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(54) Title: ANTIMICROBIAL MATERIALS AND PREPARATION THEREOF

(57) Abstract: The invention relates to a monomelic antimicrobial agent, to a copolymer and polymer compositions having antimicrobial activity and to articles and products prepared from them. The invention also relate to methods for preparing the anti microbial copolymer and polymer compositions. The monomeric antimicrobial agent of the invention has the general formula $(R)_j-(SO_3MM)_m(L)_n$ where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate, trialkyl phosphate or a thiol, R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

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Antimicrobial materials and preparation thereof

Field of invention

The invention relates to an antimicrobial agent, to copolymer and polymer compositions having antimicrobial activity and to articles and products prepared from them. The invention also relate to methods for preparing the copolymer and the polymer compositions.

Background of the invention

Polymer materials having antimicrobial activity find applications in textile, medical, food and packaging industries, especially in the manufacture of apparels, sanitary clothing, diapers, wall materials, surgical gowns, wound and burn dressings/bandages and dental compositions. Antimicrobial activity is usually imparted to these materials by incorporation into them a metal such as Ag, Cu or Zn having antimicrobial activity. Antimicrobial metal is incorporated by either adding an antimicrobial metal containing additive during polymerization and/or by treatment of polymer materials with an antimicrobial metal salt solution.

JP 02925628, JP 52092000 and WO 2006/026573 disclose methods for preparation of antimicrobial polymer materials by ion exchange treatment of materials containing alkali metal sulphonate/alkali metal carboxylate groups with silver salt solutions. Such treated polymer materials would contain a large number of unexchanged alkali metal sulphonate groups. The presence of such alkali metal sulphonate groups tend to adversely affect the mechanical, thermal and/or chemical properties of the polymer materials. Moreover, the methods described in these documents tend to concentrate the antimicrobial metal on the surface of the material leading to inhomogeneous distribution of the metal in the material.

JP 3074430 describes polycondensation of terephthalic acid and ethylene glycol in the presence of silver benzoate and a polyol or an aromatic dicarboxylic compound containing alkali metal sulphonate group. US 7052765 relates to a method to prepare polymer materials containing antimicrobial silver in the particulate form by adding a silver containing precursor and a reducing agent during polymerisation. The methods described in these patents would require additives that form leachable byproducts, that deteriorate the material quality or that adds to the material cost of the process.

There is a need to prepare polymer materials having antimicrobial activity as well as having good functional attributes.

Detailed Description

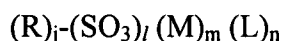
Accordingly, the invention provides a monomeric antimicrobial agent used in the polymerization of compounds selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters alkenes, alkenyl benzenes or isocyanates to yield antimicrobial copolymers, fibers, fabrics, films, containers or other articles without deterioration of other properties.

When used throughout this specification, the following terms have the meanings indicated:

The term "metal" as used herein refers to metal atom(s), metal ion(s) or group of metal atom(s) or of metal ion(s).

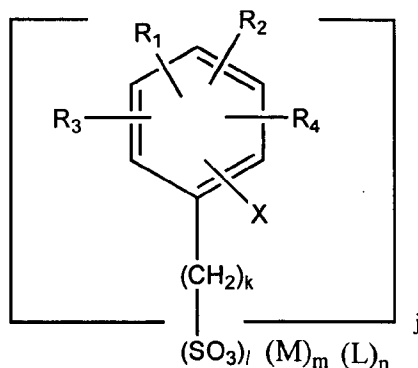
The term "antimicrobial metal" as used herein refers to metal having antimicrobial activity.

In one embodiment, the invention provides a monomeric antimicrobial agent having the general formula



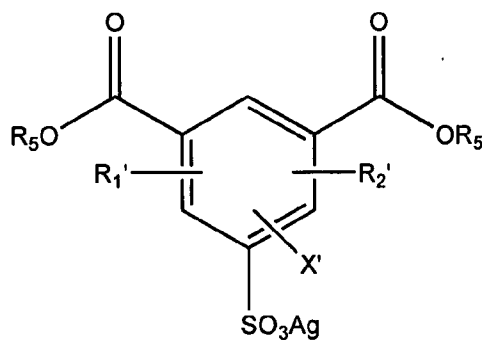
where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate, trialkyl phosphate or a thiol, R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

In another embodiment, the invention provides a monomeric antimicrobial agent having the following formula (I)



where j , l , m is an integer from 1 to 6, n , k is an integer from 0 to 6, X is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3M where M is as defined herein, R_1 , R_2 is individually H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , COR_6 where R_6 is a $(\text{C}_1\text{-C}_3)$ alkyl, aryl or substituted aryl, SO_3M where M is as defined herein or COOR_5 , R_5 being H, Na, K, $(\text{C}_1\text{-C}_3)$ alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined herein or $-(\text{CH}_2)_n\text{-OH}$ where n' is an integer from 1 to 6 or R_1 and R_2 together form an anhydride or an unsubstituted or substituted 5- or 6- membered ring and R_3 and R_4 are reactive functional groups selected from alkenyl, alkoxy, OH, CH_2OH , NH_2 , CHO, COCl or COOR_5 where R_5 is as defined herein.

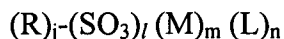
In another embodiment, the invention provides a monomeric antimicrobial agent having the following formula (II)



where R_5 is as defined herein, X' is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3Ag , R_1' , R_2' is H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , SO_3Ag , COR_6 where R_6 is a $(\text{C}_1\text{-C}_3)$ alkyl, aryl or substituted aryl or COOR_5 where R_5 is as defined herein.

