

Preparation of Thermosensitive and Superabsorbent Polymer Hydrogels from Trialkyl-4-vinylbenzyl Phosphonium Chloride-*N*-isopropylacrylamide-*N,N'*-methylenebisacrylamide Copolymers and Their Properties

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ABSTRACT: Thermosensitive and superabsorbent polymer hydrogels were synthesized by copolymerization of three kinds of tri-*n*-alkyl vinylbenzyl phosphonium chlorides (TRVB) with different lengths of alkyl chains, *N*-isopropylacrylamide (NIPAAm), and *N,N'*-methylenebisacrylamide (MBAAm). The water-absorption ability and antibacterial activity of the hydrogels against *Staphylococcus aureus* (*S. aureus*) were investigated. The water content of TRVB–NIPAAm–MBAAm copolymers decreased with increasing temperature and increased with increasing phosphonium groups in the copolymers, while it decreased with increasing chain length of the alkyl groups in the phosphonium groups as well as with an increasing degree of crosslinking in the copolymers. The TRVB–NIPAAm–MBAAm copolymers with a higher TRVB content in the copolymers exhibited higher antibacterial activity against *S. aureus*, but decreased with increasing chain length of alkyl groups in phosphonium groups. The TRVB–NIPAAm–MBAAm copolymers exhibited the highest antibacterial activity at 30°C against *S. aureus* in deionized water. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 115–124, 2001

Key words: thermosensitive polymers; superabsorbent; hydrogels; phosphonium groups; antibacterial activity

INTRODUCTION

Many kinds of superabsorbent hydrogels are commercially prepared and used in many fields, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, water-block tapes, and absorbent pads, etc.^{1–6} Most of those superabsorbent hydrogels are composed of anionic polymers such as crosslinked polymers containing so-

dium polyacrylates or sodium polysulfonates. So far only a few reports concerning cationic polymer hydrogels have been reported.^{7–9} In addition to these, many thermosensitive polymer hydrogels consisting of poly(*N*-isopropyl acrylamide) [poly(NIPAAm)] have been widely studied from both fundamental and practical points of view.^{10–14}

On the other hand, Kanazawa et al^{15,16} have reported that water-soluble polymers containing phosphonium groups have shown high antibacterial activity against bacteria such as *Staphylococcus aureus* (*S. aureus*) or *Escherichia coli* (*E. coli*). In addition, the authors have also reported on the preparation of several water-insoluble res-

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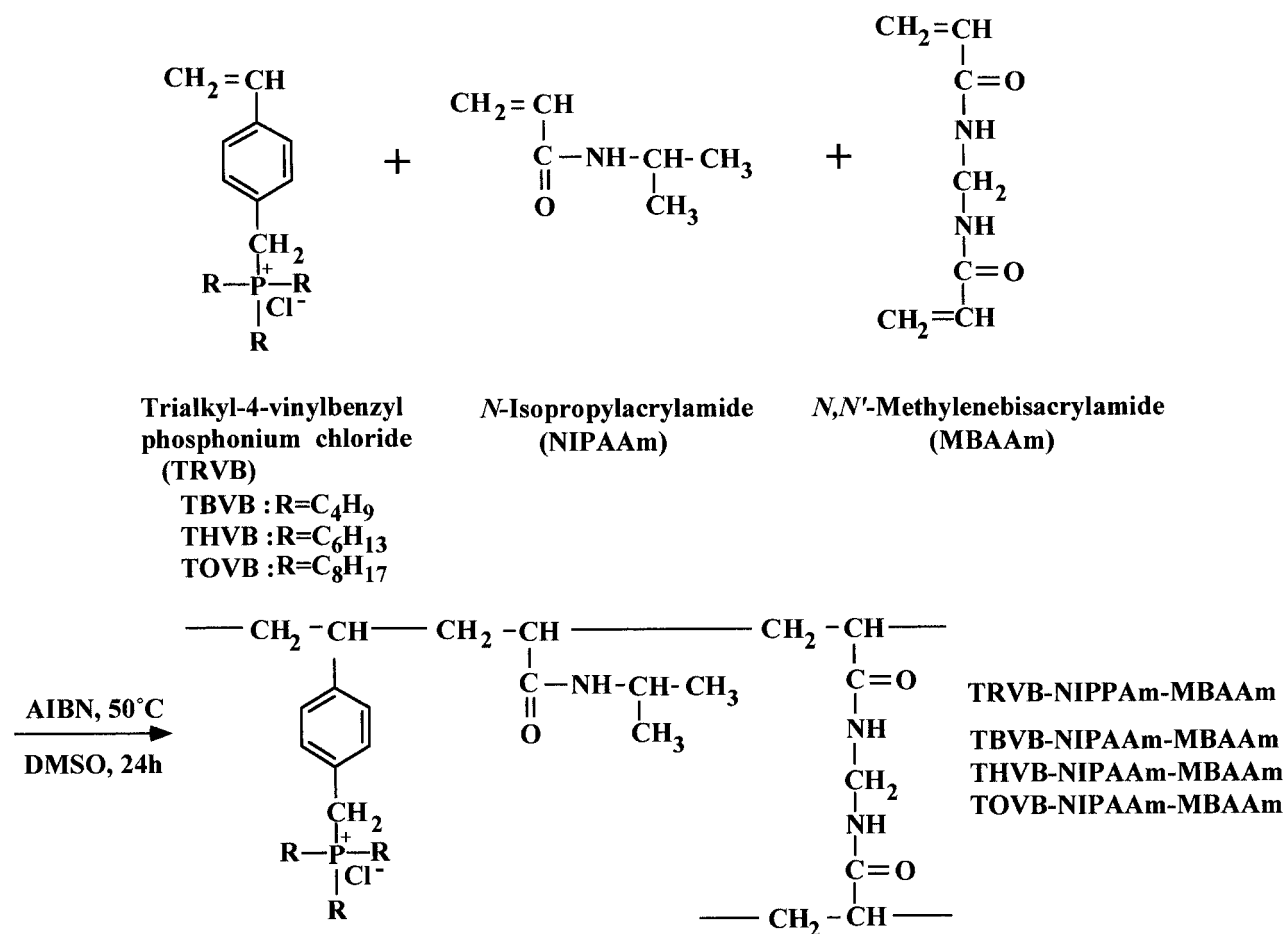


