

# Preparation of Superabsorbent Polymer Hydrogels from Trialkyl-4-vinylbenzyl Phosphonium Chloride–Acrylamide–Methylenebisacrylamide Terpolymers and Their Properties

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**ABSTRACT:** Superabsorbent polymer gels were synthesized by terpolymerization of three kinds of tri-*n*-alkyl-4-vinylbenzyl phosphonium chloride (TRVB) with alkyl chains of different lengths, with acrylamide (AAm), and with *N,N'*-methylenebisacrylamide (MBAAm). The water-absorption ability and antibacterial activity of the gels against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were investigated. The water content of TRVB–AAm–MBAAm terpolymers increased with increasing phosphonium groups in the terpolymers, while the water content decreased with increasing chain length of alkyl groups in the phosphonium groups as well as an increasing degree of crosslinking in the terpolymers. The water content of the terpolymers was depressed by the addition of NaCl. The degree of effect of NaCl addition became higher as the chain length of alkyl groups in the phosphonium groups of the terpolymers became longer. The tri-*n*-octyl-4-vinylbenzyl phosphonium chlorides (TOVB)–AAm–MBAAm terpolymers exhibited high antibacterial activity against *S. aureus* and *E. coli* in deionized water. The antibacterial activity decreased in 0.9 wt % NaCl solution. The antibacterial activity of TOVB–AAm–MBAAm terpolymers with almost the same phosphonium content increased with the increasing swelling ratio of the terpolymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1833–1844, 2000

**Key words:** superabsorbent; hydrogels; phosphonium groups; antibacterial activity

## INTRODUCTION

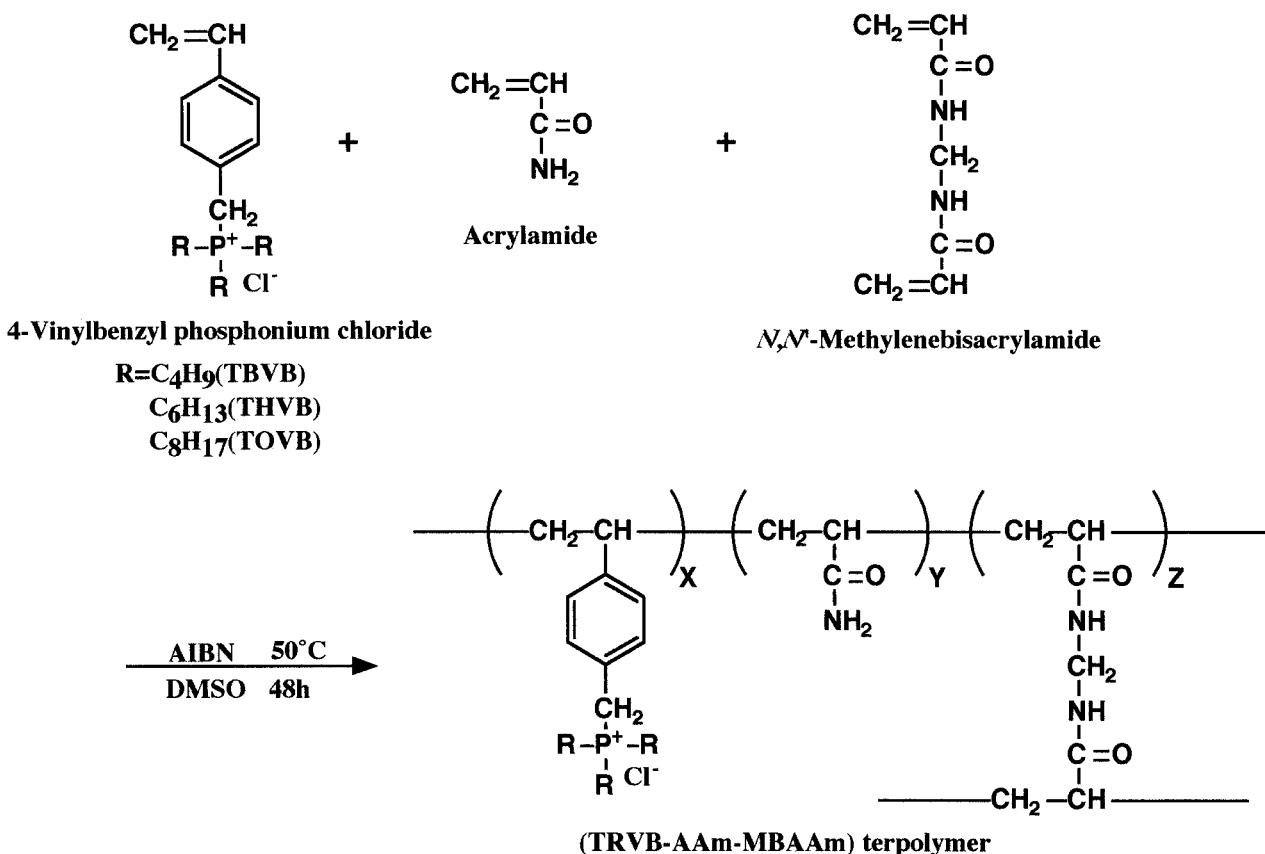
Many kinds of superabsorbent hydrogels are commercially prepared and used in a variety of fields, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, water-block tapes, and absorbent pads.<sup>1–6</sup> Most of these superabsorbent hydrogels are composed of anionic polymers such as crosslinked polymers containing sodium polyacrylates or sodium polysulfonates.

So far only a few studies concerning cationic polymer hydrogels have been reported.<sup>7–9</sup>

On the other hand, Kanazawa et al.<sup>10,11</sup> have reported that water-soluble polymers with phosphonium groups had high antibacterial activity against bacteria such as *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). We have also reported the preparation of several water-insoluble resins<sup>12–14</sup> having antibacterial activity to prevent the residual toxicity of water-soluble bactericides in water, as well as on high antibacterial activity against such bacteria and by copolymers beads containing quaternary ammonium, phosphonium, or other cationic groups, such beads having high adsorption ability for anionic

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**Figure 1** Synthesis of TRVB-AAm-MBAAm terpolymers.

surfactants such as sodium dodecyl benzenesulfonate, even from its salt solution.<sup>12,14</sup>

For this study we synthesized hydrogels having phosphonium groups by the terpolymerization of tri-4-vinylbenzyl phosphonium chloride (TRVB) with alkyl chains of different lengths, acrylamide (AAm), and *N,N'*-methylenebisacrylamide (MBAAm). We then investigated the water-absorption ability, antibacterial activity, and adsorption ability for anionic surfactants of the synthesized hydrogels.

