Graft Copolymerization of Vinyl Monomers Bearing Positive Charges or Episulfide Groups onto Loofah Fibers and Their Antibacterial Activity

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ABSTRACT: Ion exchange fibers with quaternary ammonium groups, phosphonium groups, or thiol groups etc., were prepared by graft copolymerization of vinyl monomers on loofah fiber which is one of the natural fibers. Methacryloyloxyethyl trimethyl ammonium chloride (METAC), tributyl-4-vinylbenzyl phosphonium chloride (TRVB), and epithiopropyl methacrylate (ETMA) were used as vinyl monomers. Graft copolymerization of METAC on loofah could be carried out in water using ammonium cerium (IV) nitrate. Graft copolymerization of TRVB and ETMA on loofah could be performed in water and water-dimethylsulfoxide mixed solution using hydrogen peroxide as an initiator, respectively. The optimum conditions for each graft copolymerization were investigated in detail. Ion exchange fibers (LE-TTA) having both thiol groups and triethylenetetramine side chains were obtained by treatment of L-*g*-ETMA (LE) with triethylenetetramine. LE and LE-TTA had high adsorption ability for silver ions. LE-TTA-Ag exhibited high antibacterial activity against *E. Eoli* and *S. aureus,* but LE-Ag did not. On the other hand, L-*g*-METAC and L-*g*-TRVB also exhibited high antibacterial activity against *E. Eoli* and *S. aureus.* © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1077–1086, 2000

Key words: ion exchange fibers, methacryloyloxyethyl trimethyl ammonium chloride, tributyl-4-vinylbenzyl phosphonium chloride, epithiopropyl methacrylate, loofah, antibacterial activity, adsorption of metal ions

INTRODUCTION

Natural fibers consist mostly of celluloses or proteins, and they have been widely used not only for materials in clothing but also in industry or in medical fields.[1] The loofah fiber is one of natural fibers, and it consists of celluloses. It has a strong network structure, which is easily available. The chemical modification of cellulose has been investigated by many researchers,[2–4] and modified celluloses are used for many purposes. On the other hand, we have reported the preparation of several water-insoluble resins[5–7] or hydrogels[8] having antibacterial activity to prevent the residual toxicity of water-soluble bactericides in water. This article is concerned with the graft copolymerization of vinyl monomers bearing positive charges or episulfide groups on loofah fibers and their use as adsorbents or antibacterial fibers.

EXPERIMENTAL

Materials

Dried bleached loofah fibers obtained commercially were refluxed with benzene/ethanol (1/1 volume ratio) for 6 h, then dried. The dried loofah fibers were boiled for 12 h in a 1% NaOH solution under a nitrogen atmosphere, followed by treat-

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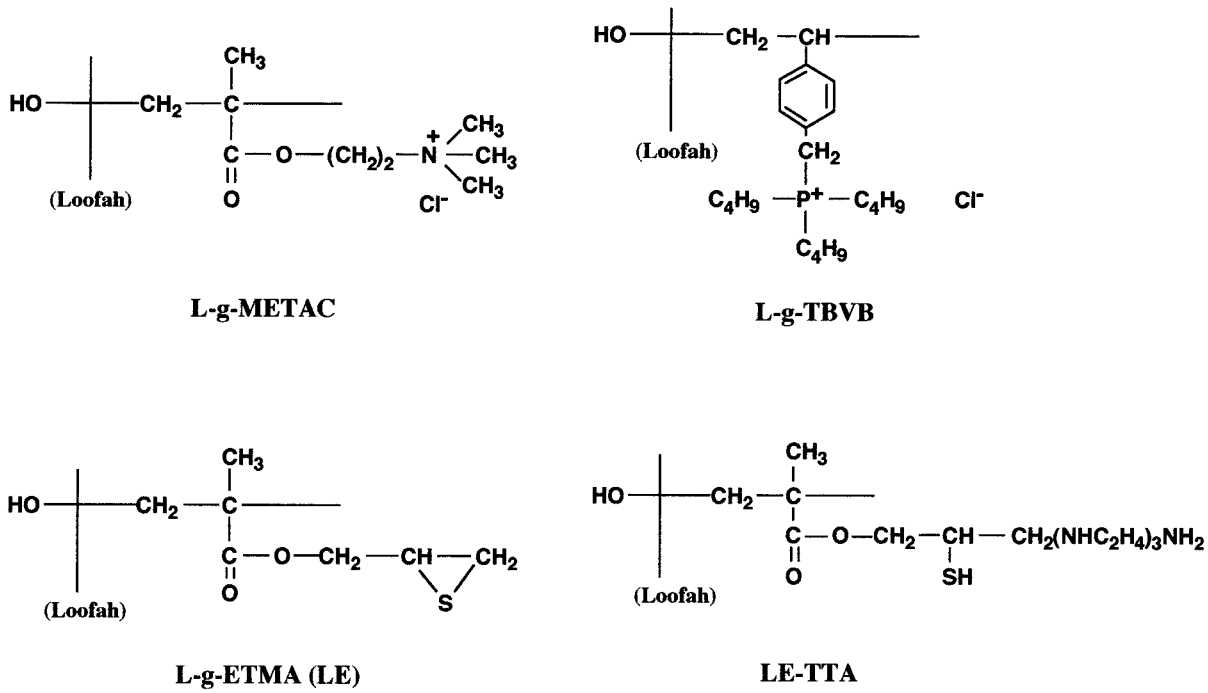

Figure 1 Structure of grafted loofah fibers.

ing three times with a 1% acetic acid solution, then washed with water until the smell of acetic acid disappeared. The loofah fibers obtained were used for experiments after complete drying. Tributyl-4-vinylbenzylphosphonium chloride (TBVB) and methacryloyloxy-ethyl trimethyl ammonium chloride (METAC) were kindly supplied by Nippon Kagaku Kogyo Co., Tokyo, Japan, and Nitto Riken Kogyo Co., Iwaki, Japan, respectively. TBVB and METAC are water-soluble monomers and have quaternary ammonium groups and phosphonium groups, respectively. They were used without further purification. 2,3-Epithiopropyl methacrylate (ETMA) was prepared by the methods reported earlier.[9] ETMA is a water-insoluble monomer. Other chemicals were of reagent grade.

