



US 20050176905A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2005/0176905 A1**

**Moon et al.** (43) **Pub. Date: Aug. 11, 2005**

(54) **MONOMER WITH ANTI-MICROBIAL CHARACTER, POLYMER USING THE SAME, AND MANUFACTURING METHOD THEREOF**

(30) **Foreign Application Priority Data**

Jan. 31, 2002 (KR) ..... 10-2002-000578  
Jun. 25, 2002 (KR) ..... 10-2002-0035792  
Feb. 3, 2003 (KR) ..... 10-2003-0006509

(76) Inventors: **Woong-Sig Moon**, Jangan-gu Suwon-city Gyeonggi (KR); **Jae-Chul Kim**, Geumgok-dong Gwonseon-gu (KR); **Kyoo-Hyun Chung**, Jongro-gu Seoul (KR); **Ki-Oh Kong**, Bupyeong-gu Incheon-city (KR); **Jung-Hwa Hwang**, Seoul (KR)

**Publication Classification**

(51) **Int. Cl.<sup>7</sup>** ..... **C08F 26/06**  
(52) **U.S. Cl.** ..... **526/259; 526/319**

(57) **ABSTRACT**

The present invention relates to a monomer with anti-microbial characteristics, a polymeric compound with anti-microbial characteristics using the same, and manufacturing methods thereof, and more particularly, to an antimicrobial monomer comprising a saturated hydrocarbon having a polymerizable functional group within its structure. Also, the present invention provides a polymeric compound using the above antimicrobial monomer, a manufacturing method thereof, and a polymeric resin composition. The compounds according to the present invention have durable antimicrobial activity and high heat resistance, they do not give rise to toxicity when added to conventional resins by not eluting the antimicrobial compounds, and they do not have an effect on the properties of molded products.

Correspondence Address:  
**ALSTON & BIRD LLP**  
**BANK OF AMERICA PLAZA**  
**101 SOUTH TRYON STREET, SUITE 4000**  
**CHARLOTTE, NC 28280-4000 (US)**

(21) Appl. No.: **10/503,040**  
(22) PCT Filed: **Feb. 3, 2003**  
(86) PCT No.: **PCT/KR03/00238**

**MONOMER WITH ANTI-MICROBIAL CHARACTER, POLYMER USING THE SAME, AND MANUFACTURING METHOD THEREOF**

**BACKGROUND OF THE INVENTION**

[0001] (a) Field of the Invention

[0002] The present invention relates to a monomer with anti-microbial characteristics, a polymeric compound with anti-microbial characteristics using the same, and manufacturing methods thereof, and more particularly, to an antimicrobial monomer that has durable antimicrobial activity and high heat resistance, does not give rise to toxicity when added to conventional polymeric resins and petrochemical products by not eluting antimicrobial compounds, and does not have an effect on the properties of molded products, an antimicrobial polymer using the same, and manufacturing methods thereof.

[0003] (b) Description of the Related Art

[0004] Recently, in line with great concerns about environmental hygiene and high-grade life style, the production of and demand for products conferring antimicrobial characteristics to petrochemical materials for use in industrial supplies such as food wrappers, containers for storage, toothbrushes, cutting boards, stationery, washing tubs, water purifiers, shampoos, soaps, cosmetics and wrappers, and medical supplies, are increasing.

[0005] In the case of organic antimicrobial substances used in these products (ex: quaternary ammonium salts, triazines, benzimidazole, triclosan, chlorohexidine, thiazoles, etc.), in order to confer antimicrobial ability to polymeric substances, the antimicrobial substances are simply added to the polymeric substances when manufacturing antimicrobial materials. However, it has been reported that the antimicrobial materials have technical limits in respect to the inherent toxicity of antimicrobial substances, the elution of antimicrobial substances, the reduction of antimicrobial ability due to the elution, and so on. Especially in the case of injecting or extruding plastics, antimicrobial substances may be decomposed by high heat, and they may also induce a yellowing phenomenon (low heat resistance).