## EXPERIMENTAL

### Materials

AAm was purified by the dissolution-precipitation method using methanol and benzene. Three kinds of trialkyl-4-vinylbenzyl phosphonium chlorides (TRVB) were kindly supplied by Nippon Kagaku Kogyo Co. and used without further purification. Azobisisobutyronitrile (AIBN) (Nakarai tesque Co.) was purified by recrystallization from etha-

nol (Wako Pure Chemical Industries, Ltd.). Other chemical compounds were reagent grade and were used as received.

### Synthesis of Polymer Gels

Polymer hydrogels used in this study were prepared by terpolymerization of TRVB, AAm, and MBAAm (Fig. 1). TRVBs with butyl, hexyl, or octyl groups in their phosphonium groups are abbreviated as TBVB, THVB, and TOVB, respectively. First, TRVB, AAm, and MBAAm were dissolved in 20 cm<sup>3</sup> of dimethyl sulfoxide (DMSO) in a glass vessel under a nitrogen atmosphere. The terpolymerization was carried out using 0.01 mol % AIBN (to total monomers) as radical initiator at 50°C for 24 h. After terpolymerization, the terpolymers obtained were purified with DMSO, propanone, and deionized water. The terpolymers were dried at room temperature in a vacuum oven. All terpolymers with particle sizes of 14–32 mesh were selected. The phosphonium content in the terpolymers was calculated from the dried terpolymers. The phosphorus content was deter-

mined as follows: Dried terpolymers (0.1 g) and 70% nitric acid (10 cm<sup>3</sup>) were placed in a Kjeldahl flask, and the mixture was heated until white steam came out; it was then cooled. After that, 60% perchloric acid (10 cm<sup>3</sup>) was added to this solution, and the mixture was heated until the solution became transparent. The concentration of phosphoric acid in the resulting solution was determined using the phosphovanadomolybdate method.<sup>15</sup>

#### Measurement of Water Content of Terpolymers

The water content of the terpolymers was measured using the tea-pack method as follows: The dried terpolymers were put into a tea pack made of nonwoven fabric, and then they were soaked in excess deionized water for 48 h at room temperature. After soaking, water on the surface of the gels and the tea pack was wiped with filter paper, and the weight ( $W_w$ ) of the tea pack containing the gels was measured.

Water content ( $Q$ )(H<sub>2</sub>Og/g- $P$ ) was calculated as

Water content ( $Q$ )(H<sub>2</sub>Og/g -  $P$ ) was

$$\text{calculated as } Q = (W_w - W_t - W_d)/W_d \quad (1)$$

where  $W_t$  and  $W_d$  are the weight of the wet tea pack and the terpolymers dried, respectively.

#### Measurement of Antibacterial Activity

##### *Organism and Growth Conditions*

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.

Calculated cell suspensions containing about 10<sup>7</sup>–10<sup>8</sup> cells/cm<sup>3</sup> were prepared for each strain and used for antibacterial tests.

##### *Contact of Polymer Gels with Bacteria*

A desired amount of the terpolymers and 10cm<sup>3</sup> of sterile deionized water were placed in a 50-cm<sup>3</sup> Erlenmeyer flask, and the terpolymers were swollen at 30°C for 24 h. After that, 10 cm<sup>3</sup> of the cell suspension were added to the flask, which was shaken for a prescribed time at 30°C.

##### *Measurement of Viable Cell Numbers After Contacting with Terpolymer Gels*

After contacting the terpolymer gels with a bacterial suspension for a prescribed time, 1 cm<sup>3</sup> of

the bacterial suspension was pipetted from the flask, and 9 cm<sup>3</sup> of sterile water was added to the bacterial suspension. The suspension was diluted several times and 0.1 cm<sup>3</sup> of the diluted suspension was spread on an agar plate made of nutrient agar. The plate was kept at 30°C for 15–24 h, and the number of viable cells was calculated from those colonies that formed on the plate.

##### *Measurement of Adsorption Capacity of Terpolymers for Sodium Dodecyl Benzenesulfonate and Sodium Benzenesulfonate*

First, the weighed terpolymer (ca. 0.1 g) was put into a 100-cm<sup>3</sup> Erlenmeyer flask and swollen completely in 30 cm<sup>3</sup> of deionized water for 48 h at room temperature, and then 30 cm<sup>3</sup> of a solution of sodium dodecyl benzenesulfonate (SDBS) or sodium benzenesulfonate (SBS) of 4 × 10<sup>-3</sup> mol/dm<sup>3</sup> was poured into the flask. Then the flask was shaken for 24 h at 30°C. A blank test was performed in the similar manner. After that, the gels were filtered; then the residual concentration of SDBS or SBS in the solution was determined by spectrophotometry (SHIMAZU UV-160A), and the amounts of SDBS or SBS adsorbed on the gels were calculated.

## RESULTS AND DISCUSSION

### Synthesis of TRVB-AAm-MBAAm Terpolymers

The scheme of the synthesis of TRVB-AAm-MBAAm terpolymers is shown in Figure 1. The water-absorption ability of polymer hydrogels is known to be affected greatly by the hydrophilicity of the polymers, charges in the polymers, and the crosslinking density in the polymers. Therefore, various TRVB-AAm-MBAAm terpolymers were obtained by changing the mole ratios of three monomers and using three kinds of tri-*n*-alkyl-4-vinylbenzyl phosphonium chloride (TRVB) with alkyl chains of different lengths.

Table I shows the mole ratios of three monomers in feed and the phosphorous contents in the terpolymers obtained for this study. The content of the phosphonium groups in TRVB-AAm-MBAAm terpolymers could be arbitrarily varied by changing the content of TRVB and keeping a constant mole ratio of MBAAm in feed. Terpolymers containing almost identical phosphorous content could be obtained with the same mole

**Table I** Synthesis of (TRVB–AAm–MBAAm) Terpolymers

Terpolymer No.	Feed (mol %)			P Content in Copolymer (meq/g)		
	TRVB	AAm	MBAAm	TRVB in Copolymer		
				TBVB	THVB	TOVB
1	1	96	3	0.13	0.13	0.10
2	2	95	3	0.25	0.25	0.21
3	3	94	3	0.33	0.32	0.31
4	4	93	3	0.44	0.35	0.33
5	5	92	3	0.51	0.49	0.48
6	2	96	2	0.21	0.23	0.25
7	2	94	4	0.20	0.23	0.23
8	2	93	5	0.19	0.21	0.21
9	1	89	10	0.12	0.12	0.12
10	3	87	10	0.34	0.33	0.32
11	5	85	10	0.45	0.43	0.42

TRVB–AAm–MBAAm ( $X - [100 - X - Y] - Y$ ) X: mol % of TRVB in feed Y: mol % of MBAAm in feed

ratio of TRVB but with different mole ratios of MBAAm in feed.