Graft Copolymerization of Vinyl Monomers onto Loofah Fibers

Pretreated loofah fibers (about 50 mg) were soaked in deionized water or deionized water–dimethylsulfoxide (DMSO) mixed solution. To each solution, water-soluble monomer (METAC, TBVB) or water-insoluble monomer (ETMA) was added, respectively. Nitrogen was introduced into this solution for 1 h in an ice/water bath, followed by addition of a desired amount of initiator (ammonium cerium nitrate for METAC, H_2O_2 for TBVB and ETMA) and by further introduction of nitrogen for 30 min. The polymerization was carried out in a sealed glass vessel. The grafted loofah fibers obtained were purified by extraction of untreated monomers and homopolymers with solvents (boiled water for METAC, methanol for TBVB, and DMSO for ETMA). The grafted loofah fibers obtained were abbreviated as L-*g*-METAC, L-*g*-TBVB, and L-*g*-ETMA (LE), respectively (Fig. 1).

Amination of LE

The LE was aminated with triethylenetetramine (TTA) in 1,4-dioxane at 90°C for 8 h under occasional shaking. The LE–TTA (Fig. 1) obtained was washed with methanol and deionized water, then washed three times with 1 mol dm^{-3} HCl solution to remove unreacted TTA, and followed by washing several times with 1 mol dm^{-3} NaOH solution, and deionized water, until washings became neutral, then dried. The polymer add-on (%) was calculated by use of equation (1), as follows:

$$\text{Polymer add-on (\%)} = 100 \times (\text{wt of grafted loofah} - \text{wt of loofah})/\text{wt of loofah} \quad (1)$$

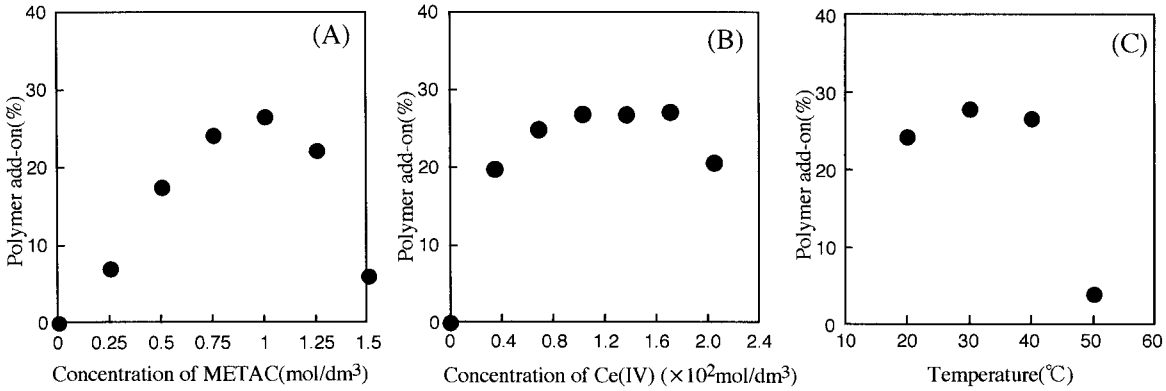

Figure 2 Graft copolymerization of METAC on loofah fibers under various conditions. (A) Effect of concentration of METAC: Ce(IV), 13.6 mmol dm^{-3}; polymerization, 40°C, 24 h. (B) Effect of concentration of initiator: METAC, 1.0 mol dm^{-3}; polymerization, 40°C, 24 h. (C) Effect of temperature: Ce(IV), 13.6 mmol dm^{-3}; METAC, 1.0 mol dm^{-3}; polymerization, 24 h.

Measurement of Adsorption Capacity of the Grafted Loofah Fibers for Ag^+ Ions

Weighed grafted loofah fibers dried (about 100 mg) and 50 cm^3 of 0.01 mol dm^{-3} $AgNO_3$ solution were placed in a 100-cm^3 glass-stoppered Erlenmeyer flask. The mixture was shaken at 30°C for 24 h. The adsorption capacity was calculated by determining the concentration of metal ions in the supernatant with inductively coupled argon plasma atomic emission spectrophotometry (Shimadzu ICPS-5000).

Measurement of Antibacterial Activity

The bacteria used in this study were *E. coli* (IFO 3301) and *S. aureus* (IFO 13276), which were obtained commercially from the Institute for Fermentation, Osaka, Japan. Cultured cell suspensions containing about 10^7–10^8 cells cm^{-3} were prepared for each strain and used for antibacterial tests.

A desired amount of grafted loofah fiber was placed in 50-cm^3 Erlenmeyer flask, and then 10 cm^3 of cell suspension and subsequent 10 cm^3 of water were added into the flask, and the flask was shaken at 30°C for a desired time.