[0006] In order to overcome the limits as described above, a simple mixing method with inorganic ceramic anti-microbial complexes is widely used. However, such a method also has the problem that the antimicrobial activities are chemically decreased when they come into contact with moisture (JAPAN NEWS Feb. 11 (Wed.), 1998, Monthly Ceramics No. 2, 1998). In addition, research on binding antimicrobial substances to polymers is in progress. Pittman disclosed a method of co-polymerizing pentachlorophenylacrylates and acrylic monomers in 1981 (Pittman et al., J. Appl. Polym. Sci., 1981, 26, 2403), and Korean Patent Application No. 97-62102 disclosed a method of directly mixing antimicrobial agents with fibers, leathers, or plastics, and molding and processing them using the chemical reaction between the antimicrobial agents and polymers. However, such methods still did not solve the problems of quality deterioration of products since the antimicrobial ability was lost due to heat

of using quinolinecarboxylic compounds as a back bone, but it also did not solve the problems owing to the elution of antimicrobial substances.

**SUMMARY OF THE INVENTION**

[0007] Therefore, the present invention has been made to solve the problems of the prior arts as described, and it is an object of the invention to provide an antimicrobial monomer having durable antimicrobial activity with excellent heat resistance and compatibility.

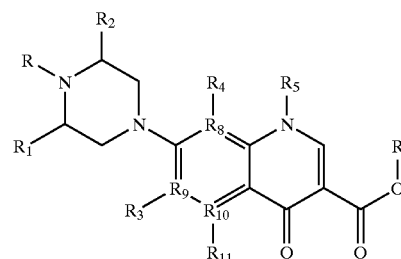
[0008] It is another object of the present invention to provide a method of manufacturing a novel antimicrobial monomer compound.

[0009] It is a still another object of the invention to provide an antimicrobial polymeric compound having durable antimicrobial activity with excellent heat resistance and compatibility using the above antimicrobial monomer compound and a manufacturing method thereof.

[0010] It is still another object of the invention is to provide a polymeric resin composition comprising the above antimicrobial monomer or the antimicrobial polymeric compound using it.

[0011] It is still another object of the invention is to provide a method of applying the antimicrobial monomer compound as a coating agent for UV light by simply adding it to petrochemical products and chemically irradiating it with UV light (by virtue of the presence of reactive groups).

[0012] In order to achieve the aforementioned objects, the present invention provides an antimicrobial monomer compound represented by the following formula 1:



[Formula 1]

[0013] wherein

[0014] R is a saturated or unsaturated C<sub>1</sub> to C<sub>150</sub> hydrocarbon comprising a polymerizable functional group and a light-curable reactive functional group;

[0015] R<sub>1</sub> and R<sub>2</sub> are each independently or simultaneously hydrogen, a halogen atom, an amine, or a C<sub>1</sub>-C<sub>20</sub> alkyl group;

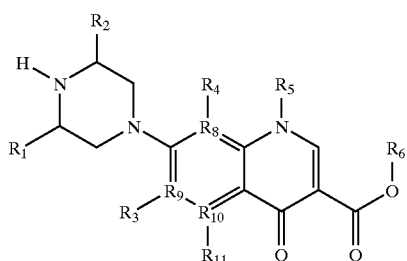
[0016] R<sub>3</sub> and R<sub>4</sub> are each independently or simultaneously hydrogen, a hydroxy group, a C<sub>1</sub>-C<sub>20</sub> alkoxide, a halogen atom, or a C<sub>1</sub>-C<sub>20</sub> alkyl group;

[0017] R<sub>5</sub> is hydrogen, a C<sub>1</sub>-C<sub>20</sub> alkyl, a cyclopropyl,

[0019]  $R_8$ ,  $R_9$ , and  $R_{10}$  are each independently or simultaneously carbon or nitrogen; and

[0020]  $R_{11}$  is hydrogen, an amine ( $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ ), a halogen atom, or a  $C_1$ - $C_{20}$  alkyl group.