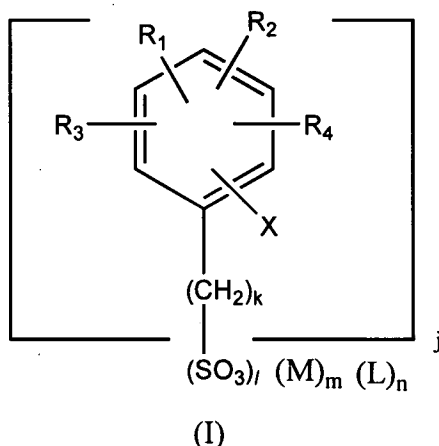
In another embodiment, the invention provides a process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid

amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



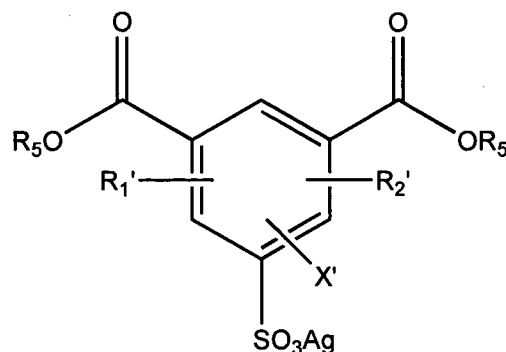
where j , l , m , n , L , M and R are as defined herein.

In another embodiment, the invention provides a process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having following formula (I)



where j , k , l , m , n , L , M , X , R_1 , R_2 , R_3 and R_4 are as defined herein.

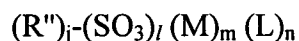
In another embodiment, the invention provides a process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of antimicrobial agent(s) having the following formula (II)



(II)

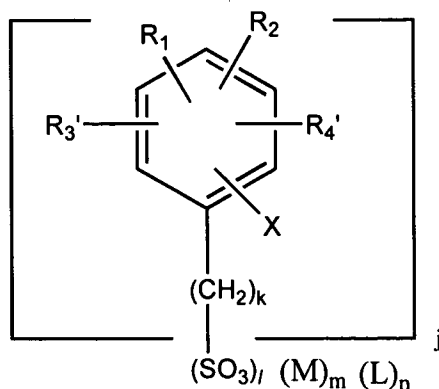
where X', R₁', R₂' and R₅ are as defined herein.

In another embodiment, the invention provides a process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



where j, l, m, n, L and M are as defined herein and R'' is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl.

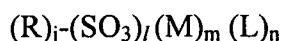
In another embodiment, the invention provides a process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the following formula (III)



(III)

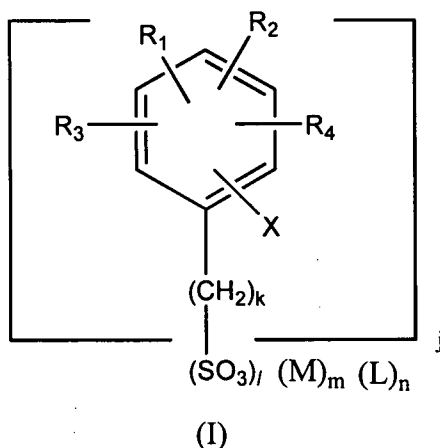
where j, k, l, m, n, X, R_1 and R_2 are as defined herein and R_3, R_4 is H, C_1 - C_{10} alkyl, alkenyl, aryl, substituted aryl, $C_6H_5N_2$, CHO, CH_2OH , COCl, $CONH_2$, COR_6 where R_6 is a (C_1 - C_3) alkyl, aryl or substituted aryl, SO_3M where M is as defined herein or $COOR_5$ where R_5 is as defined herein.

In another embodiment, the invention provides an antimicrobial polymer composition prepared by reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of $20^{\circ}C$ - $320^{\circ}C$ in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



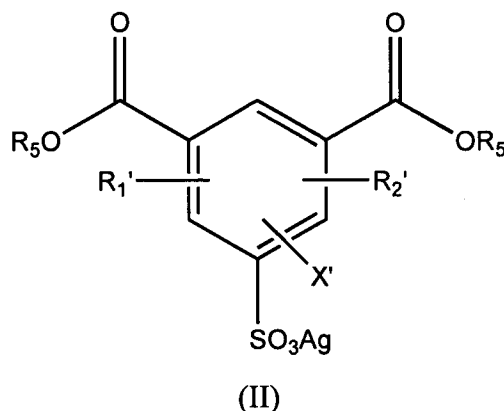
where j, l, m, n, L, M and R are as defined herein

In another embodiment, the invention provides an antimicrobial polymer composition prepared by reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of $20^{\circ}C$ - $320^{\circ}C$ in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the following formula (I)



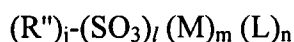
where $j, k, l, m, n, L, M, X, R_1, R_2, R_3$ and R_4 are as defined herein.

In another embodiment, the invention provides an antimicrobial polymer composition prepared by reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of $20^{\circ}C$ - $320^{\circ}C$ in the presence of a polymerisation catalyst and of antimicrobial agent(s) having the following formula (II)



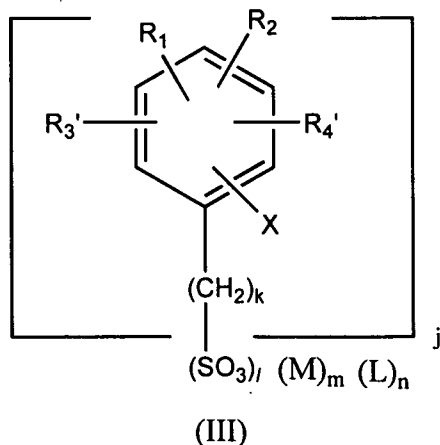
where X' , R_1' , R_2' and R_5 are as defined herein

In another embodiment, the invention provides an antimicrobial polymer composition prepared by reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20°C - 320°C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



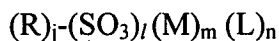
where j , l , m , n , L and M are as defined herein and R'' is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl.

In another embodiment, the invention provides an antimicrobial polymer composition prepared by reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20°C - 320°C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the following formula
(III)



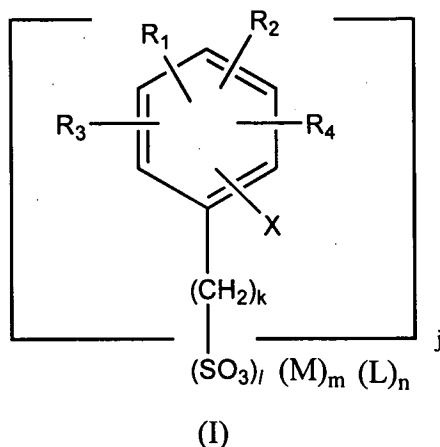
where j , k , l , m , n , L , M , X , R_1 , R_2 , R_3' and R_4' are as defined herein.