Antibacterial activity was estimated as follows. After contacting the grafted loofah fibers with a bacteria suspension for a prescribed time, 1 cm^3 of bacteria suspension was pipetted from the flask, and 9 cm^3 of sterile water was added to the bacteria suspension. The suspension was diluted several times, and 0.1 cm^3 of the diluted suspension was spread on an agar plate, which was made of nutrient agar. After the plate was kept at 30°C for 15–24 h, the numbers of viable cells were calculated by counting the numbers of the colonies formed on the plate.

The decrease coefficient (D) for bacteria by L-*g*-METAC, L-*g*-TBVB, LE–Ag, and LE–TTA–Ag was calculated by using equation (2), as follows:

$$D\ (\mathrm{cm^3\ g^{-1}\ h^{-1}}) = (V/W \cdot t)\ \log(N_0/N_t) \qquad (2)$$

where V is the volume of cell suspension (cm^3), W is the weight of the grafted loofah fibers dried (g), t is the contact time (h), N_0 is the initial viable cells (cells/cm^3), and N_t is the viable cells (cells/cm^3) after contact time $t(h)$, respectively.

RESULTS AND DISCUSSION

Graft Copolymerization of Vinyl Monomers Onto Loofah Fibers

First graft copolymerization of METAC onto loofah fibers was carried out under various conditions using ammonium cerium nitrate as an initiator. The results are shown in Figure 2. The polymer add-on increased with increasing concentration of monomer, initiator, and temperature, then decreased. This results indicate that an excess concentration of monomer and initiator, and a higher temperature than the appropriate temperature, brought about the homopolymerization of METAC. In all cases, the same percentage of polymer add-on could not be obtained for the graft copolymerization, even under the same conditions, because the graft copolymerization onto

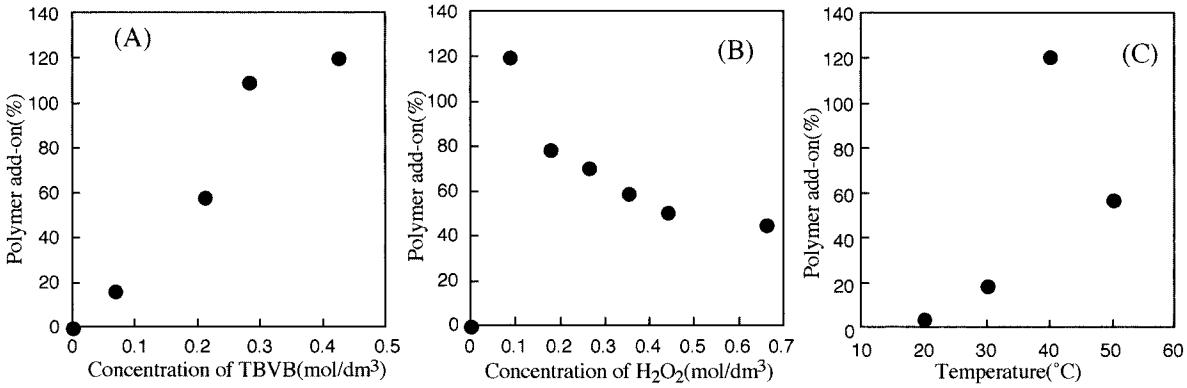

Figure 3 Graft copolymerization of TBVB on loofah fibers under various conditions. (A) Effect of concentration of TBVB: H_2O_2, 0.09 mmol dm^{-3}; polymerization, 40°C, 24 h. (B) Effect of concentration of initiator: TBVB, 0.42 mol dm^{-3}; polymerization, 40°C, 24 h. (C) Effect of temperature: H_2O_2, 0.09 mol dm^{-3}; TBVB, 0.42 mol dm^{-3}; polymerization, 24 h.

loofah fibers proceeded heterogeneously. The percentages of polymer add-on deviated within several percentages. However, the dependence of percentages of polymer add-on for the graft copolymerization on monomer concentration, initiator concentration, and temperature was a similar tendency. For the graft copolymerization of METAC onto loofah fibers, the maximum polymer add-on was obtained at the concentration of 1.0 mol dm^{-3} of METAC, 0.01–0.016 mol dm^{-3} of Ce (IV), and at 30–40°C.

In the case of TBVB and ETMA, these monomers could not be copolymerized with ammonium cerium nitrate; therefore, H_2O_2 was used as an initiator. The graft copolymerization of TBVB was also carried out under various conditions. The results on TBVB are shown in Figure 3. The polymer add-on increased with increasing concentration of TBVB in the concentration range studied from 0.01 to 0.4 mol dm^{-3}, and the maximum polymer add-on was obtained at the concentration of 0.1 mol dm^{-3} of H_2O_2 and at 40°C.

The graft copolymerization of ETMA was carried out in water–DMSO mixed solutions, as ETMA was insoluble in water (Fig. 4). The maximum polymer add-on was obtained in 20% DMSO aqueous solution. The graft copolymerization was also carried out by changing the concentration or temperature. The polymer add-on of ETMA onto loofah fibers was not affected by only the volume ratio of water–DMSO mixed solution but also the concentration of initiator and temperature. The maximum polymer add-on for the graft copolymerization of ETMA was obtained at the concentration of 0.125 mol dm^{-3} of H_2O_2 and at 50°C in the water–DMSO (4:1 volume ratio) mixed solution.