[0021] Also, the invention provides a method of manufacturing the antimicrobial monomer compound of said formula 1 comprising the step of reacting a compound of the following formula 2:



[Formula 2]

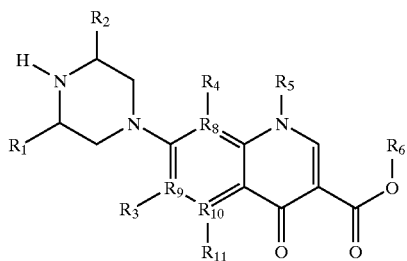
[0022] wherein  $R_1$ - $R_6$  and  $R_8$ - $R_{11}$  are as defined in formula 1 above; with a compound of the following formula 3:

R-Z [Formula 3]

[0023] wherein R is as defined in formula 1 above and Z is a halogen atom, or a leaving group comprising a tosyl or a mesyl;

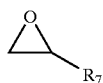
[0024] in the presence of a solvent with or without a base.

[0025] Also, the invention provides a method of manufacturing the antimicrobial monomer compound of said formula 1 comprising the epoxy ring-opening reaction of a compound of the following formula 2:



[Formula 2]

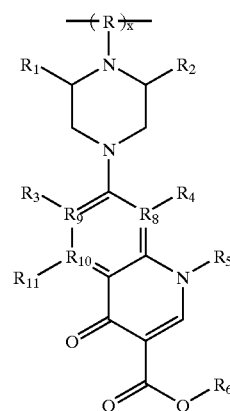
[0026] wherein  $R_1$ - $R_6$  and  $R_8$ - $R_{11}$ , are as defined in formula 1 above; with a compound of the following formula 3a:



[Formula 3a]

[0028] in the presence of a solvent with or without a base.

[0029] Also, the invention provides an antimicrobial homopolymer having an average molecular weight of 10,000~1,000,000 represented by the following formula 4:



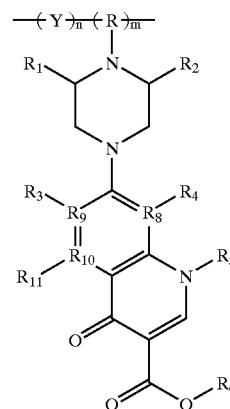
[Formula 4]

[0030] wherein R,  $R_1$ - $R_6$ , and  $R_8$ - $R_{11}$  are as defined in formula 1 above, and

[0031] X is an integer greater than zero satisfying the above molecular weight.

[0032] Also, the invention provides a method of manufacturing the antimicrobial homopolymer of formula 4 comprising the step of radically polymerizing the antimicrobial monomer compound of formula 1 as defined above in the presence of an organic solvent and a catalyst (initiator).

[0033] Also, the invention provides an antimicrobial copolymer having an average molecular weight of 10,000~1,000,000 represented by the following formula 5:



[Formula 5]

[0034] wherein

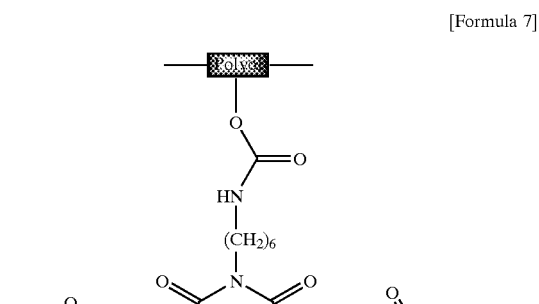
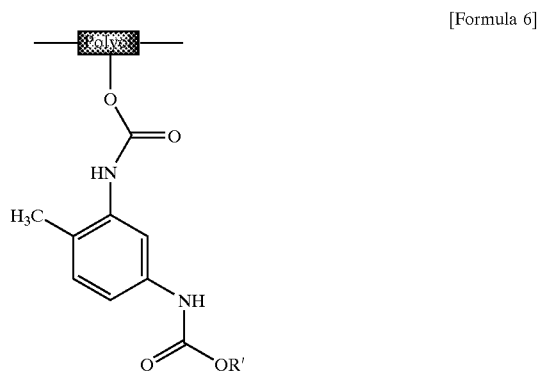
[0037] Y is a monomer group capable of reacting a radically polymerizable functional group.

