

Synthesis and Antimicrobial Activity of Some Polymers Derived from Modified Amino Polyacrylamide by Reacting It with Benzoate Esters and Benzaldehyde Derivatives

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ABSTRACT: Functionalized polymers have gained much interest in the last decades. This is due to their functional groups and their polymer nature, which give them unique properties and more advantages than the corresponding small molecules. In this trend, we modified polyacrylamide by introducing an amino group in the side chain of the polymer by reacting it with ethylenediamine. The amine-modified polymer was reacted with two classes of active compounds. The first group is aromatic aldehydes containing active groups such as *p*-hydroxybenzaldehyde, vanillin, *p*-chlorobenzaldehyde, and anisaldehyde. The second group is phenolic ester derivatives such as *p*-hydroxymethylbenzoate, 2,4-dihydroxymethylbenzoate, 2-hydroxymethylbenzoate and 3,4,5-trihydroxypropylbenzoate. The antimicrobial activity of these two classes were explored by cut plug

method against *Candida albicans* SC5314, *Aspergillus flavus*, and *Fusarium oxysporium* as fungal organisms and *Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus aureus* as bacterial organisms. It was found that the diameter of inhibition zone varied according to the active group in the modified polymer and the examined microorganism. In general, the modified polymers showed antimicrobial activity against the tested microorganisms. However, the polymer derivative of *p*-chlorobenzaldehyde being the most effective on bacteria and fungi species. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2428–2437, 2006

Key words: bioactive polymers; antimicrobial polymers, biocide, biomedical polymers; phenolic esters; phenolic aldehydes; biological applications of polymers; copolymers

INTRODUCTION

In the recent years, the infections are the most common cause of biomaterial implant failure in modern medicine.^{1–3} Also, infections associated with biomaterials represent a significant challenge to the more widespread application of medical implants.⁴ The presence of a foreign body such as a synthetic biomaterial provides a site for microbial attachment.^{5–10} A possible approach to prevent biomaterial-centered infections is to render the biomaterial surface antimicrobial properties by functionalization with suitable functional groups such as quaternary ammonium or phosphonium groups, which are widely known as disinfectants.³ Antimicrobial biomaterials would be a promising solution for the problems associated with dental applications of polymers for treatment of periodontal diseases.¹¹ Contact lenses represent another

important area for application of antimicrobial polymers, which would be able to reduce or prevent the bacterially driven adverse response associated with the contact lens wear.¹²

Antimicrobial agent-bound polymers usually exhibit their microbial activities by slowly releasing the active agents through hydrolysis, but some other polymers are antimicrobially active by themselves. They have some advantages over low-molecular-weight agents because they are more stable against volatilization, dissolution, and diffusion to the surfaces of material to be protected.^{13–23}

Polyacrylamide (PAAm), a synthetic polymer, is widely used as flocculating, paper strengthening agents, and can also be applied to enhance the recovery of the oil.²⁴ Moreover, PAAm is a water-soluble polymer of biomedical and pharmaceutical interest widely studied as hydrogel for blood compatible material.²⁵ PAAm can interact with some other functional groups, such as —COOH, —NH₂, and C=O groups, due to its backbone chain having several primary amide groups. With the purpose of producing new polyacrylamide derivatives with primary amino groups, the amine-functionalized polyacrylamide was used as a carrier for various antimicrobial agents.

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EXPERIMENTAL

Materials

Polyacrylamide (PA) was purchased from Aldrich and was used as received without further purification. Ethylenediamine (EDA) was supplied by S. D. Fine Chem. Ltd. Co. and was distilled before use. *p*-Hydroxy benzoic acid was supplied from Sigma-Aldrich Co. Ltd., and was used as received. Methyl salicylate was used as received from El-Naser Pharmaceutical Chemicals Company, Egypt. Propylgallate was purchased from Aldrich and was used as received without further purification. 4-Hydroxy-3-methoxy benzaldehyde (vanillin) was purchased from El-Gomhouria Chemicals Company, Egypt and was used without further purification. *p*-Methoxybenzaldehyde was supplied by Fluka AG and was used without further purification. Glacial acetic acid supplied from El-Gomhouria Chemicals Company, Egypt and was used as received. Absolute methanol was used as received from Merck-Schuchardt.

p-Hydroxymethylbenzoate was prepared as follows: 50 g (362 mmol) of *p*-hydroxy benzoic acid was dissolved in 250 mL absolute methanol. Dry H₂SO₄ (16 mL) was added slowly to the colorless solution with stirring. The system was fitted to a reflux at 80°C for 24 h in an oil bath with continuous stirring. The system was cooled and the excess alcohol was removed by rotary evaporator. A white precipitate was formed immediately when 300 mL of distilled water was added to the reaction mixture. The precipitate was filtered off and washed with distilled water until no more acid appear in the TLC. The ester was collected as white powder and was dried under vacuum at 40°C for 24 h. The yield was 47.5 g (95%). The product was characterized by ¹H NMR and IR spectroscopy.

2,4-Dihydroxymethylbenzoate was synthesized as follows: To a colorless solution of 50 g (324.42 mmol) of 2,4-dihydroxymethyl benzoic acid in 250 mL of absolute methanol was added 16 mL of dry H₂SO₄. The mixture was refluxed with stirring at 80°C for 24 h. The system was cooled and the excess alcohol was removed using rotary evaporator. Distilled H₂O (300 mL) was added to the mixture and a white precipitate was formed. The precipitate was filtered off and washed with hot distilled water to ensure that no more unreacted acid was still present in the precipitate. The ester was collected as white powder and it was dried under vacuum at 40°C for 24 h. The yield was 45 g (90%) and the product was characterized by IR and ¹H NMR spectroscopy.