Confirmation of Introduction of Vinyl Monomers into Loofah Fibers

The graft copolymerization was confirmed by elemental analysis and the infrared (IR) spectra of grafted loofah fibers. Figure 5 shows the IR spectra of loofah fiber, LE, and LE–TTA. It was confirmed the introduction of ETMA and TTA from the adsorption peak at 1730 cm^{-1} due to carboxyl groups and at 1550 cm^{-1} due to imino groups, respectively.

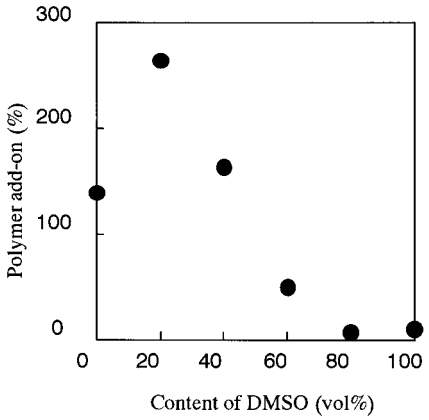

Figure 4 Effect of DMSO content on graft copolymerization of ETMA on loofah fibers under various conditions. ETMA, 0.16 mol dm^{-3}; H_2O_2, 0.18 mol dm^{-3}; polymerization, 50°C, 24 h.

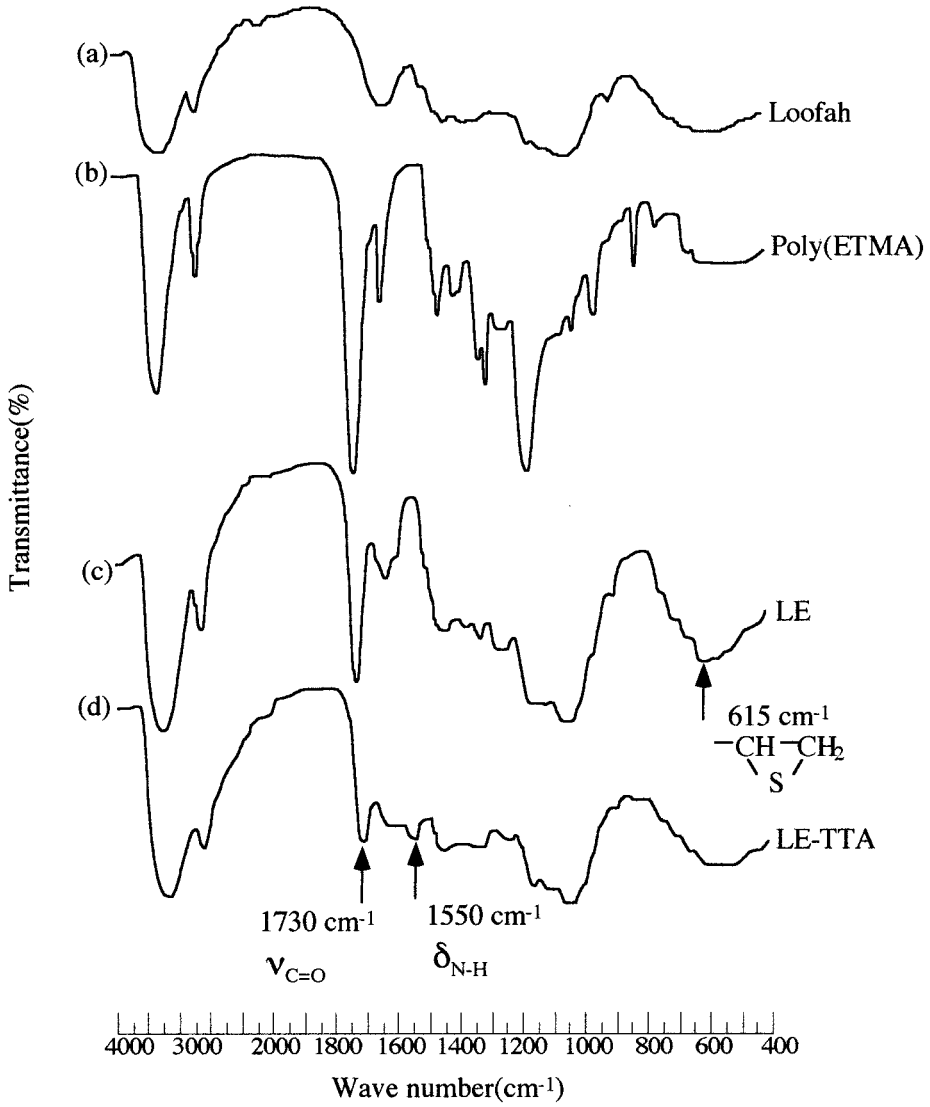

Figure 5 IR spectra of (a) loofah, (b) poly(ETMA), (c) LE (polymer add-on, 71.6%, and (d) LE (polymer add-on, 92.1%)–TTA.

Adsorption of Ag^+ on LE and LE–TTA

It is known that ligands containing sulfur coordinate strongly with Ag^+ ions. We previously reported the preparation of chelating copolymer beads containing triethylenetetramine side chains and/or thiol groups and their properties.[6]

Adsorption of Ag^+ on LE and LE–TTA with different polymer add-on was investigated. The results are shown in Figure 6. The LE and LE–TTA with about 100% of polymer add-on exhibited the maximum adsorption capacity. This indicates that all episufides or thiol groups in the grafted loofah fibers can not participate in the coordination with Ag^+ ions. Accordingly, it was found that the excess polymer add-on of ETMA was not necessary for high adsorption of Ag^+ ions.