[0038] Also, the invention provides a method of manufacturing the antimicrobial copolymer of formula 5, comprising the step of radically copolymerizing the antimicrobial monomer compound of formula 1 with monomer Y having a polymerizable functional group in the presence of an organic solvent and a catalyst (initiator).

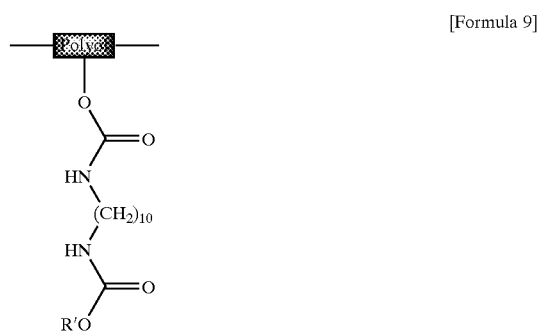
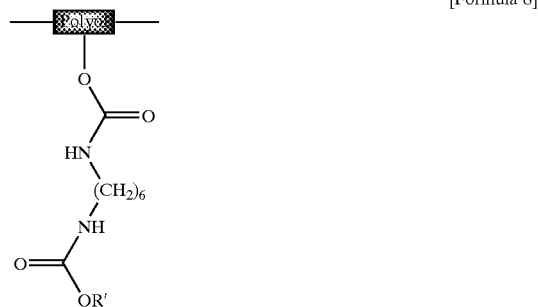
[0039] Also, the invention provides a method of manufacturing an antimicrobial polymeric compound comprising the steps of binding the antimicrobial monomer of formula 1 to a linker selected from the group consisting of an isocyanate class, a haloacylhalogenade and a compound containing an acid anhydride in the presence of an organic solvent, and then reacting it with a polyol.

[0040] Also, the invention provides an antimicrobial polymeric compound manufactured by the process as described above.

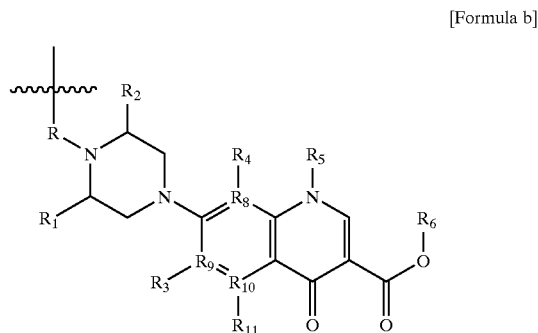
[0041] It is preferred that the above antimicrobial polymeric compound is selected from the group consisting of compounds represented by the following formula 6 to 9:



-continued

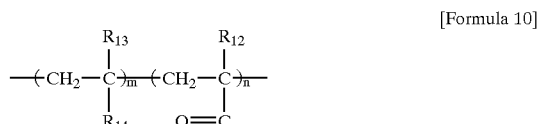


[0042] (in the formula 6 to 9, R' is a group represented by the following formula b:



[0043] wherein R<sub>1</sub> R<sub>1</sub>~R<sub>6</sub>, and R<sub>8</sub>~R<sub>11</sub> are as defined in formula 1 above.)

[0044] Also, the invention provides an antimicrobial acrylic copolymer having an average molecular weight of 10,000~1,000,000 represented by the following formula 10:



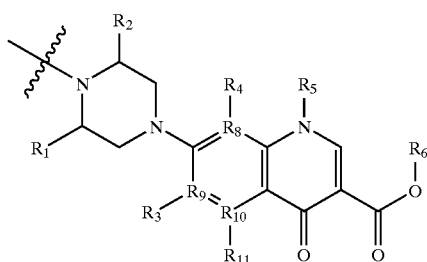
[0045] wherein

[0046]  $R_{12}$  and  $R_{13}$  are each independently or simultaneously hydrogen or a methyl group,  $R_{14}$  is a  $C_1$ - $C_{18}$  alkyl group comprising one or more selected from the group consisting of ester, carbonyl, amide, amine, cycloalkyl, ether, hydroxy, carboxylic acid,  $C_5$ - $C_{10}$  hetero ring containing N or O, sulfonyl, silane, lactone, and aldehyde groups,