In another embodiment, the invention provides a process for synthesis of a copolymer having antimicrobial activity by reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20⁰C-320⁰C with one or more antimicrobial agent(s) having the general formula



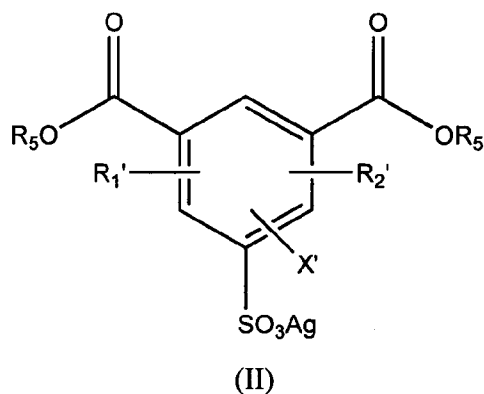
where j, l, m, n, L and M are as defined herein and R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

In another embodiment, the invention provides a process for synthesis of a copolymer having antimicrobial activity, the process comprising reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20⁰C-320⁰C with one or more antimicrobial agent(s) having the following formula (I)



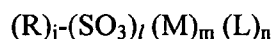
where j, k, l, m, n, L, M, X, R₁, R₂, R₃ and R₄ are as defined herein

In another embodiment, the invention provides a process for synthesis of a copolymer having antimicrobial activity the process comprising reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20⁰C-320⁰C with an antimicrobial agent having the following formula (II)



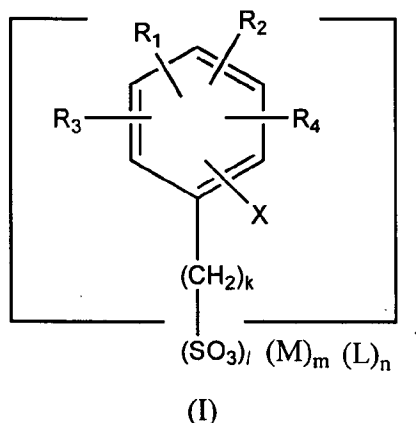
where X' , R_1' , R_2' and R_5 are as defined herein.

In another embodiment of the invention, there is provided an antimicrobial copolymer prepared by reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20°C-320°C with one or more antimicrobial agent(s) having the general formula



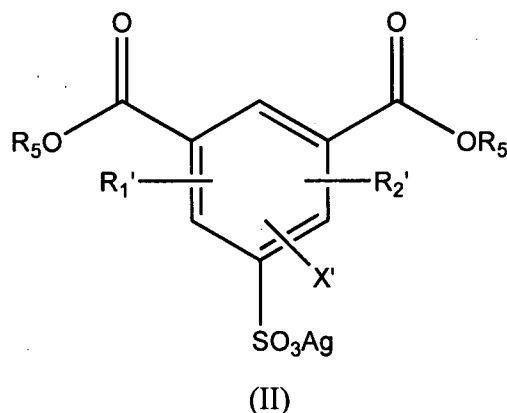
where j , l , m , n , L and M are as defined herein and R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group

In another embodiment of the invention, there is provided an antimicrobial copolymer prepared by reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20°C-320°C with one or more antimicrobial agent(s) having the following formula (I)



where j , k , l , m , n , X , L , M , R_1 , R_2 , R_3 and R_4 are as defined herein

In another embodiment of the invention, there is provided an antimicrobial copolymer prepared by reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of 20°C-320°C with an antimicrobial agent having the following formula (II)



where X', R₁', R₂' and R₅ are as defined herein

In another embodiment of the invention, there is provided an antimicrobial polymer composition prepared by using an antimicrobial agent, the composition having metal component(s) of the antimicrobial agent substantially uniformly distributed throughout, overall metal to sulphonate ratio in the composition being in the range of 1:0.8 to 1:2.2

In yet another embodiment of the invention, there is provided an antimicrobial composition comprising the copolymer wherein metal component(s) of the antimicrobial agent is substantially uniformly distributed throughout, overall metal to sulphonate ratio in the composition being in the range of 1:0.8 to 1:2.2.

In a further embodiment of the invention, there is provided filaments, fibers, yarns, fabrics, films, containers or other articles having prolonged antimicrobial activity, improved tenacity, melting point and hydrolytic stability prepared from antimicrobial polymer composition or from antimicrobial composition comprising the copolymer.

The invention provides a monomeric antimicrobial agent capable of imparting antimicrobial activity to a copolymer prepared by the reaction of the antimicrobial agent with other monomers. The monomeric antimicrobial agent of the invention contain reactive functional groups capable of participating in the polymerization reaction. The reactive functional group is selected from alkenyl,

OH, OR, CH₂OH, NH₂, CHO, COCl or COOR₅ where R₅ is as defined herein. During polymerization, the monomeric antimicrobial agent reacts with compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst. The polymerization catalyst is a metal or non-metal based catalyst conventionally used for polymerization reactions. In certain polymerization reactions, the antimicrobial agent can also provide the necessary catalytic activity and thus reduce or eliminate the requirement of using a separate polymerization catalyst. The polymerization reaction is carried out either as a batch process or as a continuous process. One or more antimicrobial agents, differing in the type of metal or differing in the organic part of the molecule, can be used simultaneously in the polymerization reactions. Moreover, the antimicrobial agent can be added to the polymerization mixture at any stage during the polymerization, i.e. the antimicrobial agent can be added at the beginning of the polymerization, during the polymerization or towards the end of polymerization. The antimicrobial agent can be mixed with the polymer in the solid, molten or dissolved form. In liquid phase polymerization reactions, if the addition of antimicrobial agent leads to decrease in the polymer molecular weight, the molecular weight is increased by further polymerization, for example by addition of chain extenders or by polymerization in the solid state.