The adsorption capacity (meq g^{-1}) of the LE for Ag^+ was higher than that of the LE–TTA. This is due to both the introduction of TTA side chains, which have a lower affinity for Ag^+ ions than ligands bearing sulfur[10] and a lower sulfur content in LE–TTA than LE because LE–TTA was obtained by amination of LE with TTA.

Antibacterial Activity of L-*g*-METAC and L-*g*-TBVB

First, the antibacterial activity of L-*g*-METAC with almost the same polymer add-on against *E. coli* and *S. aureus* was investigated by addition of different amount of L-*g*-METAC. *E. coli* and *S. aureus* are gram-negative and gram-positive bacteria, respectively. The results are shown in Fig-

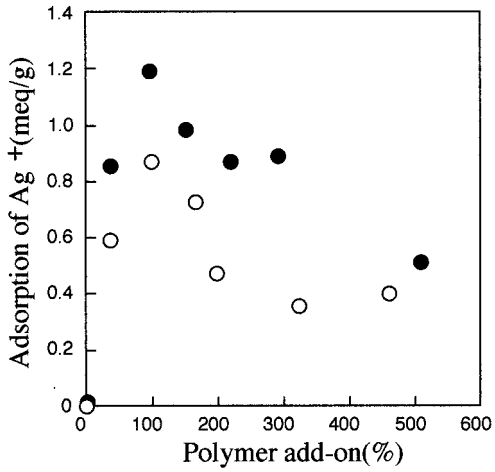

Figure 6 Relation between polymer add-on and the adsorption of Ag^+: (●) LE; (○) LE-TTA; initial Ag^+ concentration, 0.01 mol dm^{-3}; shaking at 30°C, 24 h.

ure 7. The L-*g*-METAC exhibited high antibacterial activity both against *E. coli* and *S. aureus,* and the antibacterial activity increased with increasing amount of L-*g*-METAC added. Next, the antibacterial activity of L-*g*-TBVB with almost the same polymer add-on against *E. coli* and *S. aureus* was investigated (Fig. 8). The L-*g*-TBVB also exhibited high antibacterial activity against *E. coli* and *S. aureus* and increased with increasing amount of L-*g*-TBVB added. We confirmed that supernatant after contacting with grafted loofah fibers exhibited no antibacterial activity, although it contained a very small amount of total organic carbon (TOC), as shown in Figures 7 and 8. Furthermore, they exhibited higher antibacterial activity against *S. aureus* than *E. coli.* It is known that the surfaces of the bacteria such as *E. coli* and *S. aureus* have negative charges in water. Therefore, it is said that the antibacterial activity of the polymers with positive charges, such as quaternary ammonium or phosphonium groups, is brought about by interaction between positive charges on the resins and negative charges on the cell walls of the bacteria.[11,12] The antibacterial activity of L-*g*-TBVB was higher than that of LE–METAC. This is due to the higher polymer add-on of the L-*g*-TBVB than that of the L-*g*-METAC. On the other hand, it is known that the cell wall of *S. aureus* is thinner than that of *E. coli.*[13] Therefore, this difference of activity against both bacteria is due to the difference of the thickness of the cell walls between *S. aureus* and *E. coli.*

Antibacterial Activity of LE–Ag and LE–TTA–Ag

First, antibacterial activity of LE–Ag, which adsorbed different amount of Ag^+, was investigated

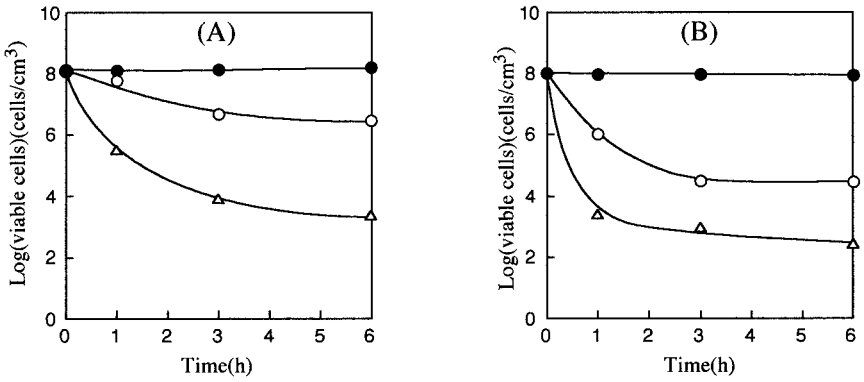

Figure 7 Changes in viable cell number after contacting with L-*g*-METAC. Suspension of (A) *E. coli* or (B) *S. aureus:* 20 cm^3 (water)

Symbol	Sample	Polymer Add-On (%) (A)	Polymer Add-On (%) (B)	Weight (g) (A)	Weight (g) (B)	Final pH (A)	Final pH (B)	TOC* (mg dm^{-3}) (A)	TOC* (mg dm^{-3}) (B)
●	Blank	—	—	—	—	7.49	6.72	11.3	10.3
○	L-*g*-METAC (I)	9.1	9.3	0.054	0.056	6.72	6.44	17.5	11.1
△	L-*g*-METAC (II)	12.6	11.8	0.115	0.118	6.36	6.41	11.5	12.1

Shaking at 30°C.
* TOC indicates total organic carbon.