#### Water-Absorption Ability of TRVB–AAm–MBAAm Terpolymers

In general, the swelling ratio, which corresponds to water content, of hydrogels can be expressed by following equation:<sup>16</sup>

$$Q^{5/3} = \left\{ \left[ \frac{1}{2} \times \frac{i}{Vu} \times \frac{1}{S^{1/2}} \right]^2 + \frac{(1/2 - X_1)}{V_1} \right\} / \frac{\nu}{V_0} \quad (2)$$

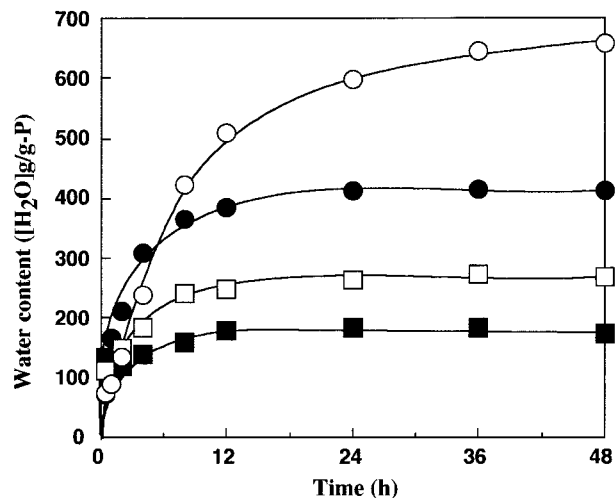
where  $Q$  is the swelling ratio,  $i/Vu$  is the charge density attached to the polymer matrix,  $(1/2 - X_1)$  is the affinity between the polymer matrix and water,  $S^{1/2}$  is the ionic strength of the outer solution, and  $\nu/V_0$  is the crosslinking density.

This equation indicates that the water content of the hydrogels depends on the hydrophilicity, crosslinking density, charges of the terpolymers, and concentration of neutral salts in an aqueous solution.

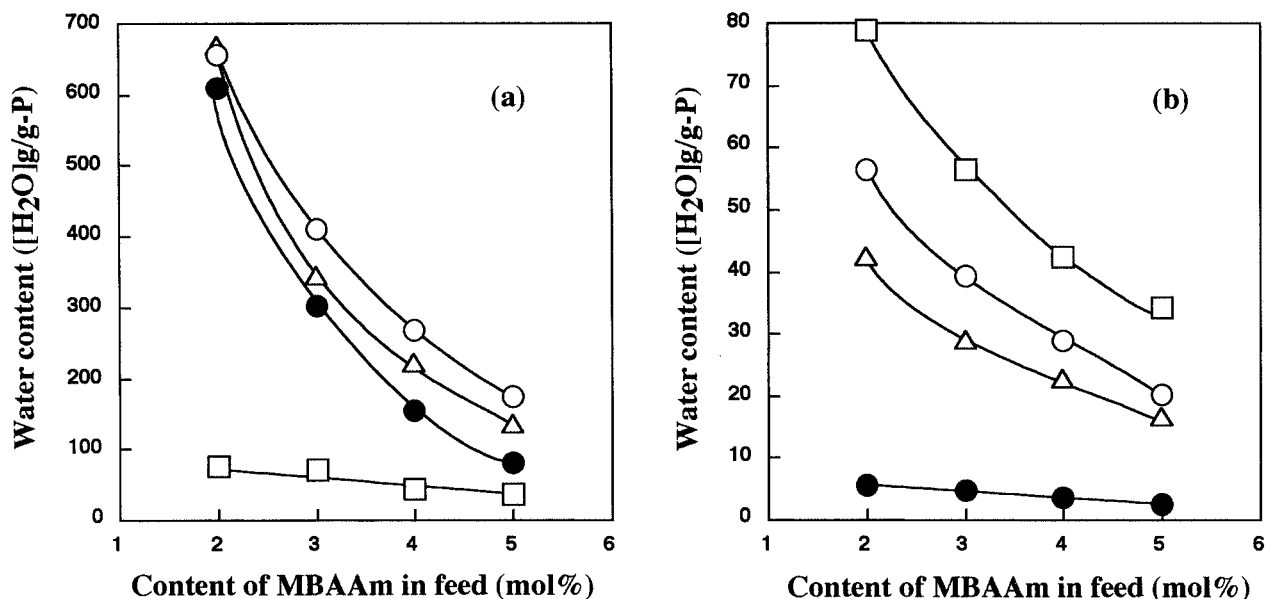
#### Time Dependence of Water-Absorption Ability

Figure 2 shows the measurement of time dependence of water-absorption ability of TBVB–AAm–MBAAm terpolymers with almost the same phosphonium content but different degrees of crosslinking. The water content of the terpolymers leveled off after 24 h except for the TBVB–AAm–MBAAm (2–96–2) terpolymer, which had

the lowest degree of crosslinking in the terpolymers measured. Because of these results, it was decided to measure the water content of all the terpolymers after 48 h. The water content of the TBVB–AAm–MBAAm terpolymers decreased with the increasing content of the crosslinking agent in feed. The exact degree of crosslinking in the terpolymers could not be determined. Therefore, the degree of crosslinking of the terpolymers



**Figure 2** Water content of TBVB–AAm–MBAAm terpolymers with various MBAAm contents after immersing various times (deionized water, polymer 0.1 g, room temperature). TBVB–AAm–MBAAm: (○) 2–92–2, (●) 2–95–3, (□) 2–94–4, (■) 2–93–5.



**Figure 3** Water content of TRVB-AAm-MBAAm terpolymers with various MBAAm contents: (a) deionized water, (b) 0.9 wt % NaCl solution. TRVB:AAm:MBAAm = 2:98 - Y:Y (mole ratio in feed). Polymers: (○) TBVB-AAm-MBAAm, (△) THVB-AAm-MBAAm, (●) TOVB-AAm-MBAAm, (□) AAm-MBAAm.

was represented using the mol % of MBAAm in feed.

#### *Effect of the Degree of Crosslinking in TRVB-AAm-MBAAm terpolymers on Water-Absorption Ability*

The water content of the terpolymers obtained at a constant mol % (2 mol %) of each vinyl monomer of phosphonium salt and different mol % (2–5 mol %) of MBAAm was measured in deionized water and a 0.9 wt % NaCl aqueous solution. The results are shown in Figure 3(a,b). In Figure 3 the results from the AAm-MBAAm copolymer carrying no phosphonium group are also shown for comparison.

In deionized water [Fig. 3(a)], the water content of the terpolymers containing phosphonium groups decreased remarkably with an increasing degree of crosslinking in the terpolymers. However, the water content of the AAm-MBAAm copolymer carrying no phosphonium group was fairly low compared with those of the terpolymers, and it decreased slightly with an increasing degree of crosslinking in the copolymers.