The invention also provide compositions having antimicrobial activity prepared by using an antimicrobial agent. The antimicrobial agent used for preparing the composition of the invention may or may not contain reactive functional groups. If the antimicrobial agent contain a reactive functional group, the antimicrobial agent can react with other monomers or polymers to form a copolymer. The antimicrobial agent containing reactive functional groups can also be present in unreacted form in the composition of the invention. If the antimicrobial agent does not contain reactive functional groups, the composition would contain free antimicrobial agent dispersed therein. Further, the antimicrobial metal component of the antimicrobial agent can be present in the composition in the particulate form. Essentially, the antimicrobial compositions of the invention contain the antimicrobial metal substantially uniformly distributed, overall antimicrobial metal to sulphonate ratio in the composition being in the range of 1:0.8 to 1:2.2.

The polymer compositions of the invention comprise polymer(s)/copolymer(s) which include, but are not limited to polyester, polycarbonate, polyamide, polystyrene, polyolefin or polyurethane. Exemplary polyester polymer(s)/copolymer(s) include, but are not limited to polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate and poly (cyclohexane dimethylene terephthalate), each of them containing antimicrobial comonomer units. Typically a polyester copolymer is formed by the reaction between antimicrobial agent with dicarbonyl

compound(s) and glycols. The dicarbonyl compounds include, but are not limited to terephthalic acid, isophthalic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, naphthalene dicarboxylic acid and cyclohexane dicarboxylic acid. Examples of glycols include, but are not limited to ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexane diol, 8-octane diol, 1,10 decanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexane dimethanol, diethylene glycol, polyethylene glycol, polypropylene glycol or polytetramethylene glycol or combinations thereof

The antimicrobial compositions of the invention can contain one or more conventional additives which include, but are not limited to, a colorant including a dye or a pigment, a mold release agent, an antioxidant, a flame retardant, a filler, a reinforcing agent, a UV protective agent, a plasticizer, a water transporting/absorbing agent or cationic dyeability agents. Concentrated master batches of the compositions are prepared and subsequently blended, as portions, to additional quantities of base polymer to achieve the final desired composition.

The copolymer and compositions of the invention, optionally blended with other polymers and additives, can be formed into various durable articles and structures having antimicrobial activity. The copolymer and compositions described herein can be used to prepare molded products such as telephones, switches, computer accessories, key boards, wrist-rests and also to prepare kitchen appliances, cookwares, cutting boards, kitchen mats, water filters, fridge lining, food packaging materials, films and baby feed bottles. They can also be used to prepare conveyor belts, food processing equipments, containers, furnitures, appliances or parts thereof, medical devices such as catheters or implants and to prepare bedding, floor covering and wound dressing products. The copolymer and compositions of the invention can be used to provide antimicrobial coating on articles. The copolymer and compositions of the invention can also be formed into filaments, fibers or yarn including monofilaments, staple fiber or continuous filament yarn. Polymer filaments are prepared by extruding a molten mixture of copolymer or compositions described herein and the base polymer optionally along with other blends/ master batches yielding a homogenous melt which is spun through a spinneret and taken on a wind-up roll, developing a morphology in the filament, suitable for further downstream processing. The processing can include thermo-mechanical operations such as hot/cold drawing, annealing/relaxation or texturizing depending upon the final applications. Alternatively, the blended melt of the copolymer with other polymers is spun to obtain polymer strands or fast quenched and then converted to chips. Further, the molten polymeric chips are extruded and melt spun to obtain polymer strands. The polymer strands can have various known cross sections to impart certain specific characteristics, for example, to impart wicking characteristics. Filaments and fibers in various configurations like core-sheath, side by side

etc are also prepared by bi- or multi-component spinning of the copolymer or composition of the invention with another polymer. Fibers described herein can be used in the production of yarns, woven fabrics, carpets and nonwoven fabrics. Fabrics made from the fibers described herein can be used in a variety of end-use applications, like in the manufacture of consumer products, hygiene products, medical products, operating room products including gowns, drapes, sterile wraps, footcovers, towels and related articles. Other exemplary products that can be produced from fabrics made from the fibers described herein include active wears, hosiery/socks, rubber gaskets and seals, fiberfills, feminine care products, diapers and incontinence products.

The invention is further illustrated by way of the following non limiting examples. In the examples and the results that follow, the Ag content of the samples was calculated from the amount added during polymerization and from the loading of polymerization product during filament extrusion. Intrinsic viscosity (IV) was obtained according to ASTM D4603-03 using 0.5 g/cc solution of the polymer in phenol-tetra chloro ethane solvent (60:40 wt ratio, 30°C). Tenacity was determined on a table model Statimat M (TexTechno), using gage length 150 mm, and elongation rate 600 mm/min. Melting point (T_m) was determined by using differential scanning calorimetry. The percentage weight loss during alkaline hydrolysis was determined by exposing 1 g sample of knitted hose to 50 mL aqueous solution of sodium hydroxide (1 g) at 130 °C for 30 min followed by washing, drying and weighing the sample to determine the percentage weight loss.

Example 1: Synthesis of antimicrobial agent

A sodium sulphonate of dimethylisophthalate was dissolved in demineralized water. The solution was passed through an ion exchange column containing beads of T-42 cation exchange resin to form dimethylisophthalate sulphonic acid (having the structure: $H^+SO_3^- - C_6H_3O_4$). 30.5 g of silver oxide (Ag_2O) was added to 71.9 g of the acid and stirred for 5 min at ~ 60-70°C till the brown/black powder of silver oxide disappeared resulting in silver sulphonate of dimethylisophthalate (Ag-DMS). The product solution was concentrated by evaporation of water under partial vacuum. The solution was concentrated further and cooled to crystallize the Ag – DMS salt (antimicrobial agent) which was filtered, dried in nitrogen atmosphere and vacuum and then stored in a dark environment.