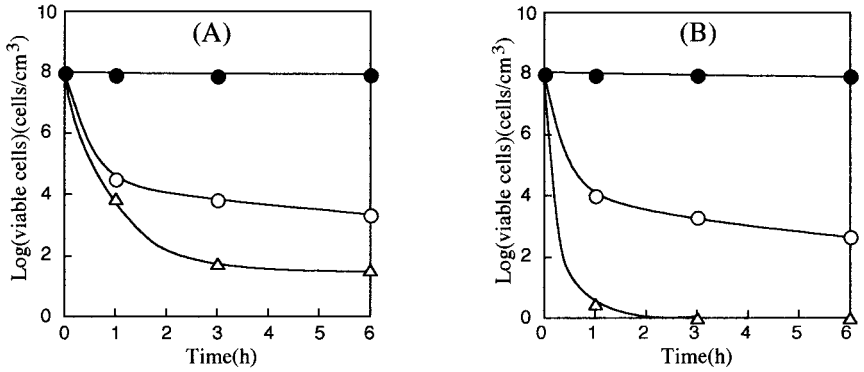

Figure 8 Changes in viable cell number after contacting with L-*g*-TBVB. Suspension of (A) *E. coli* or (B) *S. aureus:* 20 cm^3 (water)

		Polymer Add-On (%)		Weight (g)		Final pH		TOC* (mg dm^{-3})	
Symbol	Sample	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
●	Blank	—	—	—	—	6.19	6.72	12.9	10.3
○	L-*g*-TBVB (I)	74.6	70.4	0.092	0.090	6.14	6.24	11.3	11.5
△	L-*g*-TBVB (II)	77.7	75.0	0.170	0.179	6.35	6.13	11.9	8.4

Shaking at 30°C.
* TOC indicates total organic carbon.

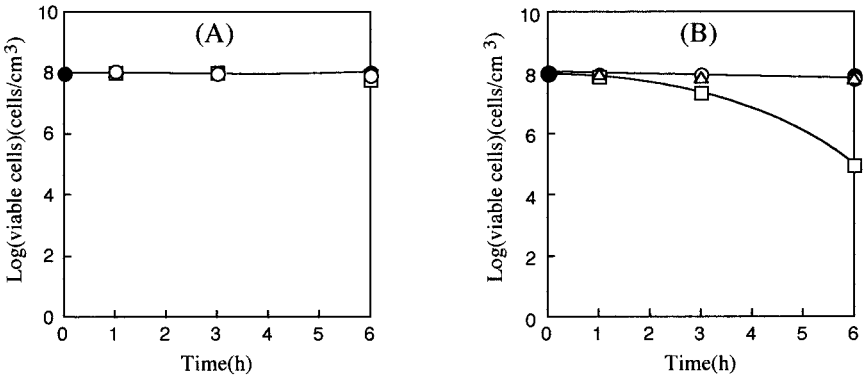

Figure 9 Changes in viable cell number after contacting with LE–Ag. Suspension of (A) *E. coli* or (B) *S. aureus:* 20 cm^3 (water).

		Polymer Add-On (%)		Ag^+ Content (meq g^{-1})		Weight (g)		Final pH		TOC (mg dm^{-3})		Ag^+ (ppm)[a]	
Symbol	Sample	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
●	Blank	—	—	—	—	—	—	7.26	6.72	18.7	10.3	—	—
○	LE–Ag (I)	103.3	105.6	0.044	0.044	0.106	0.106	6.00	6.47	20.3	11.1	0	0
△	LE–Ag (II)	105.1	105.6	0.079	0.079	0.104	0.106	6.04	6.52	14.2	13.6	0	0
□	LE–Ag (III)	105.5	106.0	0.20	0.19	0.104	0.100	6.14	6.02	13.8	7.8	0.015	0

Shaking at 30°C. TOC indicates total organic carbon.
[a] Concentration of Ag^+ in water after the experiment.

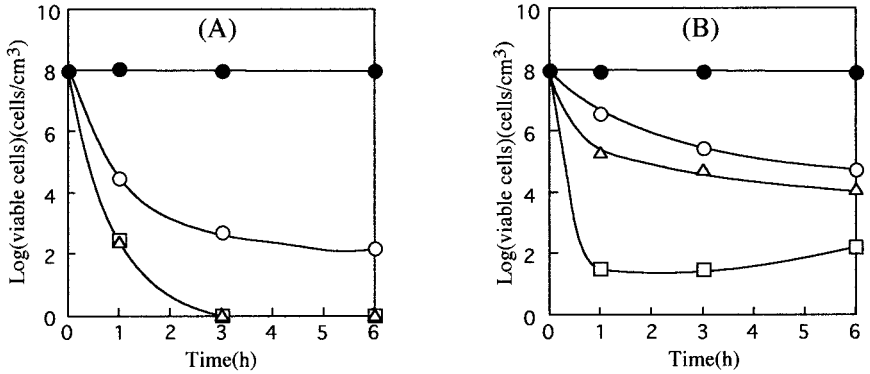

Figure 10 Changes in viable cell number after contacting with LE–TTA–Ag. Suspension of (A) *E. coli* or (B) *S. aureus:* 20 cm^3 (water).