Instruments

Infrared spectra were recorded on a PERKIN-ELMER 1430 Ratio Recoding Infrared Spectrophotometer from KBr pellets. Elemental analyses were determined on

Heraeus (microanalysis Center, Cairo University, Giza, Egypt). Rotary Evaporator was supplied from Buchi, Switzerland. Vacuum oven was supplied by Lab-Line Instruments, Inc.

Polyacrylamide modification

Modification of PA with EDA

In 500 mL round-bottomed flask, 30 g (0.42 mol) of (PA) were added portionwise to 282.2 mL of EDA. After the addition was completed, the system was fitted to reflux at 80°C for 2 days with continuous stirring. The modified PA (MPA) was filtered off and washed five times with methyl alcohol to remove the unreacted EDA. The product (MPA) was collected as white powder; it was dried in vacuum oven at 40°C overnight. The yield was 47.2 g (98%). The product was characterized by IR and elemental analysis (*cf.* Scheme 1).

Modification of the EDA MPA with vanillin

To a solution of vanillin (13.63 g, 0.09 mol) in 30 mL of absolute methanol was added with stirring 3.41 g (0.05 mol) of MPA and 1 mL of glacial acetic acid. Stirring was continued at room temperature for 48 h and then the system was fitted to reflux at 80°C for 10 h. The formed precipitate was filtered off and washed with methanol to remove the excess vanillin and acetic acid. The product (MPA₁) was collected as brown powder, dried in vacuum oven at 40°C for 48 h. The yield was 84.16% (6.24 g). The product was characterized by elemental analysis and IR (*cf.* Scheme 2).

Modification of EDA MPA with *p*-hydroxybenzaldehyde

A mixture of 4-hydroxybenzaldehyde (10.94 g, 0.09 mol), MPA (3.41 g, 0.05 mol) and 1 mL glacial acetic acid in 30 mL methanol was stirred at room temperature for 48 h. The system was fitted to reflux for 10 h at 80°C. The product was filtered off and washed with methanol to remove the unreacted species. The modified polymer (MPA₂) was collected as dark orange powder, dried under vacuum oven at 40°C for 48 h. The yield was 5.78 g (88.65%). MPA₂ was characterized by IR and elemental analysis (*cf.* Scheme 2).

Modification of EDA MPA with *p*-hydroxymethylbenzoate

In a 500 mL round-bottomed flask was added *p*-hydroxymethylbenzoate (13.62 g, 0.09 mol) in 30 mL DMSO. The amine MPA (3.41 g, 0.05 mol) was added portionwise to the stirred *p*-hydroxymethylbenzoate solution. The reaction mixture was stirred for 2 days

and the color turned buff. The system was fitted to reflux at 80°C for 10 h. The product was washed with DMSO to remove the unreacted ester. The product (MPA₃) was collected as buff powder and dried in vacuum oven at 40°C overnight. The yield was 3.66 g (52%), and structure of the product was characterized by IR and elemental analysis (*cf.* Scheme 3).

Modification of EDA MPA with 2,4-dihydroxymethylbenzoate

To a solution of (15.1 g, 0.09 mol) of 2,4-dihydroxymethylbenzoate in 30 mL DMSO was added 3.41 g (0.05 mol) of MPA portionwise with continues stirring. The reaction mixture was stirred for 2 days at room temperature. The system was fitted to reflux at 80°C for 10 h to ensure that the reaction was completed. The product was filtered off and washed with DMSO to remove the unreacted ester. The product MPA₄ was collected as buff powder, dried in vacuum oven at 40°C for 2 days. The yield was 3.7 g (49.3%). The product MPA₄ was characterized by IR and elemental analysis (*cf.* Scheme 3).

Modification of EDA MPA with 2-hydroxymethylbenzoate

To a solution of 2-hydroxymethylbenzoate (13.62 g, 0.09 mol) in 30 mL chloroform, MPA (3.41 g, 0.05 mol) was added portionwise with stirring. The reaction mixture was stirred for 2 days. The color became buff after 2 days. The system was fitted to reflux at 80°C for 10 h to ensure that the reaction was completed. The product was filtered off and washed with chloroform to remove the unreacted ester. The collected polymer (MPA₅) was collected as buff powder, dried in vacuum oven at 40°C overnight. The yield was 5.91 g (84.5%) (*cf.* Scheme 3). Structure of the product was confirmed by elemental analysis and IR.

Modification of EDA MPA with p-chlorobenzaldehyde

To a stirred solution of *p*-chlorobenzaldehyde (12.6 g, 0.09 mol) in methanol (30 mL) was added MPA (3.41 g, 0.05 mol) and 1 mL acetic acid. Stirring was continued at room temperature for 28 h. The system was refluxed at 80°C for 10 h. The modified polymer was filtered off and washed five times with methanol to remove the excess aldehyde. The collected Schiff base (MPA₆) was collected as yellowish powder, dried in vacuum at 40°C for 2 days (*cf.* Scheme 2). Structure of the product was confirmed by elemental analysis and IR.