Example 2: Preparation of polymer product

Slurry of purified terephthalic acid (6 kg) in ethylene glycol (4.5 kg) was esterified for 3.5 hrs upto 260°C at 2 bar nitrogen pressure. 24.45 g of Ag–DMS salt of Example 1 (containing 6.93 g Ag) was dissolved in ethylene glycol and added to the molten esterification product. After an interval of 20 minutes, antimony trioxide catalyst (300 ppm Sb in PET) dissolved in ethylene glycol 250 ml

was added. The mixture temperature was increased to $\sim 285^{\circ}\text{C}$, while gradually reducing the pressure over 45 minutes to 1 mm of Hg to obtain the polymeric product.

Example 3: Preparation of antimicrobial master batches

The polymeric product obtained in example 2 was extruded out of the reactor in the form of a strand, quenched in a water bath and sliced into chips (called 'antimicrobial masterbatch') containing 1000 ppm of silver. The intrinsic viscosity of the polymer was determined as 0.635 (ASTM D4603).

Example 4: Manufacture of polymer yarns (Control experiment)

The crystallized 'base' polyester chips (using polyester prepared without antimicrobial comonomer) were extruded from a 36 hole spinneret at 280°C , quenched using cold air at 18°C , and taken up at a spinning speed of 1133 m/min on first godet maintained at 80°C , and further drawn 2.85 X to second roller at 3230 m/min maintained at 145°C , and then wound up to produce a fully drawn yarn (FDY) at a spinning throughput of 1.615 kg/hr. The yarn was knitted into a hose and was used as the 'control' sample. Antimicrobial testing was carried out following the JIS L 1902 method. The properties of the yarn are displayed in table 1.

Example 5: Manufacture of antimicrobial polymer yarns with 100 ppm Ag

(a) The antimicrobial masterbatch chips of example 3 were crystallized at 140°C for 3 hours and then fed to an extruder with similarly crystallized base (free of antimicrobial agent) polyester (polyethylene terephthalate) chips having intrinsic viscosity of 0.62 while using a K-Tron feeder to maintain a masterbatch to base polyester ratio of 1:9 and total throughput of 1.615 kg/hr. The molten polymer mixture was extruded from a 36 hole spinneret at 280°C , quenched using cold air at 18°C , and taken up at a spinning speed of 1133 m/min on first godet maintained at 80°C , and further drawn 2.85 X to second roller at 3230 m/min maintained at 145°C , and then wound up to produce a fully drawn yarn (FDY) of 75 denier. The yarn was knitted into a hose, containing 100 ppm silver. Antimicrobial testing was carried out following the JIS L 1902 method. The properties and activity of the material are displayed in table 1.

(b) The knit hose (20 g) of example 5 was dyed at 110°C for 45 min in a 500 mL bath containing high energy dye blue-79 dye at a level of 1% (based on knit hose), and dried.

(c) The knit hose (20 g) of examples 5(a) and 5(b) were subjected to washing for 20 times according to ISO 6630: 6A 2000 using front loading IFB Washing machine with 2 kg dummy

weight, soft water, and ECE non phosphate reference detergent. The hose was then subjected to antimicrobial test method JISL 1902. The activity of the materials are displayed in table 2.

Example 6: Manufacture of antimicrobial polymer yarns with 25 ppm Ag

Melt spinning to FDY was carried out as in example 5 but maintaining a masterbatch to base polyester ratio of 1:39 to obtain a hose containing 25 ppm silver. The hose was then subjected to antimicrobial test method JIS L 1902. The properties and activity of the material are displayed in table 1.

Example 7: Manufacture of conventional cationic dyeable (CD) polyester yarns Commercial cationic dyeable polyester chips containing 1.7 mole% of the terephthalates groups replaced by 5 sodium sulfoisophthalate groups were obtained and spun into FDY 75 den / 36 following the procedure in Example 5. The properties of the yarn are displayed in table 1.

Example 8: Silver salt treatment of conventional CD polyester yarns

The FDY sample of example 7 was knitted into a hose as in example 4, and then subjected to AgNO_3 treatment as in example 21 of JP 02925628. 25 g of the knitted hose was dipped into 375 g of water containing 100 ppm acetic acid and 0.016 g of silver-nitrate, and boiled under pressure at 120°C for 1 hr. After cooling and washing the knitted hose with water, it was dried by churning for 20 minutes. A polyester cloth which has a silver sulfonate group was obtained. The properties and activity of the material are displayed in table 1.

Example 9: Manufacture of polymer film (Control experiment)

The crystallized and dried 'base' polyester (poly(ethylene terephthalate-co-ethylene-isophthalate) of $\text{IV} = 0.76\text{ dL/g}$ prepared without antimicrobial comonomer) chips were extruded as a film from a 'Brabender' single screw extruder (Barrel Dia = 19, L/D=25) attached with a film die (slit width = 150 mm, slit height = 0.5 mm) at 280°C at screw rpm = 40, and quenched by passing over chilled water cooled roller rotating at surface speed 0.5 m/min, to obtain film with width = 100 mm and thickness of 0.25 mm. The film was used as the 'control' sample for antimicrobial testing following the JIS Z 2801 method.

Example 10: Manufacture of antimicrobial polymer film with 100 ppm Ag

The antimicrobial masterbatch chips of example 3 were crystallized and dried and then tumble mixed with similarly crystallized and dried base (free of antimicrobial agent) polyester

(poly(ethylene terephthalate – co- ethylene isophthalate), IV = 0.76 dL/g) chips to maintain a masterbatch to base polyester ratio of 1:9 and extruded as a film in a ‘Brabender’ single screw extruder (Barrel Dia =19, L/D=25) attached with a film die (slit width = 150 mm, slit height = 0.5 mm) at 280⁰ C at screw rpm = 40, and quenched by passing over chilled water cooled roller rotating at surface speed 0.5 m/min, to obtain film with width = 100 mm and thickness of 0.25 mm. The film containing 100 ppm silver was tested for antimicrobial testing following the JIS Z 2801 method. The film showed bacteriostatic activity for Escherichia coli (ATCC-11229).