The order of the water content of the terpolymers and the copolymer was: TBVB-AAm-MBAAm > THVB-AAm-MBAAm > TOVB-AAm-MBAAm terpolymers >> AAm-MBAAm

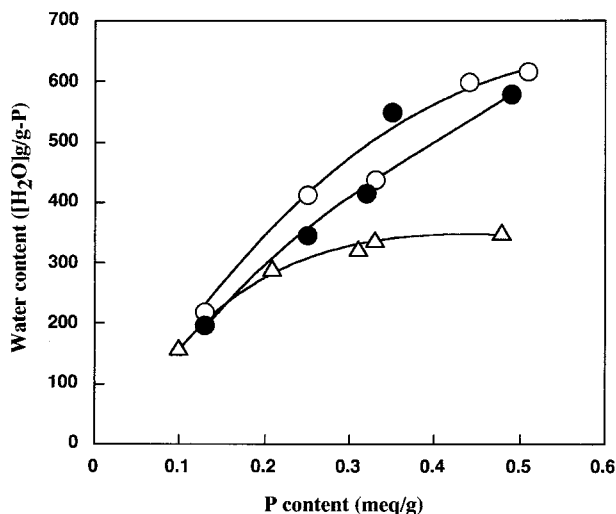
copolymer. This result indicates that the introduction of phosphonium groups into the AAm-MBAAm copolymer increases the water content by a remarkable amount, and the terpolymers carrying shorter alkyl chains in the phosphonium groups have a higher water content.

In a 0.9 wt% NaCl solution [Fig. 3(b)], the water content of the terpolymers containing phosphonium groups decreased to one-tenth of those in deionized water, but the order of water content was the same as those in deionized water. And, in particular, the water content of the TOVB-AAm-MBAAm terpolymer was significantly depressed. In this case, the water content of AAm-MBAAm copolymer, which had no phosphonium group, was hardly affected by the addition of NaCl.

The decrease in water content of terpolymers in NaCl solutions is because the difference in osmotic pressure between the inner and outer side of the terpolymer hydrogels became very low because of the addition of NaCl into the outer solution.

On the other hand, it is known that the addition of neutral salt brings about the flocculation of colloidal particles by dehydration of colloidal particles, and the dehydration effect on the more hydrophobic colloidal particles is higher than that on less hydrophobic colloidal particles.<sup>17</sup> There-





**Figure 4** Water content of TRVB-AAm-MBAAm terpolymers with various phosphonium chlorides (in deionized water, room temperature). TRVB:AAm:MBAAm = X:97 - X:3 (mole ratio in feed). Terpolymers: (○) TBVB-AAm-MBAAm, (●) THVB-AAm-MBAAm, (△) TOVB-AAm-MBAAm.

fore, the largest degree of water-content depression, in the terpolymer containing TOVB, indicates that the dehydration effect of NaCl is largest in the terpolymers with the most hydrophobic octyl groups.

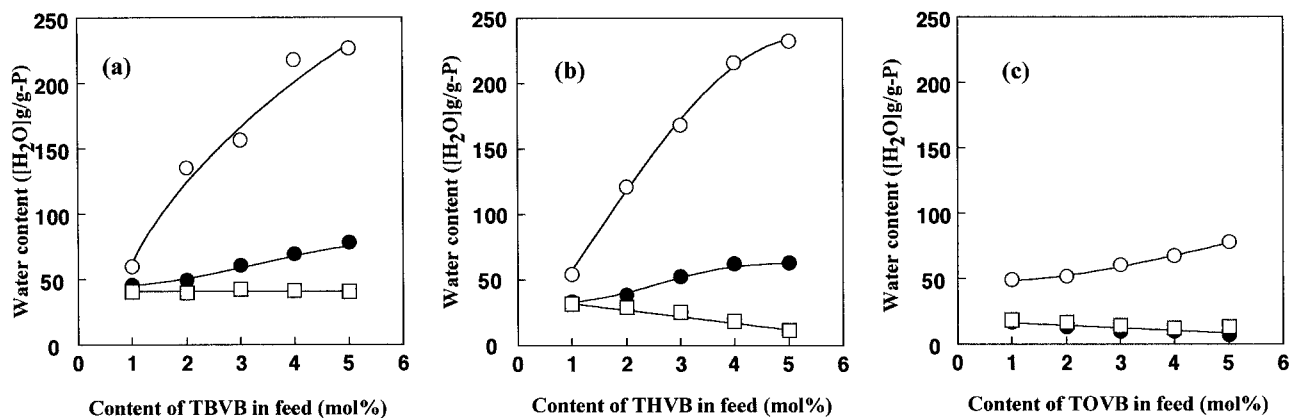
#### Effect of Phosphonium Content of Terpolymers on Water-Absorption Ability

The water content of the TRVB-AAm-MBAAm terpolymers obtained at 3 mol % of MBAAm and

1–5 mol % of TRVB were measured in deionized water (Fig. 4). The water content of the TRVB-AAm-MBAAm terpolymers was represented as a function of the phosphorus content in the terpolymers. The water content increased with increasing phosphonium content in the terpolymers, although the water content of terpolymers was different, depending the chain length of the alkyl groups in the phosphonium groups. This increase in water content with increasing phosphonium content in the terpolymers is the result of the increase in osmotic pressure between the inner and outer side of the polymer gels. Figure 4 also shows that the water contents increased in the order of: TBVB-AAm-MBAAm > THVB-AAm-MBAAm > TOVB-AAm-MBAAm terpolymers.

#### Water Content of Terpolymers in NaCl Solutions of Various Concentrations

- (1) The water content of the TRVB-AAm-MBAAm terpolymers obtained at 3 mol % of MBAAm and 1–5 mol % of TRVB were measured in 0.009, 0.09, and 0.9 wt % NaCl solutions. The results are shown in Figure 5. The water contents of each terpolymer decreased with increasing concentration of NaCl in solutions, and they were considerably depressed in NaCl solutions above 0.009 wt %. This decrease in water content by the addition of NaCl is a result of both the decrease in the difference of osmotic pressure between the inner side and outer side of the polymer gels and of dehydration of polymer hydrogels.



**Figure 5** Water content of TRVB-AAm-MBAAm terpolymers in NaCl solutions of various concentrations. TRVB:AAm:MBAAm = X:97 - X:3 (mole ratio in feed). Terpolymers: (a) TBVB-AAm-MBAAm, (b) THVB-AAm-MBAAm, (c) TOVB-AAm-MBAAm. NaCl concentration (wt %): (○) 0.009, (●) 0.09, (□) 0.9.