Modification of EDA MPA with anisaldehyde

To a solution of 4-methoxybenzaldehyde (anisaldehyde) (12.2 g, 0.09 mol) in methanol (30 mL) was

added MPA (3.41 g; 0.05 mol) and 1 mL glacial acetic acid. Stirring was continued at room temperature for 2 days. The system was then refluxed at 80°C for 10 h. The color became darker on heating, and the formed precipitate was filtered off and washed five times with methanol to remove unreacted aldehyde. The product (MPA₇) was collected as yellowish powder, dried in vacuum oven at 40°C for 48 h. The yield was 5.35 g (76.91%). Structure of the product was confirmed by elemental analysis and IR (*cf.* Scheme 2).

Modification of EDA MPA with 3,4,5-trihydroxypropylbenzoate

To a stirred solution of 3,4,5-trihydroxy propylbenzoate (13.93 g, 65.71 mmol) in 30 mL DMSO was added MPA (1.5 g, 13.16 mmol) portionwise with stirring. The reaction mixture was stirred for 48 h and the color became buff. The system was fitted to reflux at 80°C for 10 h to ensure that the reaction was completed. The product was filtered off and washed with DMSO to remove the unreacted ester. The polymer (MPA₈) was collected as buff powder, dried in vacuum oven at 40°C overnight. The yield was 2.18 g (62.21%) (Scheme 3). Structure of the product was confirmed by elemental analysis and IR.

Antimicrobial assessment

Microorganisms

The fungal microorganisms chosen to test the antimicrobial activity of the synthesized polymers were *Candida albicans* SC5314, *Aspergillus flavus*, and *Fusarium oxysporium*. To evaluate the antimicrobial activity of the synthesized polymers, *Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus aureus* were used.

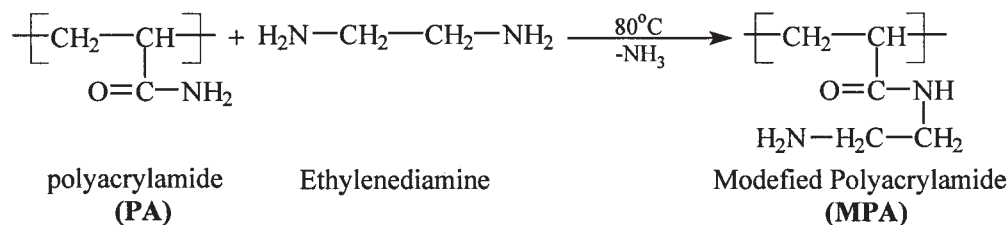
Media

Nutrient agar and Nutrient broth were used for growing bacterial cultures. On the other hand, Sabouraud dextrose agar was used for the growth of *C. albicans*, and Czapek's dox agar was used for the growth of *A. flavus* and *F. oxysporium*.

Antimicrobial activity test

Cut plug method

The tested polymers were water insoluble; the cut plug method was employed to determine the antimicrobial activity of the synthesized polymers. A 0.5 mL spores or cell suspension were prepared and counted, then mixed with 9.5 mL of the corresponding sterilized melted media, and left to solidify at room temperature. Wells are made in seeded agar plate with different organisms under investigation by cork borer



Scheme 1 Modification of PA with EDA.

and each one was filled with 20 mg of the tested polymers. All the plates were incubated at proper temperature for 36 h, and then the inhibition zone diameters were measured.

Measuring the organism's surviving ratio

Each standard organism suspension (0.5 mL) was mixed with 9.5 mL of 10-fold diluted corresponding media in sterile test tube that contained the tested polymer to give concentration of 1.25, 2.5, 5, 10, and 20 mg/mL. The seeded tubes were shaken at 250 rpm overnight, the threefold dilution was carried out, and 100 mL of each dilution was spread into agar plate of corresponding media. Controls without the polymers were run and the plates were incubated at proper temperature for 24 h, and then the colony forming units was recorded. The surviving ratio was calculated for each organism at different polymers concentration and compared with the control.

RESULTS AND DISCUSSION

In these studies, development of new polymers with antimicrobial activity is described. This was achieved by modification of PA to produce polymers with the suitable active functional groups. A series of modified polymers (MPA₁₋₈) were synthesized and their antimicrobial activity against different tested organisms was investigated.

Synthesis of the MPA polymers

The modification of PA was carried out by introducing active amino group to the PA by reacting it with EDA.

The aminated PA is expected to be highly active than PA itself when reacted with aldehydes and esters.

