy diacrylate.
12. The method of claim 10 or 11, wherein the one or more radical initiators are selected from the group consisting of *tert*-amyl peroxybenzoate; 4,4'-azobis(4-cyanovaleric acid); 2,2'-azobisisobutyronitrile; benzoyl peroxide; 2,2-bis(*tert*-butylperoxy)butane; 1,1-bis(*tert*-butylperoxy)cyclohexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane; 2,5-bis(*tert*-butylperoxy)-2,5-dimethyl-3-hexyne; bis(1-(*tert*-butylperoxy)-methylethyl)benzene; 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane; *tert*-butyl hydroperoxide; *tert*-butyl peracetate; *tert*-butyl peroxide; *tert*-butyl peroxybenzoate; *tert*-butylperoxy isopropyl carbonate; cumene hydroperoxide; cyclohexanone peroxide; dicumyl peroxide; lauroyl peroxide; 2,4-pentanedione peroxide; peracetic acid; and potassium persulfate.
13. The method of claim 12, wherein the one or more radical initiator is benzoyl peroxide.
14. The method of any of claims 10 to 13, wherein the solid substrate composition further comprises iii) one or more grafting agents.
15. The method of any of claims 10 to 14, wherein the solid substrate is pre-treated with a corona treatment or plasma discharge treatment.
16. The method of any of claims 1 to 15, wherein the solid substrate is porous.
17. The method of any of claims 1 to 15, wherein the solid substrate is a non-woven or woven textile.
18. The method of claim 17, wherein the solid substrate is a non-woven textile and the non-woven textile is a cleaning wipe.
19. The method of any of claims 1 to 15, wherein the solid substrate comprises a plastic.

20. The method of any of claims 1 to 15, wherein the solid substrate is a medical gauze or bandage.
- 5 21. The method of any of claims 1 to 15, wherein the solid substrate is a water filtration medium.
22. The method of claim 21, wherein the water filtration medium comprises plastic, ceramic, glass, diatomaceous earth, or sand.
- 10 23. The method of claim 21, wherein the water filtration medium comprises filter cartridges.
24. The method of any of claims 1 to 15, wherein the solid substrate is a diaper.
- 15 25. The method of any of claims 1 to 15, wherein the solid substrate is a medical or surgical mask or a respirator.
26. The method of any of claims 1 to 15, wherein the solid substrate comprises a surface used in a pharmaceutical clean room.
- 20 27. The method of any of claims 1 to 15, wherein the solid substrate comprises a surface used in a bathroom.
28. The method of claim 27, wherein the surface used in a bathroom is a wall, a ceiling, a floor, a door, a toilet seat, or a flush handle.