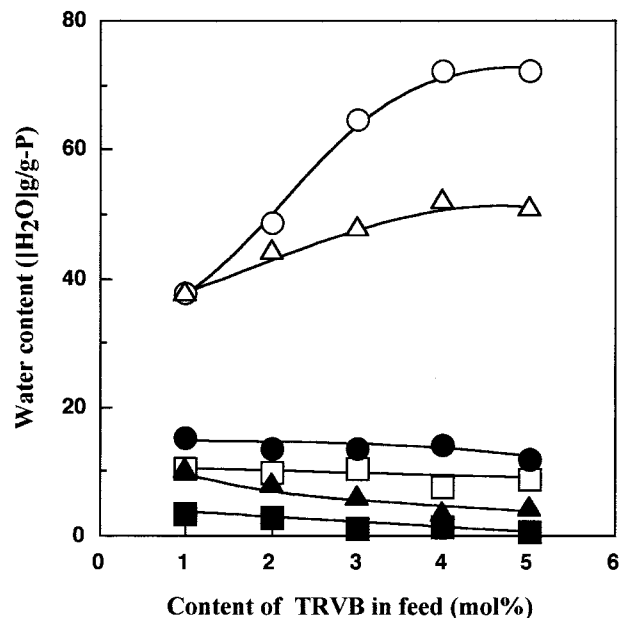
In the case of TOVB–AAm–MBAAm terpolymers in 0.09 wt % NaCl solution, the water content decreased with the increasing phosphonium content in the terpolymers. This indicates that the TOVB–AAm–MBAAm terpolymers became less hydrophilic by the addition of NaCl irrespective of the introduction of more phosphonium groups because the phosphonium group in the TOVB–AAm–MBAAm terpolymers had the most hydrophobic octyl groups. In the case of THVB–AAm–MBAAm terpolymers with a shorter alkyl chain in the phosphonium group than TOVB–AAm–MBAAm terpolymers, the water content of the terpolymers decreased with increasing phosphonium content in the terpolymers in only 0.9 wt % NaCl solution. These results indicate that the dehydration effect of NaCl became stronger against terpolymers with more hydrophobic alkyl groups in the terpolymers.

- (2) The water content of the terpolymers obtained at 10 mol % MBAAm in feed were also measured in deionized water and 0.9 wt % NaCl solution. The results are shown in Figure 6. These TRVB–AAm–MBAAm terpolymers were used for estimating the antibacterial activity, as mentioned later. The water content of the TBVB–AAm–MBAAm (5–85–10) terpolymer was below 80 g H<sub>2</sub>O/g–P. The water content of the TBVB–AAm–MBAAm (5–85–10) and THVB–AAm–MBAAm (5–85–10) terpolymers increased with increasing phosphonium groups. However, in the case of the TOVB–AAm–MBAAm (5–85–10) terpolymers, the water content of the terpolymers did not increase with increasing TOVB content in the terpolymers, even in deionized water. They had almost the same water content of 10 g H<sub>2</sub>O/g–P. The water contents of all the terpolymers were depressed by the addition of NaCl, as shown in Figure 6.

#### Antibacterial Activity of TRVB–AAm–MBAAm Terpolymers

##### Antibacterial Activity of TRVB Monomers

First, antibacterial activity of TRVB monomers was measured against *S. aureus* in deionized water and saline (0.9 wt % NaCl; Fig. 7). It was found that terpolymers with longer alkyl chains in the phosphonium groups showed higher anti-

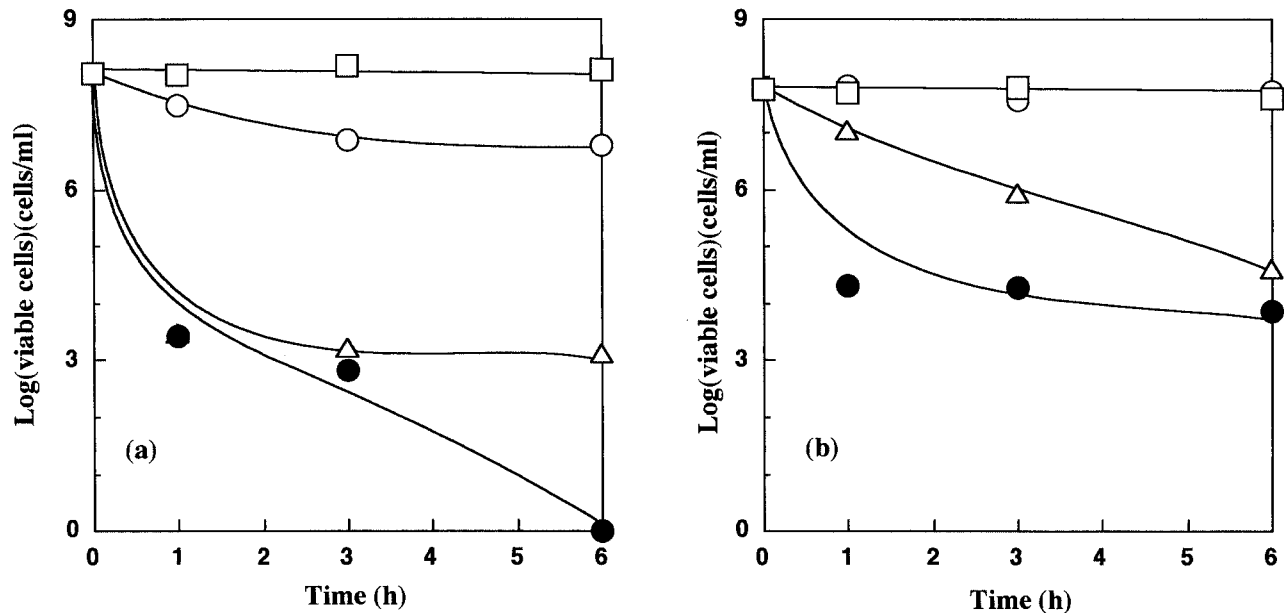


**Figure 6** Water content of TRVB–AAm–MBAAm terpolymers with various TRVB contents. TRVB:AAm:MBAAm = X:90 – X:10 (mole ratio in feed). Terpolymers in deionized water: (○) TBVB–AAm–MBAAm, (△) THVB–AAm–MBAAm, (□) TOVB–AAm–MBAAm; terpolymers in 0.9 wt % NaCl solution: (●) TBVB–AAm–MBAAm, (▲) THVB–AAm–MBAAm, (■) TOVB–AAm–MBAAm.

bacterial activity against *S. aureus*. That is, the antibacterial activity was in the order of: TOVB > THVB > TBVB. This result indicates the antibacterial activity of TRVBs is affected not only by the positive charges of phosphonium groups but also by the alkyl chains in TRVBs. It was also found that the antibacterial activity of the TRVBs in deionized water was higher than that in saline. These TRVBs are water soluble; therefore, the residual toxicity of TRVBs dissolved in water after using as bactericides cannot be avoided.