Example 11: Manufacture of antimicrobial polymer film with 10 ppm Ag

The antimicrobial masterbatch chips were prepared in accordance with example 3 except that instead of 1000 ppm of Ag, 100 ppm Ag was used. The master batch chips were crystallized and dried and then tumble mixed with similarly crystallized and dried base (free of antimicrobial agent) polyester (poly(ethylene terephthalate–co-ethylene isophthalate), IV = 0.76 dL/g) chips to maintain a masterbatch to base polyester ratio of 1:9 and extruded as a film in a ‘Brabender’ single screw extruder (Barrel Dia =19, L/D=25) attached with a film die (slit width = 150 mm, slit height = 0.5 mm) at 280⁰ C at screw rpm = 40, and quenched by passing over chilled water cooled roller rotating at surface speed 0.5 m/min, to obtain film with width = 100 mm and thickness of 0.25 mm. The film containing 10 ppm silver was tested for antimicrobial testing following the JIS Z 2801 method. The film showed bacteriostatic activity for Escherichia coli (ATCC-11229).

Example 12: Manufacture of antimicrobial polyester bottles with 25 ppm Ag

The antimicrobial masterbatch chips of example 3 were crystallized and dried and then tumble mixed with similarly crystallized and dried base (free of antimicrobial agent) polyester (poly(ethylene terephthalate-co-ethylene isophthalate), IV = 0.76 dL/g) chips to maintain a masterbatch to base polyester ratio of 1:39, and injection molded using 2 cavity Arburg injection molding machine (Model Allrounder 420C) operated at cylinder temperature of 287-292 ⁰C and runner temperature of 293-295 ⁰C, into 32 g perform. These performs were blown into bottles of 0.5 L volume using SIDEL SB01 single cavity blow moulding machine.

Table 1: Comparison of physical properties, antimicrobial activity and hydrolytic stability of polymeric materials prepared according to different examples

Sample of	Ag content (ppm)	IV (dL/g)	Tenacity (gpd)	Tm (°C)	Bacteriostatic activity (as shown towards Staphylococcus Aureus MTCC 6538 P)	Bacteriostatic activity (as shown towards Candida albicans MTCC 227)	% weight loss (during alkaline hydrolysis)
Example 4	0	0.62	4.3	258	-	-	31
Example 5 (a)	100	0.58	4.0	258	3.54	3.0	32
Example 6	25	0.59	4.3	257	2.99	3.09	26
Example 7	0	0.46	3.6	249	-	-	83
Example 8	Not known	0.37	-	249	3.54	3.53	89

Table 2: Antimicrobial activity of knitted polymeric yarns on washing and dyeing

Sample of	Processing after knitting	Bacteriostatic activity (as shown towards Staphylococcus Aureus MTCC 6538 P)	Bacteriostatic activity (as shown towards Candida albicans MTCC 227)
Example 5 (c)	Washed 20 times	2.89	2.88
Example 5 (c)	Dyed, Washed 20 times	2.96	2.97

Table 1 compares the properties of polyester yarns of the invention containing 100 ppm and 25 ppm of silver (Prepared according to the procedures in example 5 (a) and example 6 respectively) with fibers containing no silver prepared by a control experiment (example 4). The table also compares the properties of the polyester yarns of the invention with untreated as well as AgNO₃ treated cationic dyeable (CD) polyester yarns (Prepared according to example 7 and example 8 respectively). It is clear from the table 1 that the tenacity, melting point, intrinsic viscosity and hydrolytic stability of the antimicrobial polyester yarns of the invention (yarns of examples 5 (a) & 6) are high and are comparable to those of the polyester yarns of the control experiment (yarns of example 4). In comparison, however, the tenacity, heat of melting, intrinsic viscosity and hydrolytic

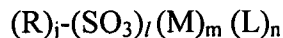
stability of cationic dyeable polyester yarns (of example 7) having alkali metal sulphonate groups are lower. Particularly, the hydrolytic stability of the polymer yarns of the invention is significantly higher as compared to the CD yarns (of example 7) or to the AgNO₃ treated CD yarns (of example 8). Table 2 demonstrates the prolonged antimicrobial activity of knitted polymer yarns of the invention. It could be seen from the table that the knitted polymer yarns of the invention exhibit high bacteriostatic activity (higher than 2.2) even after repeated washings.

The antimicrobial activity along with other functional attributes exhibited by the antimicrobial materials of the invention presumably results from having metal component of the antimicrobial agent substantially uniformly distributed throughout the material at an overall metal to sulphonate ratio in the range of 1:0.8 to 1:2.2 as well as from the absence of alkali metal sulphonate groups in the material. The CD yarns contain large number of alkali metal sulphonate groups which deteriorate its properties. The process of preparing antimicrobial copolymer of the invention through addition, during polymerization, of an antimicrobial agent having reactive functional groups, avoids the requirement of first having large number of [exchangeable] alkali metal sulphonates in the polymer and then carrying out exchange treatment of the polymer with antimicrobial metal salt solution. Further, the process of polymerisation according to the invention does not require additives that would leach out of or deteriorate the quality of the polymer material. The invention, therefore, provide materials that are durable and are suitable for preparing quality antimicrobial products including packaging materials and containers that would improve the shelf life of the packaged or contained food/drinks.

The above description is illustrative only and is not limiting. The present invention is defined by the claims which follow and their full range of equivalents.

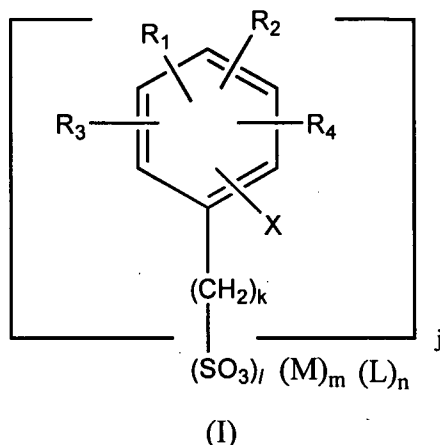
Claims :