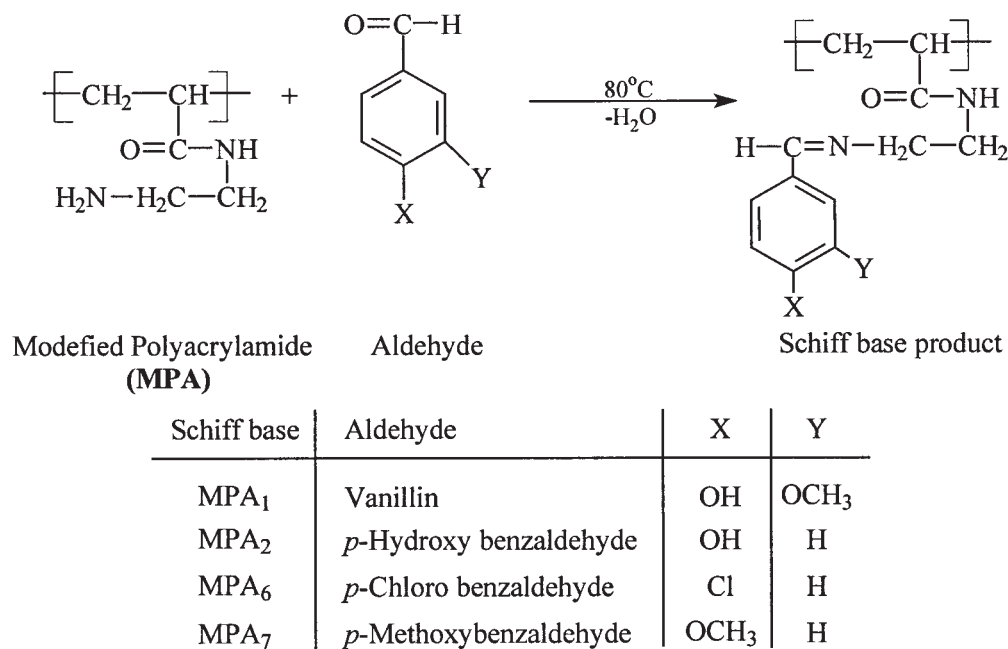
Modification of PA with EDA

Modification of PA with EDA was carried out to create active amino group as the functional group in the PA. The reactivity of the MPA toward aldehydes and esters was found to be higher than that of the PA itself. The amination reaction takes place in absolute methanol as a solvent. Many attempts were carried to determine the molar ratio between the polymer and the diamine. It was found that, when 1 : 10 Molar ratio for the polymer:diamine was used, the reaction gives the highest degree of amination at this molar ratio. The reaction yield was about 98%. At lower ratios for PA and the diamine, the reaction yields a crosslinked polymer. It was also noticed that the reaction proceeds better at higher temperature (70°C) than at lower temperature. Also, addition of solvent promotes the reaction to yield uncrosslinked polymer. This may be due to the dilution factor. Absolute methanol was also used to remove the unreacted diamine. The MPA was collected as white fine powder and was dried under vacuum for 24 h (Scheme 1).

The elemental analysis is as shown in Table I and it was in a good agreement with the calculated values. The IR spectrum of polymer MPA showed peaks at 3294.3 and 3346.8 cm⁻¹ for (—NH₂) primary amine, 3071.9 cm⁻¹ for secondary amide (—NH—), and 1653.5 cm⁻¹ for (C=O) carbonyl of amide.

TABLE I
Elemental Microanalysis for MPA and the Synthesized Polymers MPA₁₋₈

Polymer	C %		H %		N %		Cl %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
PA	50.69	49.84	7.09	7.03	19.71	15.50	—	—
MPA	52.61	51.14	8.83	8.91	24.54	19.70	—	—
MPA ₁	62.89	60.30	6.50	6.35	11.28	11.10	—	—
MPA ₂	66.04	65.80	6.47	6.35	12.84	11.00	—	—
MPA ₃	61.53	60.2	6.02	6.00	11.96	10.35	—	—
MPA ₄	57.59	56.4	5.64	6.2	11.19	11.20	—	—
MPA ₅	61.53	60.2	6.02	6.0	10.52	10.5	—	—
MPA ₆	60.89	59.90	5.54	5.30	11.83	11.60	14.98	12.40
MPA ₇	67.22	66.10	6.94	6.10	12.06	12.00	—	—
MPA ₈	56.13	56.00	5.30	5.34	10.52	9.60	—	—



Scheme 2 Schiff base formation between MPA and various aldehydes.

Modification of MPA with various aldehydes (schiff base formation)

The Schiff base formation between the MPA and various aldehydes was carried out in absolute methanol and glacial acetic acid as a catalyst. A series of four different modified polymers was prepared by reacting the aminated PA with vanillin, *p*-hydroxy benzaldehyde, *p*-chlorobenzaldehyde, and *p*-methoxybenzaldehyde. In all condensation reactions, excess amounts of the aldehyde were used to ensure complete condensation. The condensation reaction was carried out in an oil bath at 80–90°C with stirring. The Schiff base does form at room temperature, but heating and stirring was used to increase the reaction yield. The product was washed with absolute methanol to remove the excess aldehyde (Scheme 2).

The elemental analysis data for these derivatives are listed in Table I and are in a good agreement with the calculated values. The characteristics bands of the IR

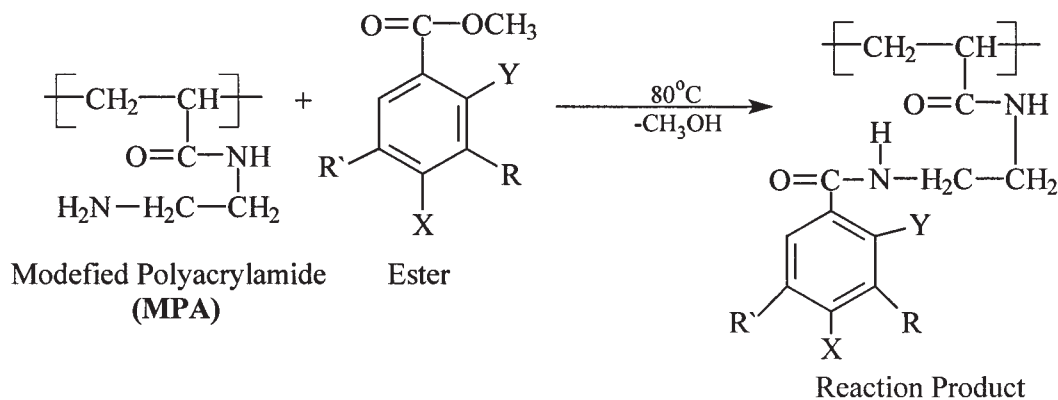
spectra of polymers MPA₁, MPA₂, MPA₆, and MPA₇ are listed in Table II.