#### Antibacterial Activity of TOVB–AAm–MBAAm Terpolymers

The antibacterial activity of TOVB–AAm–MBAAm terpolymers was investigated against *S. aureus* because TOVB exhibited the highest antibacterial activity against *S. aureus*. For the measurement of antibacterial activity, TOVB–AAm–MBAAm terpolymers obtained at 10 mol % of MBAAm and 1–5 mol % of TOVB in feed were used because terpolymers obtained below 5 mol % of MBAAm and above 5 mol % of TOVB were too swellable to pipette the bacterial suspension after

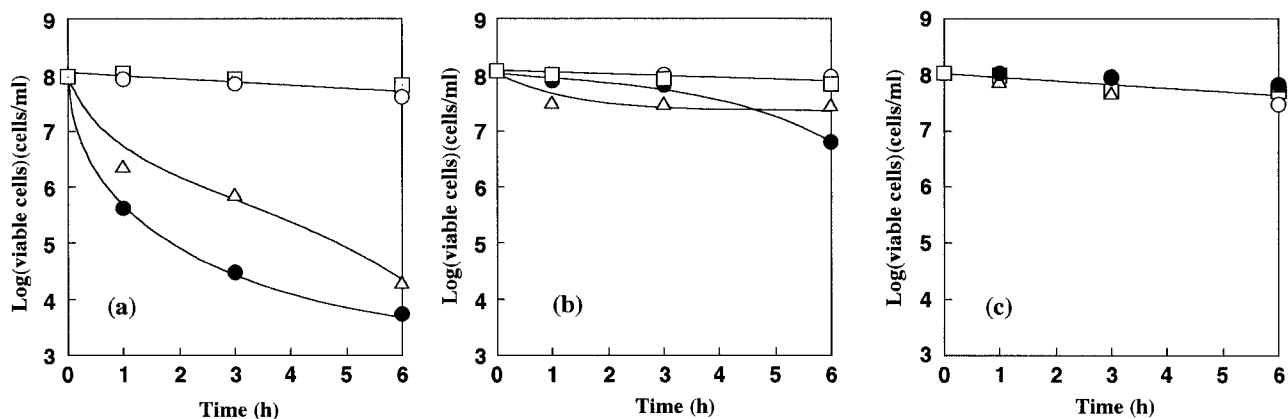


**Figure 7** Changes in viable cell number after contacting with TRVB monomers suspension of *S. aureus*: 20 cm<sup>3</sup>; concentration of TRVB monomer: 5 ppm; (a) deionized water, (b) 0.9% NaCl. TRVB monomer: (○) TBVB, (△) THVB, (●) TOVB, (□) blank.

contacting with the terpolymer gels. The water content of terpolymers obtained at 10 mol % MBAAm in feed was low, as shown previously in Figure 6.

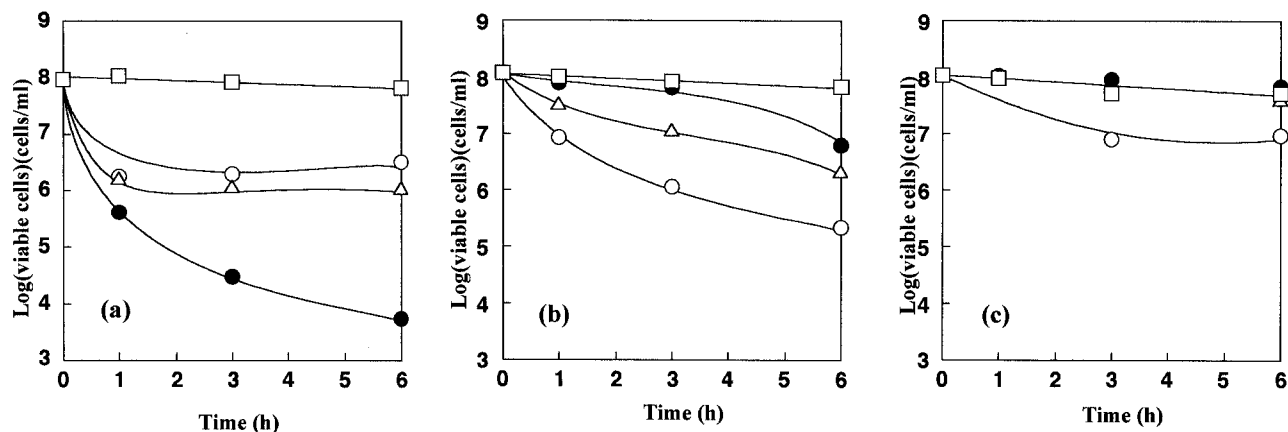
The antibacterial activity of terpolymers obtained at 10 mol % of MBAAm and 1–5 mol % of TOVB was measured in deionized water, 0.09 wt %, and 0.9 wt % NaCl solutions (Fig. 8). In deion-

ized water [Fig.8(a)] the TOVB–AAm–MBAAm terpolymer exhibited the highest antibacterial activity against *S. aureus*, and antibacterial activity increased with increasing phosphonium content in the terpolymers. However, in NaCl solutions [Fig. 8(b,c)] antibacterial activity was hardly observed. This decrease in antibacterial activity in NaCl solutions is from the effect of the addition



**Figure 8** Changes in viable cell number after contacting with TOVB–AAm–MBAAm terpolymers with various TOVB contents in NaCl solution of various concentrations; suspension of *S. aureus*: 20 cm<sup>3</sup>; (a) deionized water with 0.1 g added terpolymer, (b) 0.09 wt % NaCl solution with 0.2 g added terpolymer, (c) 0.9 wt % NaCl solution with 0.5 g added terpolymer. TOVB–AAm–MBAAm (X–Y–Z) terpolymers: (○) 1–89–10, (△) 3–87–10, (●) 5–85–10, (□) blank.





**Figure 9** Changes in viable cell number after contacting with TRVB–AAm–MBAAm terpolymers with different phosphonium groups in NaCl solution of various concentrations; suspension of *S. aureus*: 20 cm<sup>3</sup>; (a) deionized water with 0.1 g added terpolymer, (b) 0.09 wt % NaCl solution with 0.2 g added terpolymer, (c) 0.9 wt % NaCl solution with 0.5 g added terpolymer. TRVB–AAm–MBAAm (5–85–10) terpolymers: (○) TBVB–AAm–MBAAm, (△) THVB–AAm–MBAAm, (●) TOVB–AAm–MBAAm, (□) blank.

of NaCl in shielding terpolymers from positive charges.

#### Antibacterial Activity of Various TRVB–AAm–MBAAm Terpolymers

The antibacterial activity of various TRVB–AAm–MBAAm (5–85–10) terpolymers, which were obtained using TBVB, THVB, or TOVB and had almost the same phosphonium content, was measured against *S. aureus* in deionized water, 0.09 wt %, and 0.9 wt % NaCl solutions. The results are shown in Figure 9.