1. A monomeric antimicrobial agent having the general formula



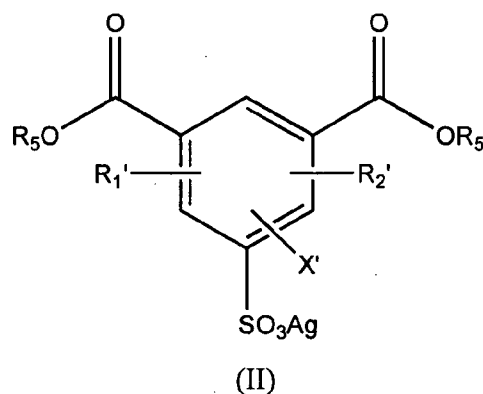
where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate, trialkyl phosphate or a thiol, R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

2. The monomeric antimicrobial agent as claimed in claim 1 having the following formula (I)



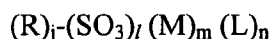
where j, l, m is an integer from 1 to 6, n, k is an integer from 0 to 6, X is H, halo, alkoxy, NH_2 , OH , SH , CN , NO_2 , CH_2OH or SO_3M where M is a metal selected from Ag, Cu or Zn, R_1, R_2 is individually H, C_1 - C_{10} alkyl, alkenyl, aryl, substituted aryl, $C_6H_5N_2$, CHO , CH_2OH , $COCl$, $CONH_2$, COR_6 where R_6 is a $(C_1$ - $C_3)$ alkyl, aryl or substituted aryl, SO_3M where M is as defined above, $COOR_5$, R_5 being H, Na, K, $(C_1$ - $C_3)$ alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(CH_2)_n-OH$ where n' is an integer from 1 to 6 or R_1 and R_2 together form an anhydride or an unsubstituted or substituted 5- or 6- membered ring and R_3 and R_4 are reactive functional groups selected from alkenyl, alkoxy, OH , CH_2OH , NH_2 , CHO , $COCl$ or $COOR_5$ where R_5 is as defined above.

3. The monomeric antimicrobial agent as claimed in claim 1 having the following formula (II)



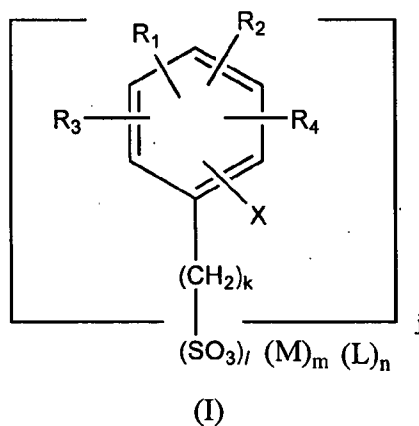
where X' is H, halo, alkoxy, NH₂, OH, SH, CN, NO₂, CH₂OH or SO₃Ag, R₁', R₂' is H, C₁-C₁₀ alkyl, alkenyl, aryl, substituted aryl, C₆H₅N₂, CHO, CH₂OH, COCl, CONH₂, SO₃Ag, COR₆ where R₆ is a (C₁-C₃) alkyl, aryl or substituted aryl or COOR₅, R₅ being H, Na, K, (C₁-C₃) alkyl, aryl, substituted aryl, COR₆ where R₆ is as defined above or -(CH₂)_n-OH where n' is an integer from 1 to 6.

4. A process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20⁰C-320⁰C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



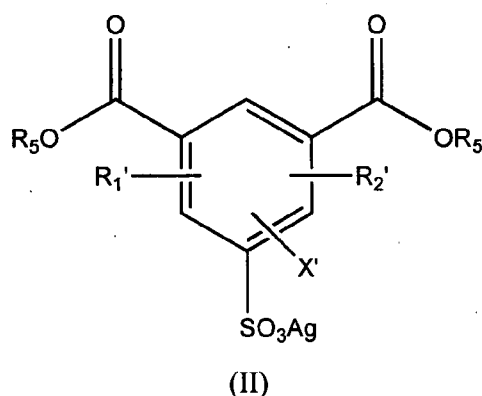
where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate, trialkyl phosphate or a thiol, R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

5. The process as claimed in claim 4 wherein the antimicrobial agent has the following formula (I)



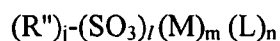
where j, l, m is an integer from 1 to 6, n, k is an integer from 0 to 6, X is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3M where M is a metal selected from Ag, Cu or Zn, R_1, R_2 is individually H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , COR_6 where R_6 is a $(\text{C}_1\text{-C}_3)$ alkyl, aryl or substituted aryl, SO_3M where M is as defined above or COOR_5 , R_5 being H, Na, K, $(\text{C}_1\text{-C}_3)$ alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(\text{CH}_2)_n\text{-OH}$ where n' is an integer from 1 to 6 or R_1 and R_2 together form an anhydride or an unsubstituted or substituted 5- or 6- membered ring and R_3 and R_4 are reactive functional groups selected from alkenyl, alkoxy, OH, CH_2OH , NH_2 , CHO, COCl or COOR_5 where R_5 is as defined above.

6. The process as claimed in claim 4 wherein the antimicrobial agent has the following formula (II)



where X' is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , SO_3Ag or CH_2OH , n is as defined above, R_1', R_2' is H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , COR_6 where R_6 is a $(\text{C}_1\text{-C}_3)$ alkyl, aryl or substituted aryl, SO_3Ag , COOR_5 , R_5 being H, Na, K, $(\text{C}_1\text{-C}_3)$ alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(\text{CH}_2)_n\text{-OH}$ where n' is an integer from 1 to 6.

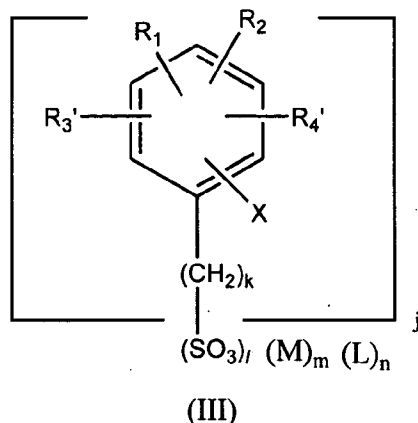
7. A process for preparing a polymer composition having antimicrobial activity, the process comprising reacting one or more compound(s) selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenes, alkenyl benzenes or isocyanates at a temperature in the range of 20°C - 320°C in the presence of a polymerisation catalyst and of one or more antimicrobial agent(s) having the general formula



where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate,

trialkyl phosphate, or a thiol and R'' is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl.