Modification of MPA with various esters

These compounds were prepared to examine the effect of such phenolic groups on the antibacterial activity of the unmodified polymer. Various phenolic esters were prepared by reacting the corresponding acid with absolute methyl alcohol in the presence of sulfuric acid. The esterification was carried out in high conversion yield (90–95%). The ¹H NMR spectrum of 4-hydroxymethylbenzoate in DMSO showed peaks at 10.3 ppm (1H, singlet, OH in position 4); 7.8 ppm (2H, doublet, CH in position 3 and 5); 6.8 ppm (2H, doublet, CH at positions 2 and 6); and at 3.8 ppm (3H, singlet, CH₃). The ¹H NMR spectrum of 2,4-dihydroxymethylbenzoate in DMSO showed peak at 10.7 ppm (1H, singlet, OH in position 2); 10.42 ppm (1H,

TABLE II
IR Analysis of Modified Polyacrylamide MPA₁₋₈

Polymer	N—H 2° amide	C=O	O—H aromatic	C—H in CH ₃ O—	C=N imine	C—Cl
MPA ₁	3060.9	1645.0	3254.7	2927.0 & 2843.7	1593.4	—
MPA ₂	3066.7	1645.1	3246.3	—	1584.5	—
MPA ₃	3076.0	1647.7	3294.7	—	—	—
MPA ₄	3072.0	1655.1	3287.4	—	—	—
MPA ₅	3061.5	1635.0	3266.7	—	—	—
MPA ₆	3063.0	1643.0	3280.7	—	1594.7	692.1
MPA ₇	3066.7	1644.7	3281.9	2838.3 & 2930.9	1605.3	—
MPA ₈	3066.0	1654.9	3421.6	—	—	—



Product	Ester	X	Y	R	R'
MPA ₃	<i>p</i> -Hydroxy methyl benzoate	OH	H	H	H
MPA ₄	2,4-Dihydroxy methyl benzoate	OH	OH	H	H
MPA ₅	2-Hydroxy methyl benzoate	H	OH	H	H
MPA ₈	3,4,5-TriHydroxy propylbenzoate	OH	H	OH	OH

Scheme 3 Modification of MPA with various esters.

singlet, OH in position 4); 7.62 ppm (1H, singlet, CH in position 3); 6.25 ppm (1H, doublet, CH in position 5); 6.35 ppm (1H, doublet, CH in position 6); and at 3.82 ppm (3H, singlet, —CH₃).

Reaction of aminated PA with phenolic esters was carried out to introduce the phenolic group to the side chain of the polymer. Compounds MPA₃₋₅ and MPA₈ were synthesized in similar conditions. The reactions involved the removal of alcohol from the reactants and the formation of new amide group. MPA₃, MPA₄, and MPA₈ were prepared in DMSO and an excess of the ester was used to ensure that the reaction was completed. Washing with DMSO and methanol removed the unreacted ester. The reaction with methyl salicylate was carried out in chloroform with 84.5% yield. The modified polymers were then collected and dried in vacuum oven at 30–40°C for 24 h. Generally, the reactions occurred easily with higher yields (Scheme 3).

The characteristic bands of the IR spectra of polymers MPA₃, MPA₄, MPA₅, and MPA₈ are listed in Table II.

Antimicrobial activity of the modified polymers

The antimicrobial activity of the modified polymers is investigated. It was found that the diameter of inhibition zone varied from polymer to another, according to the substitutions and also the microorganisms tested. The MPA derivatives (MPA₁₋₈) have greater

effect on the fungi species more than bacterial species based on the larger, clear inhibition zones with the tested fungi species on solid agar media (diameters of inhibition zones ranged between 12.0 and 49.0 mm) after incubation [Fig. 1(a,b)].