In deionized water [Fig.9(a)] the antibacterial activity of the TRVB–AAm–MBAAm terpolymers against *S. aureus* increased with increasing alkyl chain length in the phosphonium groups. However, in 0.09 wt % NaCl solution [Fig.9(b)] antibacterial activity decreased with increasing alkyl chain length in the phosphonium groups, although the antibacterial activity in 0.09 wt % NaCl solution was lower than that in deionized water. In 0.9 wt % NaCl solution [Fig.9(c)] only the TBVB–AAm–MBAAm (5–85–10) terpolymer exhibited low antibacterial activity, although a larger amount of terpolymers was added into the bacterial suspension containing NaCl of a higher concentration. This decrease in antibacterial activity in NaCl solution resulted from both the shielding of positive charges and the contracting of the terpolymers by the addition of NaCl into polymer solutions. The high antibacterial activity of TOVB–AAm–MBAAm terpolymers in deion-

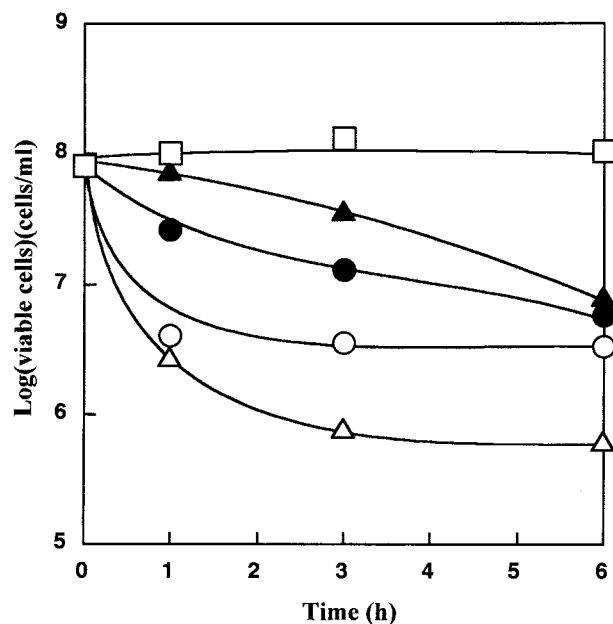
ized water indicates that antibacterial activity is affected both by positive charges and by hydrophobicity of alkyl groups in the terpolymers.

#### Antibacterial Activity of TOVB–AAm–MBAAm Terpolymers with Different Degrees of Crosslinking

It was previously mentioned that the TOVB–AAm–MBAAm terpolymer obtained at 10 mol % of MBAAm in feed was used for the measurement of antibacterial activity because the terpolymers obtained below 5 mol % of MBAAm and above 5 mol % of TOVB were too swellable to pipette a bacterial suspension after contacting with terpolymer gels. In order to study the effect of the degree of crosslinking of terpolymers on antibacterial activity, we made the terpolymers below 10 mol % of MBAAm and at 3 mol % of TOVB in feed, and the antibacterial activity of the terpolymers obtained was measured against *S. aureus* and *E. coli*. Different amounts of terpolymers and volumes of bacterial suspension were used for this experiment in order to estimate clearly the antibacterial activity because the swelling ratios of the terpolymers depended on the degree of crosslinking in the terpolymers. The results against *S. aureus* are shown in Figure 10.

From these results the decrease coefficients of the terpolymers against *S. aureus* were calculated by using eq. (3)

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



**Figure 10** Changes in viable cell number after contacting with TOVB-AAm-MBAAm terpolymers with various MBAAm contents; suspension of *S. aureus*: 20 or 60 cm<sup>3</sup>; shaking at 30°C.

Symbol	TOVB-AAm-MBAAm (X-Y-Z) Terpolymer	Amount of Terpolymer (g)	Suspension (cm <sup>3</sup> )
○	3-94-3	0.025	60
△	3-92-5	0.05	20
●	3-90-7	0.05	20
▲	3-87-10	0.1	20
□	Blank	—	20

where  $V$  is the volume of cell suspension (cm<sup>3</sup>),  $W$  is the weight of dry terpolymers (g),  $t$  is the contact time (h),  $N_o$  is the initial viable cell numbers (cells/cm<sup>3</sup>), and  $N_t$  is the viable cell numbers after

contact time ( $t$ , cells/cm<sup>3</sup>). The decrease coefficients against *E. coli* are also shown in Table II.

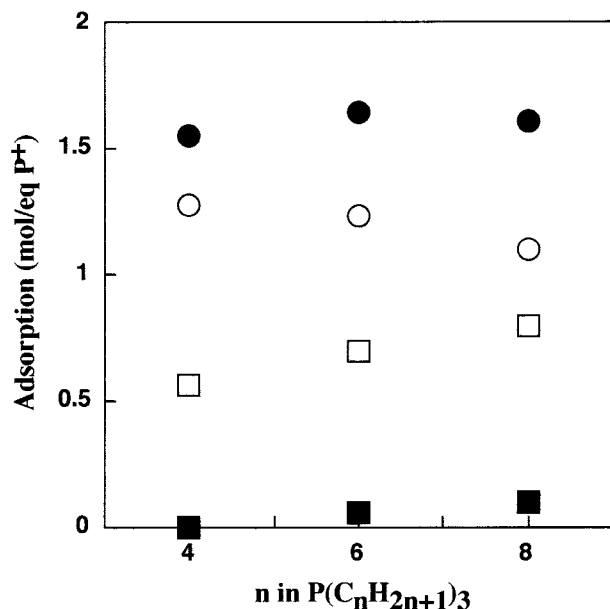
The decrease coefficients of the terpolymers increased with the decreasing degree of the crosslinking agent in the feed, although all the terpolymers had almost the same phosphonium content in the dry state. Table II also shows that the terpolymers with a lower degree of crosslinking have a higher water content. This means that the terpolymers with a lower degree of crosslinking swelled more highly than those with a higher degree of crosslinking. We mentioned before that the antibacterial activity of the terpolymers was affected by both the positive charges and the hydrophobicity of alkyl groups of the terpolymers. In this case, the terpolymers have the same octyl groups in the phosphonium groups. Therefore, the increase in the decrease coefficient with a decreasing degree of crosslinking is thought to result from the appearance of more positive charges on the surface of the polymer hydrogels by the swelling of terpolymers in deionized water. However, at present we have no data confirming this phenomena.