		Polymer Add-On (%)		Ag^+ Content (meq g^{-1})		Weight (g)		Final pH		TOC (mg dm^{-3})		Ag^+ (ppm)[a]	
Symbol	Sample	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
●	Blank	—	—	—	—	—	—	7.26	6.72	18.7	10.3	—	—
○	LE–TTA–Ag (I)	94.4	96.4	0.043	0.043	0.101	0.105	5.98	6.55	21.4	12.7	0	0
△	LE–TTA–Ag (II)	95.4	97.9	0.083	0.073	0.098	0.104	5.45	6.37	13.8	13.1	0	0
□	LE–TTA–Ag (III)	96.5	98.4	0.21	0.20	0.101	0.099	5.13	5.61	13.8	13.4	0.93	0.47

Shaking at 30°C. TOC indicates total organic carbon.
[a] Concentration of Ag^+ in water after experiment.

against *E. coli* and *S. aureus.* The results are shown in Figure 9. The LE–Ag, which adsorbed Ag^+ ions from 0.04 to 0.08 meq g^{-1}, exhibited no antibacterial activity against both bacteria. However, only the LE–Ag, which adsorbed Ag^+ ions of 0.20 meq g^{-1}, showed small antibacterial activity against *S. aureus.* In this case, the LE–Ag exhibited no antibacterial activity against *E. coli,* although a very small concentration of residual Ag^+ ions were observed in solution after contacting of the LE–Ag with bacteria.

The antibacterial activity of LE–TTA–Ag, which adsorbed different amounts of Ag^+, was also investigated against *E. coli* and *S. aureus* (Fig. 10). The LE–TTA–Ag, which adsorbed Ag^+ ions above 0.04 meq g^{-1}, exhibited high antibacterial activity against both *E. coli* and *S. aureus.* The antibacterial activity increased with the increasing amount of Ag^+ ions adsorbed. In the case of the LE–TTA–Ag, which adsorbed Ag^+ ions below 0.08 meq g^{-1}, no Ag^+ ions were observed in the solution after contacting with bacteria. In the case of the LE–TTA–Ag, which adsorbed Ag^+ ions of 0.20 meq g^{-1}, about 0.9 and 0.5 ppm of Ag^+ ions were observed in the solution after contacting with *E. coli* and *S. aureus,* respectively. This

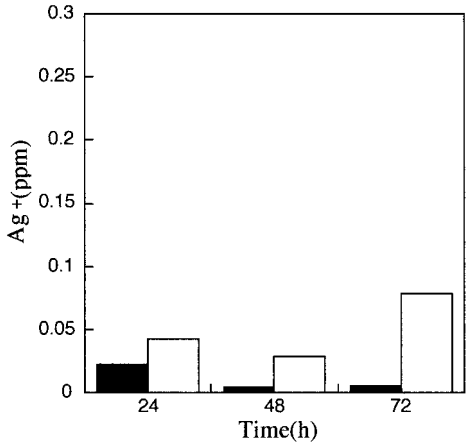

Figure 11 Concentration of released Ag^+ from LE–Ag and LE–TTA–Ag in deionized water (50 cm^3). **Shaking at 30°C**

Sample	Polymer Add-On (%)	Weight (g)	Initial Ag^+ (mmol dm^{-3})	Adsorption of Ag^+ (meq g^{-1})
■ LE–Ag	108.9	0.108	0.21	0.086
□ LE–TTA–Ag	90.7	0.095	0.21	0.087

higher antibacterial activity of LE–TTA–Ag than LE–Ag is due to the fact that LE–TTA is easier to release Ag^+ ions than LE because it has triethylenetetetramine side chains besides thiol groups. This thought could be confirmed by the experiment shown in Figure 11. Figure 11 shows the release of Ag^+ ions from RE–Ag and LE–TTA–Ag in water. The release of Ag^+ ions from RE–Ag is smaller than that from RE–TTA–Ag.

In addition to this, the LE–TTA–Ag containing Ag^+ ions exhibited higher antibacterial activity against *E. coli* than *S. aureus,* as shown in Figure 10. It is well known that Ag^+ ions combine easily with enzymes. We have previously reported that Ag^+ ions were combined more largely with *E. coli* than with *S. aureus.*[6] The exact mechanism of antibacterial activity is not clear at present. Considering the mechanism that was proposed at this time, the tentative mechanism is as follows. When the grafted loofah fibers bearing Ag^+ made contact with a bacteria suspension, Ag^+ ions on the grafted loofah fibers were released, and they penetrated into bacteria, then combined with enzymes in the cell membranes. This results in the inhibition of enzymatic reaction and the death of bacteria.

Table I Decrease Coefficient of Grafted-Loofah Fibers for Bacteria

	Polymer Add-On (%)		D ($cm^3\ g^{-1}\ h^{-1}$)	
Sample	E. coli	S. aureus	E. coli	S. aureus
L-*g*-METAC	12.6	11.8	452	778
L-*g*-TBVB	77.7	75.0	486	839
LE–Ag	105.1	105.6	0	0
LE–TTA–Ag	95.4	97.9	1141	517

$D = \frac{V}{W \cdot t} \log \frac{N_o}{N_t}$, in which V is the volume of cell suspension (cm^3), W is the weight of the dried sample (g), t is the contact time (h), N_o is the initial viable cells (cells/cm^3), and N_t is the viable cells after contact time t (cells/cm^3).