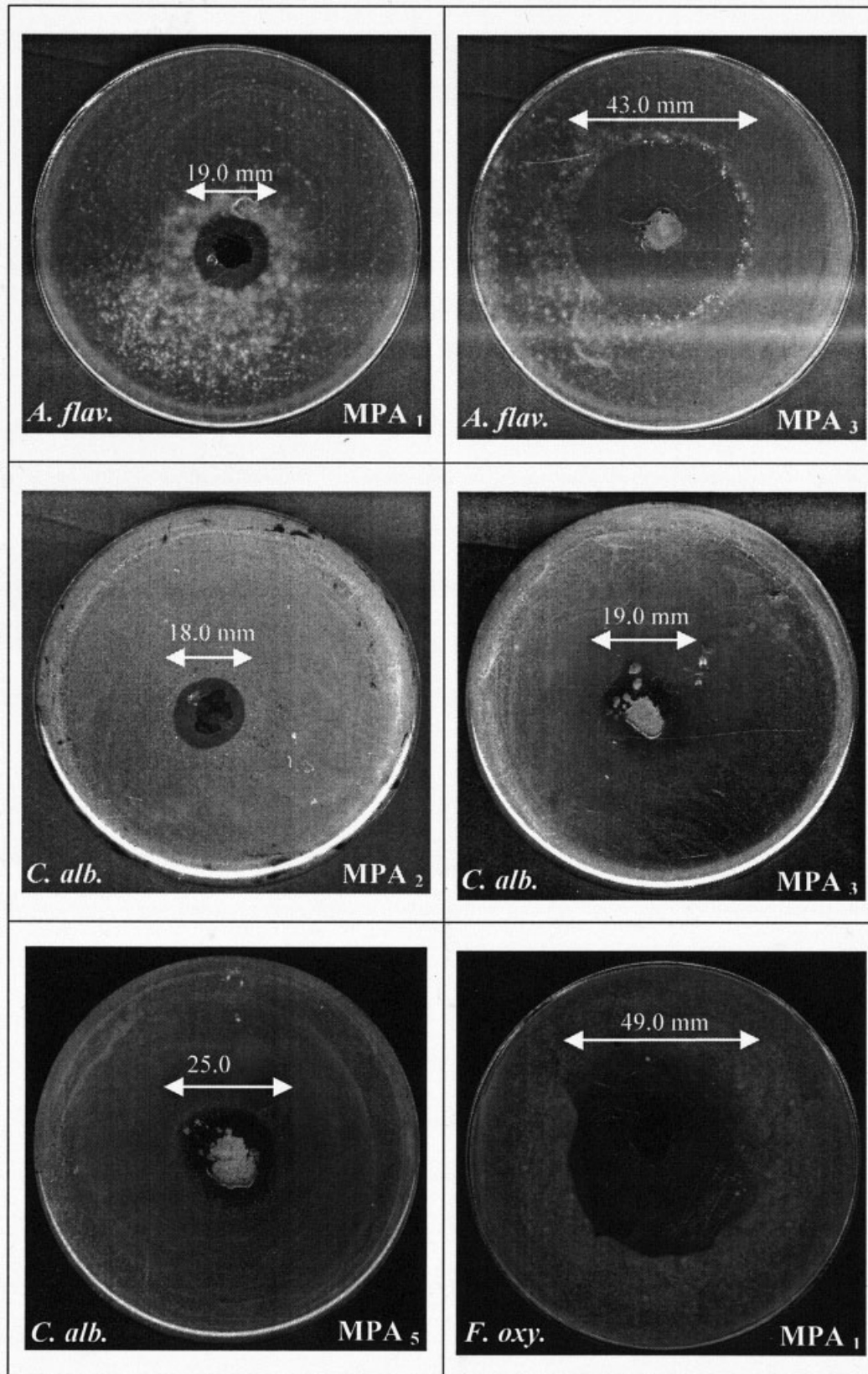
Antimicrobial assessment of MPA₂

The antimicrobial activities of MPA derivative MPA₂ against *C. albicans*, *A. flavus*, *F. oxysporium*, *B. subtilis*, *E. coli*, and *S. aureus* were examined using cut plug method and visible count methods as described before in the Materials and Methods.

The growth inhibiting effect was quantitatively determined by the ratio (*M/C*) of the surviving cell number and the results were recorded. As shown in Figure 2, the growth inhibitory effects of MPA₂ differed among the bacteria and fungi species. The inhibition becomes stronger in the order *S. aureus* < *F. oxysporium* < *C. albicans*. The results showed also that the inhibitory effect increased by increasing the concentration of the polymer.