#### Adsorption Ability of TRVB-AAm-MBAAm terpolymers for SDBS and SBS

It is known that bacteria in water have negative charges because of many phosphoric acid derivatives present in tissue, such as the cytoplasmic membranes of bacteria cells. Therefore, the electrostatic interactions between terpolymers containing phosphonium groups and bacteria such as *S. aureus* or *E. coli* is thought to contribute to the antibacterial activity of the terpolymers. In order to investigate the interaction between terpolymer hydrogels and bacteria, the adsorption of SDBS as an anionic surfactant on TRVB-AAm-MBAAm (5-85-10) terpolymers with different alkyl chains in the phosphonium groups was stud-

**Table II** Decrease Coefficient for Bacteria by TOVB-AAm-MBAAm Terpolymers Having Various MBAAm Contents

TOVB-AAm-MBAAm Terpolymer	P Content (mmol/g)	Water Content ([H <sub>2</sub> O]g/g-P)	$D$ (cm <sup>3</sup> /g · h)	
			<i>S. aureus</i>	<i>E. coli</i>
3-94-3	0.31	323.8	560	1444
3-92-5	0.31	90.2	142	253
3-90-7	0.31	51.4	77	32
3-87-10	0.32	10.4	34	24



**Figure 11** Adsorption of SDBS or SBS with TRVB-AAm-MBAAm (5–85–10) terpolymers in deionized water or in saline; concentration of SDBS and SBS:  $2.0 \times 10^{-3}$  mol/dm<sup>3</sup>; weight of polymer: 0.100 g; shaking at 30°C.

In Deionized Water		○ SDBS	□ SBS
In Saline		● SDBS	■ SBS
Terpolymer	P Content in Terpolymer (meq/g)		
$n = 4$	TBVB-AAm-MBAAm	0.45	
$n = 6$	THVB-AAm-MBAAm	0.43	
$n = 8$	TOVB-AAm-MBAAm	0.42	

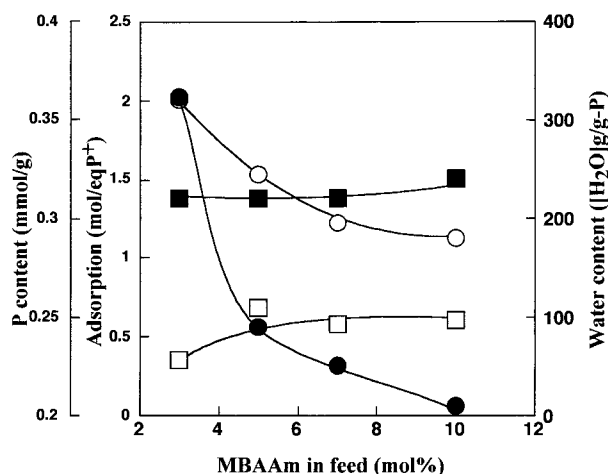
ied in deionized water and 0.9 wt % NaCl solution. For comparison the adsorption of SBS was also measured. The results are shown in Figure 11. In deionized water both SDBS and SBS were adsorbed on the terpolymers, although the adsorption capacities for SDBS were higher than those for SBS. And the adsorption capacities (mol/eq P<sup>+</sup>) for SDBS were more than unity and decreased slightly with increasing alkyl chain length in the phosphonium groups, while the adsorption capacities for SBS were less than unity and increased with increasing alkyl chain length in the phosphonium groups.

In addition to this phenomena, the adsorption capacities for SDBS in 0.9 w t% NaCl solution increased in comparison with those in deionized water and those for SBS decreased significantly,

to almost zero. These results indicate that the adsorption of SBS on terpolymers occurs mainly because of the electrostatic interaction between SBS and terpolymers and that the adsorption of SDBS on the terpolymers is brought about not only by electrostatic interaction but also by hydrophobic interaction between SDBS and terpolymers. We have reported that similar behavior was observed with copolymer beads carrying phosphonium groups.<sup>14</sup>

Next, the adsorption ability for SDBS and SBS of terpolymers obtained at 3 mol % of TOVB and 3–10 mol % of MBAAm in feed was measured in deionized water (Fig. 12). The adsorption capacities for SDBS on the terpolymers decreased with a increasing degree of crosslinking, while those for SBS did not depend on the degree of crosslinking in the terpolymers. The reason for the difference in adsorption behavior between SDBS and SBS is thought to be as follows:

SBS is thought to be able to penetrate easily into polymer hydrogels because of its small molecular size and to be adsorbed with polymers. On the other hand, SDBS is thought to make micelles at this concentration ( $2 \times 10^{-3}$  mol/dm<sup>3</sup>) because critical micelle concentration of SDBS in water is  $1.2 \times 10^{-3}$  mol/dm<sup>3</sup> at 25°C. Therefore, SDBS was not thought to be able to penetrate easily into the polymer hydrogels because of its larger size. So the adsorption of SDBS was thought to occur



**Figure 12** Adsorption of SDBS or SBS with TOVB-AAm-MBAAm terpolymers with various degrees of crosslinking in deionized water; concentration of SDBS and SBS:  $2.0 \times 10^{-3}$  mol/dm<sup>3</sup>; TOVB-AAm-MBAAm (3–[97–Y]–Y) terpolymers; shaking at 30°C: (○) SDBS, (□) SBS, (●) water content, (■) P content in terpolymers.

mostly on the surface of polymer hydrogels. Low water content means low swelling of the terpolymers. Therefore, the decrease in adsorption capacities with an increasing degree of crosslinking of the terpolymers indicates the terpolymers with a lower water content have less positive charges on the surface of the terpolymer hydrogels in water because of low swelling, although they have almost the same phosphonium content in the dry state. Thus it was found that antibacterial activity was also affected by the swelling ratio of the terpolymers.

## CONCLUSIONS

The water content of TRVB–AAM–MBAAM terpolymers increased with increasing phosphonium groups in terpolymers, while water content decreased with an increasing chain length of alkyl groups in phosphonium groups as well as with an increasing degree of crosslinking in the terpolymers.

The water content of terpolymers in NaCl solutions decreased with an increasing concentration of NaCl. The degree of the effect of the addition of NaCl on water content of terpolymers increased as the chain length of alkyl groups in the phosphonium groups became longer.

The TOVB–AAM–MBAAM terpolymers exhibited high antibacterial activity against *S. aureus* and *E. coli* in deionized water, an effect that increased with increasing content of TOVB in the terpolymers. Antibacterial activity was decreased by the addition of NaCl. These TRVB–AAM–MBAAM terpolymers can be separated by filtration after contacting with bacterial suspensions because they are water-insoluble polymer hydrogels. Therefore, residual toxicity of bactericides in water can be prevented.

Furthermore, it was found that the antibacterial activity of TOVB–AAM–MBAAM terpolymers having almost the same phosphonium content increased with an increasing swelling ratio of the

terpolymers and that the terpolymers could adsorb anionic surfactant such as SDBS by both electrostatic interaction and hydrophobic interaction.

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