[0047]  $m$  and  $n$  are each an integer more than zero satisfying the above molecular weight, and

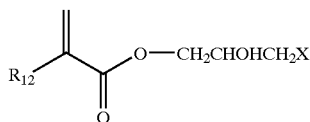
[0048] X is a compound of the following formula 2a:

[Formula 2a]



[0049] Also, the invention provides a method of manufacturing an antimicrobial acrylic copolymer of formula 10 comprising the step of radically polymerizing a compound of the following formula 11:

[Formula 11]

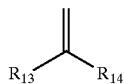


[0050] wherein  $R_{12}$  is hydrogen or a methyl group, and

[0051] X is the compound of formula 2a as defined above;

[0052] with a compound of the following formula 12:

[Formula 12]



[0053] wherein  $R_{13}$  is hydrogen or a methyl group, and  $R_{14}$  is a  $C_1$ - $C_{18}$  alkyl group comprising one or more selected from the group consisting of ester, carbonyl, amide, amine, cycloalkyl, ether, hydroxy, carboxylic acid,  $C_2$ - $C_{10}$  hetero ring containing N or O, sulfonyl, silane, lactone, and aldehyde groups.

[0054] Also, the invention provides an antimicrobial polymeric resin composition in which

bial monomer compound of formula 1, the antimicrobial homopolymer compound of formula 4, the antimicrobial copolymer compound of formula 5, the antimicrobial polymeric compounds of formula 6 to 9, and the acrylic copolymer of formula 10 are uniformly mixed.

[0057] Also, the invention provides a light-curable resin composition comprising an acrylic light-curable oligomer, a property-fortified monomer, a light initiator, and an additive,

[0058] in which the light-curable resin composition comprises one or more antimicrobial compounds selected from the group consisting of the antimicrobial monomer compound of formula 1, the antimicrobial homopolymer compound of formula 4, the antimicrobial copolymer compound of formula 5, the antimicrobial polymeric compounds of formula 6 to 9, and the acrylic copolymer of formula 10.

[0059] Also, the invention provides a molded and processed product comprising the polymeric resin composition. It is preferred that the molded and processed products are industrial supplies, various wrappers, consumer supplies or medical supplies, and they can be applied to interior materials such as blinds, wall papers and floor coverings; food related products such as films for wrapping, storage containers, and cutting boards; appliances such as humidifiers, washers, and dish washers; engineering materials such as water supply and drain pipes, and concrete; core materials in medical fields; and products for industrial purposes such as coatings. They are particularly useful for medical supplies, that is, medical devices/products for insertion into the human body such as catheters for medical purposes, prostheses, and products for repairing bones, or blood transfusion bags for medical purposes.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0060] The present invention is hereafter described in detail.

[0061] The inventors found a novel antimicrobial monomer during the process of researching polymeric substances with anti-microbial characteristics, verified that polymeric compounds manufactured from the above antimicrobial monomer using a light-curable, homopolymerizable/copolymerizable or intermediate-binding linker solved toxic problems due to elution, had durable anti-microbial effects and high heat resistance, and had high durability when manufactured into products, and thus completed the present invention.

[0062] In the present invention, R in formula 1 is preferably a saturated or unsaturated  $C_1$ - $C_{20}$  hydrocarbon comprising a light-curable reactive functional group and a polymerizable functional group, and  $R_6$ , which comprises a polymerizable functional group, is preferably a  $C_1$ - $C_{20}$  alkyl group.

[0063] The above polymerizable functional group is one or more selected from the group consisting of carbon-carbon double bond ( $C=C$ ) and carbon-carbon triple bond ( $C\equiv C$ ).

# Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

## Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

## Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

## Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

## API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

## LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

## FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

## E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.