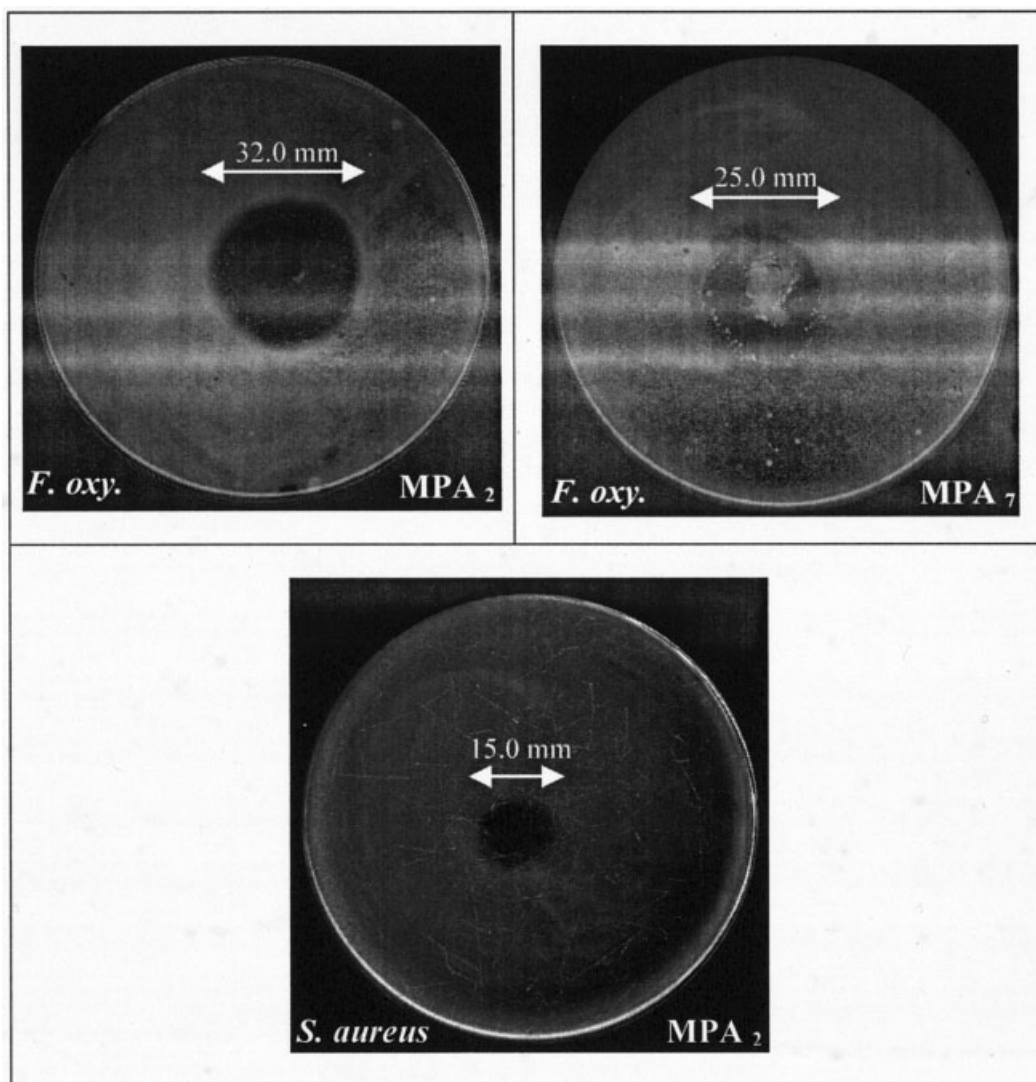
Antimicrobial assessment of MPA₃

The antimicrobial activities of MPA derivative MPA₃ against *C. albicans*, *A. flavus*, *F. oxysporium*, *B. subtilis*, *E. coli*, and *S. aureus* were examined using cut plug method and visible count methods as described before in the Materials and Methods.



(a)

Figure 1 Inhibition zone of polymers (MPA₁₋₈) against different species of microorganisms.



(b)

Figure 1 (Continued from the previous page)

The growth inhibiting effect was quantitatively determined by the ratio (M/C) of the surviving cell number. As shown in Figure 3, the growth inhibitory effect of MPA_3 varied among the bacteria and fungi species. The inhibition becomes stronger in the order *S. aureus* < *C. albicans*. The results showed that the inhibitory effect increased by increasing the concentration of the polymer on *S. aureus* and *C. albicans*.

Antimicrobial assessment of MPA_5

The antimicrobial activities of MPA derivative MPA_5 against *C. albicans*, *A. flavus*, *F. oxysporium*, *B. subtilis*, *E. coli*, and *S. aureus* were examined using cut plug method and visible count methods as described before in the Materials and Methods.

The growth inhibiting effect was quantitatively determined by the ratio (M/C) of the surviving cell number and the results were recorded. As shown in Figure 4, the growth inhibitory effect of MPA_5 differed among the bacteria and fungi species. The inhibition becomes stronger in the order *C. albicans* < *S. aureus* < *F. oxysporium*. It was found that at concentration <5 mg/mL, MPA_5 was more effective against *F. oxysporium* than *S. aureus*. The results also showed that the inhibitory effect increased by increasing the concentration of the polymer.

It is quite clear that the inhibition potency of the tested polymer varied according to the polymer and the tested microbial strain. Many researchers stated that quaternary ammonium salts are active against microorganisms by interacting with the cell membrane.^{1,3,15,19,21} We anticipate that the inhibitory effect

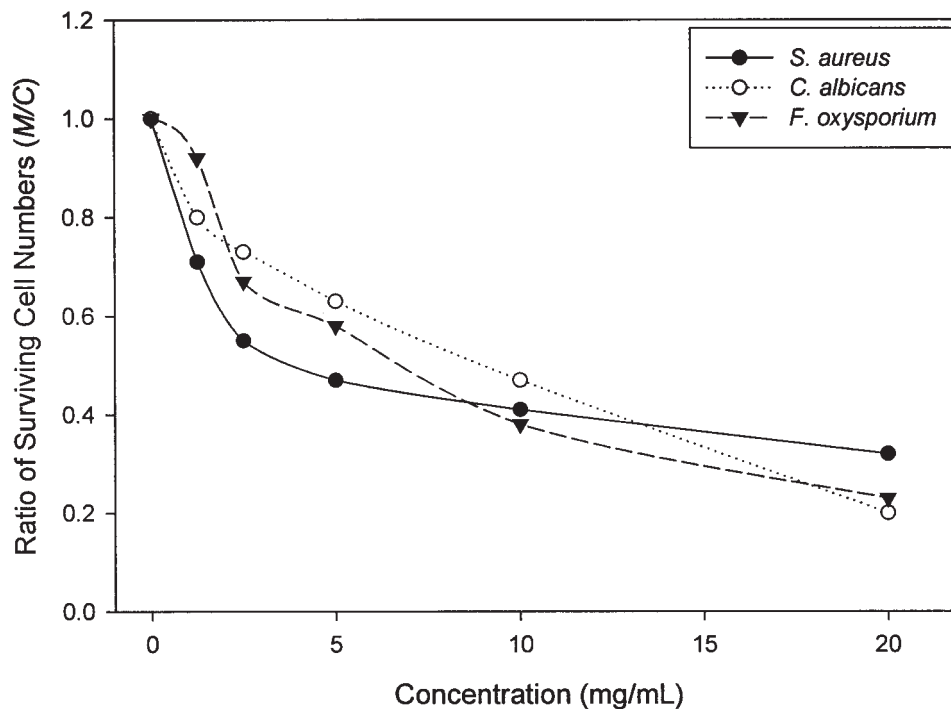


Figure 2 Growth inhibition of different concentration of MPA₂.

of MPA appears to be explicable in terms of the effective charge density of the active sites. It is reasonable to assume that the charge density of the MPA with various aldehydes leads to enhanced adsorption into the microbial cells. There are many negatively charged species present in the cytoplasmic membranes such as

acidic phospholipids and some membrane proteins. Microbial activity of the biocides arises mainly from the disruption of the plasma membrane. Therefore, it is reasonable to assume that larger the amount of the bound biocide, the more induced is the disruption, which consequently leads to higher inhibitory effect.