Figure 1 Synthesis of TRVB-NIPAAm-MBAAm copolymers.

ins^{17,18,19} having antibacterial activity. These resins were used to prevent residual toxicity of water-soluble bactericides in water. It was found that the copolymers beads with cationic groups, such as quaternary ammonium groups or phosphonium groups, exhibited high antibacterial activity against such bacteria^{17,18} and had high adsorption ability for anionic surfactants such as sodium dodecyl benzenesulfonate even from its salt solution.^{17,19}

In the current study we synthesized thermo-sensitive polymer hydrogels containing phosphonium groups via the copolymerization of trialkyl-4-vinylbenzyl phosphonium chloride (TRVB) containing different lengths of alkyl chains, NIPAAm, and *N,N'*-methylenebisacrylamide (MBAAm) as crosslinking agent. We then investigated the water-absorption ability, antibacterial activity, adsorption ability for anionic surfactants of the copolymers obtained, and temperature dependence of these hydrogels.

EXPERIMENTAL

Materials

Three kinds of trialkyl-4-vinylbenzyl phosphonium chlorides (TRVB)—butyl, hexyl, octyl— and *N*-isopropylacrylamide were kindly supplied by Nippon Kagaku Kogyo Co. and Kohjin Co., respectively, and used without further purification. Azobisisobutyronitrile (AIBN) (Nacalai Tesque Co.) was purified by recrystallization from ethanol (Wako Pure Chemical Industry, 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 copolymerization of TRVB, NIPAAm, and MBAAm (Fig. 1). TRVBs with either a butyl, hexyl, or octyl group in their phosphonium groups

are abbreviated as TBVB, THVB, and TOVB, respectively. First, TRVB, NIPAAm, and MBAAm were dissolved in 20 cm³ of dimethyl sulfoxide (DMSO) in a glass vessel under a nitrogen atmosphere. The copolymerization was carried out using 0.01 mol % AIBN (to total monomers) as a radical initiator at 50°C for 24 h. After copolymerization, the copolymers obtained were purified with DMSO, propanone, and deionized water. The copolymers were dried at room temperature in a vacuum oven. The copolymers with particle sizes of 14–32 mesh were selected. The phosphonium content in the copolymers was calculated from the phosphorus content of the dried copolymers. The phosphorus content was determined as follows: Dried copolymers (0.1 g) and 70% nitric acid (10 cm³) were placed in a Kjeldahl flask, and the mixture was heated until white steam came out and then was cooled. After that, 60% perchloric acid (10 cm³) 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 by the phosphovanadomolybdate method.²⁰

Measurement of Water Content of Copolymers

The water content of the copolymers was measured by a tea bag method as follows: The dried copolymers were put into a tea bag made of non-woven fabric. Then they were soaked in excess deionized water for 48 h at a low temperature (1°C–3°C). After that, the solution's temperature was raised to that at which the water content should be measured. After the tea bag containing the copolymers was soaked at each temperature for 6 h, the water unabsorbed into gels was removed by putting the tea bag in air for a short time. Then water on the surface of the gels and the tea bag was immediately wiped with filter paper, and the weight (W_w) of the tea bag containing the gels was measured. The water content of the copolymers was calculated using eq. (1)

$$Q = (W_w - W_t - W_d)/W_d \quad (1)$$

where W_t and W_d are the weight of the wet tea bag and the dried copolymers, respectively.