8. The process as claimed in claim 7 wherein the antimicrobial agent has the following formula (III)

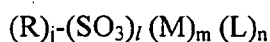


where j, l, m is an integer from 1 to 6, n, k is an integer from 0 to 6, X is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3M where M is a metal selected from Ag, Cu or Zn, R_1, R_2, R_3', R_4' is individually H, C_1 - C_{10} alkyl, alkenyl, aryl, substituted aryl, $C_6H_5N_2$, CHO, CH_2OH , COCl, $CONH_2$, COR_6 where R_6 is a (C_1-C_3) alkyl, aryl or substituted aryl, SO_3M where M is as defined above, $COOR_5$, R_5 being H, Na, K, (C_1-C_3) alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(CH_2)_{n'}-OH$ where n' is an integer from 1 to 6 or R_1 and R_2 together form an anhydride or an unsubstituted or substituted 5- or 6- membered ring.

9. Antimicrobial polymer composition prepared by the process as claimed in any one of the claims 4 to 8.

10. The composition as claimed in claim 9 wherein metal component(s) of the antimicrobial agent(s) is substantially uniformly distributed throughout, overall metal to sulphonate ratio in the composition being in the range of 1:0.8 to 1:2.2.

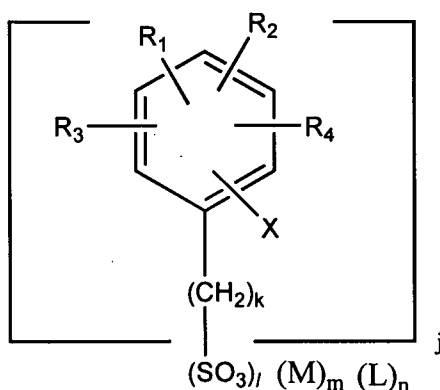
11. A process for synthesis of a copolymer having antimicrobial activity, the process comprising reacting at least one compound selected from the group consisting of carboxylic acids, their salts, acid chlorides, acid anhydrides, acid amides, alcohols, phenols, amines, esters, alkenyl benzenes or isocyanates in the presence of a polymerization catalyst and at a temperature in the range of $20^{\circ}C$ - $320^{\circ}C$ with one or more antimicrobial agent(s) having the general formula



where j, l, m is an integer from 1 to 6, n is an integer from 0 to 6, M is a metal selected from Ag, Cu or Zn, L is a nitrogen, phosphorus or sulphur containing ligand selected from ammonia, an

amine, pyridine, imidazole, pyrazole, triaryl phosphine, trialkyl phosphine, triaryl phosphate, trialkyl phosphate or a thiol, R is a linear or branched unsubstituted or substituted alkyl or alkenyl, an aryl or a substituted aryl carrying at least one reactive functional group.

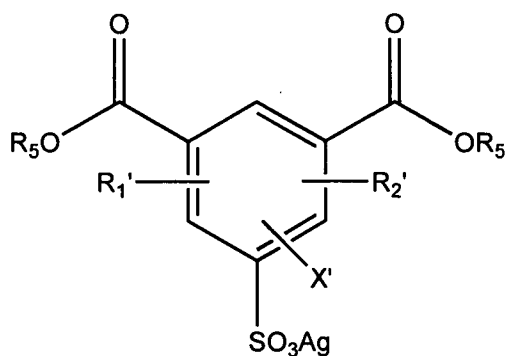
12. The process as claimed in claim 11 wherein the antimicrobial agent has the following formula (I)



(I)

where j , l , m is an integer from 1 to 6, n , k is an integer from 0 to 6, X is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3M where M is a metal selected from Ag, Cu or Zn, R_1 , R_2 is individually H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , COR_6 where R_6 is a $(\text{C}_1\text{-C}_3)$ alkyl, aryl or substituted aryl, SO_3M where M is as defined above, COOR_5 , R_5 being H, Na, K, $(\text{C}_1\text{-C}_3)$ alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(\text{CH}_2)_n\text{-OH}$ where n' is an integer from 1 to 6 or R_1 and R_2 together form an anhydride or an unsubstituted or substituted 5- or 6- membered ring and R_3 and R_4 are reactive functional groups selected from alkenyl, alkoxy, OH, CH_2OH , NH_2 , CHO, COCl or COOR_5 where R_5 is as defined above.

13. The process as claimed in claim 11 wherein the antimicrobial agent has the following formula (II)



(II)

where X' is H, halo, alkoxy, NH_2 , OH, SH, CN, NO_2 , CH_2OH or SO_3Ag , R_1' , R_2' is H, $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl, aryl, substituted aryl, $\text{C}_6\text{H}_5\text{N}_2$, CHO, CH_2OH , COCl, CONH_2 , SO_3Ag , COR_6 where R_6 is a ($\text{C}_1\text{-C}_3$) alkyl, aryl or substituted aryl or COOR_5 , R_5 being H, Na, K, ($\text{C}_1\text{-C}_3$) alkyl, aryl, substituted aryl, COR_6 where R_6 is as defined above or $-(\text{CH}_2)_n\text{-OH}$ where n is an integer from 1 to 6.

14. Antimicrobial copolymer prepared by the process as claimed in any one of the claims 11 to 13

15. Antimicrobial composition comprising the copolymer as claimed in claim 14 wherein metal component(s) of the antimicrobial agent is substantially uniformly distributed throughout, overall metal to sulphonate ratio in the composition being in the range of 1:0.8 to 1:2.2.

16. Filaments, fibers, yarns, fabrics, films, containers or other articles having prolonged antimicrobial activity, improved tenacity, melting point and hydrolytic stability prepared from the composition as claimed in the claims 9 or 10.

17. Filaments, fibers, yarns, fabrics, films, containers or other articles having prolonged antimicrobial activity, improved tenacity, melting point and hydrolytic stability prepared from the composition as claimed in claim 15.