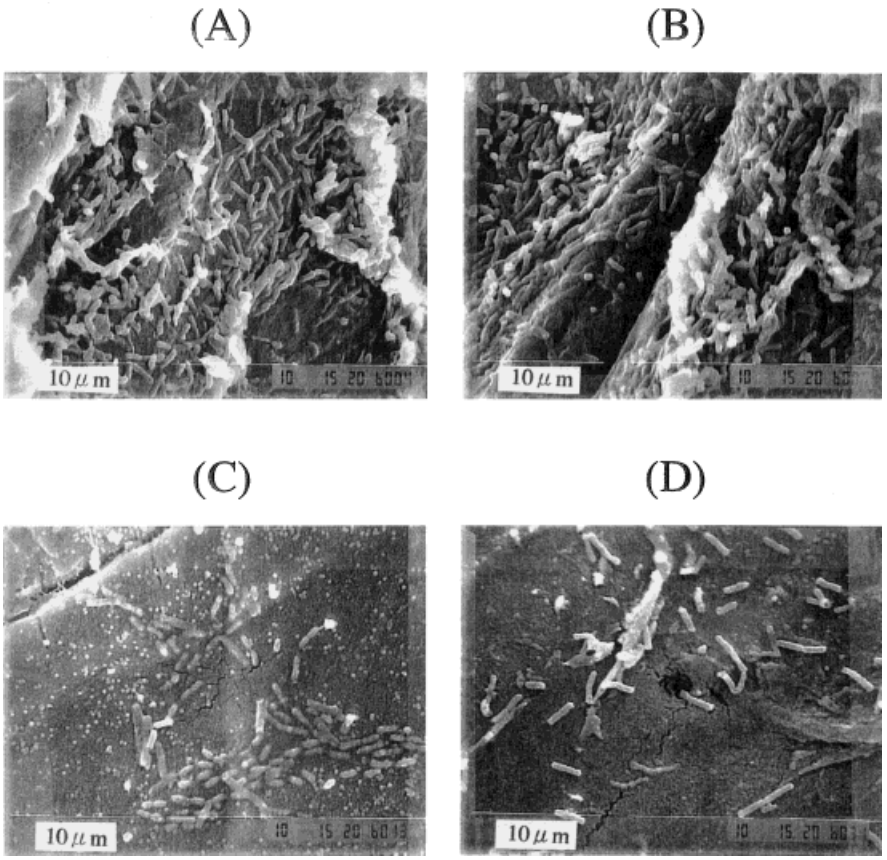

Figure 12 Scanning electron micrographs of (A) L-*g*-METAC (9.0%; ×3500), (B) L-*g*-TBVB (74.6%; ×3500), (C) LE (100.2%)–Ag ×3500) and (D) LE (98.4%)–TTA–Ag (×3500) after contacting with *E. coli.* The numbers after the abbreviations of grafted loofah fibers represent the polymer add-on of each fiber.

The same phenomena were observed with the copolymer beads containing triethylenetetranine side chains and/or thiol groups.[6]

Decrease Coefficient of Grafted Loofahs for Bacteria

Decrease coefficient of grafted loofah fibers for bacteria was calculated by using equation (2). The results are shown in Table I. As mentioned before, L-*g*-TBVB showed higher antibacterial activity than L-*g*-METAC; therefore, L-*g*-TBVB had a larger decrease coefficient than L-*g*-METAC, and both L-*g*-TBVB and L-*g*-METAC exhibited higher antibacterial activity for *S. aureus* than for *E. coli.* Accordingly, the grafted loofah fibers have a larger decrease coefficient for *S. aureus* than for *E. coli.* Furthermore, LE–TTA–Ag had a larger decrease coefficient for *E. coli* than L-*g*-METAC and L-*g*-TBVB, and it had larger decrease coefficient for *E. coli* than for *S. aureus.* However, the decrease coefficient of LE–TTA–Ag for *S. aureus* is smaller than those of L-*g*-METAC and L-*g*-TBVB. This difference of the decrease coefficients is derived from the difference of the mechanism of antibacterial activity between LE–TTA–Ag and L-*g*-METAC (or L-*g*-TBVB). LE–Ag exhibited no activity against both *E. coli* and *S. aureus.* So the decrease coefficients of LE–Ag were zero for both bacteria.

Adsorption of Bacteria on L-*g*-METAC, L-*g*-TBVB, LE–Ag, and LE–TTA–Ag

The surface on the grafted loofah fibers after contacting with bacteria was observed by scanning electron microscopy. Figure 12(A)–(D) show scanning electron micrographs of L-*g*-METAC, L-*g*-TBVB, LE–Ag, and LE–TTA–Ag after contacting with *E. coli,* respectively. It is observed that many bacteria are adsorbed on both L-*g*-METAC and L-*g*-TBVB, whereas a few bacteria are adsorbed on LE–Ag and LE–TTA–Ag. These results indicate that the interaction between surface of both L-*g*-METAC or L-*g*-TBVB and cell walls of *E. coli* is fairly strong, but the interaction between surface of both LE–Ag and LE–TTA–Ag and cell walls of *E. coli* is weak. This result also indicates that the mechanism of antibacterial activity of the grafted loofah fibers having positive charges, such as L-*g*-METAC and L-*g*-TBVB is different from that of LE–Ag and LE–TTA–Ag adsorbed Ag^+ ions.

CONCLUSIONS

1. L-*g*-METAC, L-*g*-TBVB, or L-*g*-ETMA(LE) could be obtained by graft copolymerization of METAC, TBVB, or ETMA onto loofah fibers.
2. LE–TTA, having both thiol groups and triethylenetetramine side chains, was obtained by amination of LE fibers.
3. LE and LE–TTA had high adsorption capacity for Ag^+ ions.
4. L-*g*-METAC and L-*g*-TBVB, having positive charges, exhibited high antibacterial activity against *E. coli* and *S. aureus.*
5. LE–TTA–Ag bearing Ag^+ ions exhibited high antibacterial activity without residual Ag^+ ions in water after contacting with bacteria, while LE–Ag did not.

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