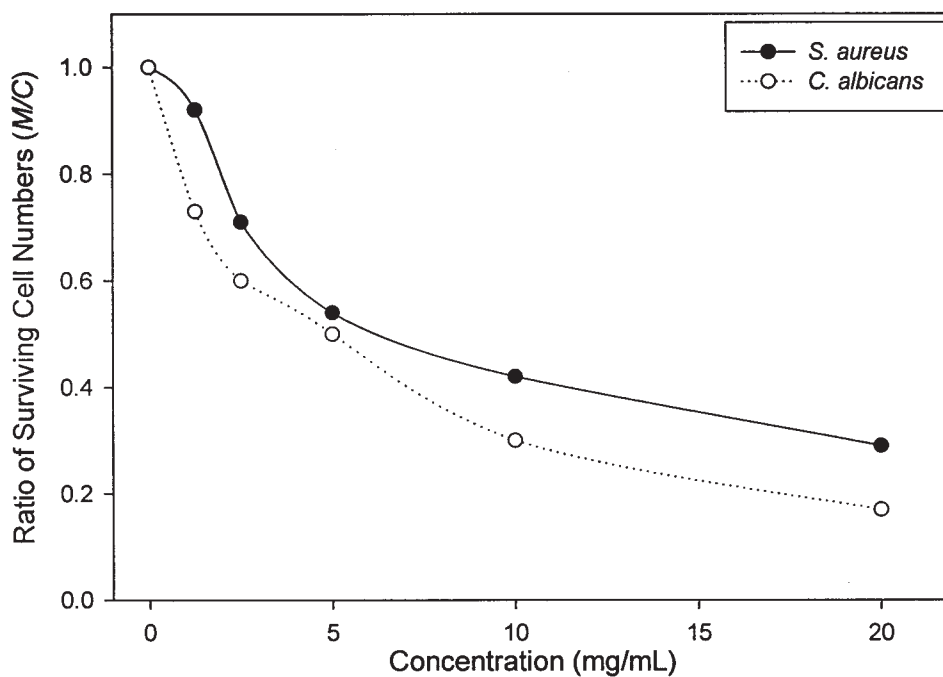


Figure 3 Growth inhibition of different concentration of MPA₃.

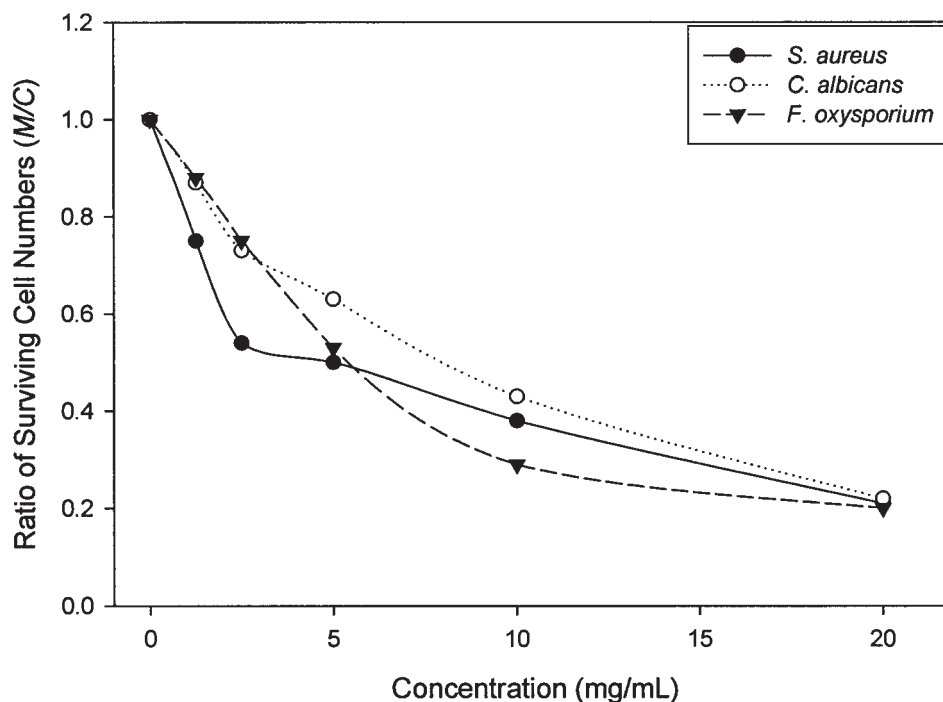


Figure 4 Growth inhibition of different concentration of MPA₅.

The mode of action of these polymers is currently under intensive investigation.

CONCLUSIONS

These studies have demonstrated the feasibility of using the amine-MPA as a carrier for antimicrobially active benzoic acid derivatives. The antimicrobial activity of the prepared polymers were explored against *C. albicans* SC5314, *A. flavus*, and *F. oxysporium* as fungal organisms and *B. subtilis*, *E. coli*, and *S. aureus* as bacterial organisms. The antimicrobial activities of the modified polymers (MPA₁₋₈) have higher effect on the fungal species more than bacterial species examined.

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