Measurement of Antibacterial Activity

Organism and Growth Conditions

The bacterium used in this study was *Staphylococcus aureus* (*S. aureus*; IFO 13276), which was

obtained commercially from the Institute for Fermentation, Osaka, Japan.

Calculated cell suspensions containing bacteria of about 10⁷–10⁸ cells/cm³ were prepared and used for antibacterial tests.

Contact of Polymer Gels with Bacteria

A desired amount of the copolymers and 10 cm³ of sterile deionized water were placed in a 50-cm³ Erlenmeyer flask, and the copolymers were swollen at various temperatures for 24 h. After that, 10 cm³ of cell suspension was added into the flask, and the flask was shaken at various temperatures for a prescribed time.

Measurement of Viable Cell Numbers after Contacting with Copolymer Gels

After contacting the copolymer gels with a bacterial suspension for a prescribed time, 1 cm³ of the bacterial suspension was pipetted from the flask, and 9 cm³ of sterile water was added to the bacterial suspension. The suspension was diluted several times, and 0.1 cm³ 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 of the colonies formed on the plate.

Measurement of Adsorption Capacity for Sodium Dodecyl Benzenesulfonate and Sodium Benzenesulfonate

First the weighed copolymer (about 0.1 g) was put into a 100 cm³ Erlenmeyer flask and swollen completely in 30 cm³ of deionized water for 48 h at various temperatures, and then 30 cm³ of the solution of sodium dodecyl benzenesulfonate (SDBS) or sodium benzenesulfonate (SBS) of 4 × 10⁻³ mol/dm³ was poured into the flask. Then the flask was shaken at 30°C for 24 h. A blank test was performed in a similar manner. After that, the gels were filtered, and then the residual concentration of SDBS or SBS in the solution was determined by spectrophotometry (SHIMADZU UV-160A), and the amount of SDBS or SBS adsorbed on the gels was calculated.

Measurement of Surface Charges of Polymer Hydrogels in Water

A smaller excess of water than the maximum water-absorption capacity of each copolymer was

added to the weighed dry copolymer in a flask, and then the flask was allowed to stand for 48 h. To this solution, an amount of potassium poly(vinyl sulfate) (PVSK) solution (degree of polymerization: 2000) equal to the amount of phosphonium groups in the dried copolymers was added using 1/400 mol/dm³ PVSK solution (Wako Pure Chemical Co. Osaka, Japan) and shaken at various temperatures for 24 h. After that, 5 cm³ of supernatant was pipetted and 5 cm³ of a 1/200 mol/dm³ methyl glycol chitosan (degree of polymerization: 600) solution (Wako Pure Chemical Co. Osaka, Japan) were added to this solution. This solution was titrated with a 1/400 mol/dm³ PVSK solution using toluidine blue as an indicator. The same procedure was performed in the absence of polymers. The surface charges on the polymer hydrogels in water were calculated using eq. (2)

$$X = (V_1 - V_2) \times 1/400 \times F \times V_3/5 \times 1/W \quad (2)$$

where X is the surface charge of the polymer gel (meq/g), F is the factor of 1/400 mol/dm³ PVSK solution given by Wako Pure Chemical Co., V_1 is the titration volume of the 1/400 mol/dm³ PVSK solution (cm³), V_2 is the titration volume of 1/400 mol/dm³ PVSK solution in the blank test (cm³), V_3 is the volume of 1/400 mol/dm³ PVSK solution added to the polymer gel (cm³) + the volume of water outside the polymer gel (cm³), and W is the weight of dry polymer (g).

RESULTS AND DISCUSSION

Synthesis of TRVB–NIPAAm–MBAAm Copolymers

The scheme of the synthesis of TRVB–NIPAAm–MBAAm copolymers is shown in Figure 1. It is known that the water-absorption ability of polymer hydrogels is greatly affected by the hydrophilicity of the polymers, the charges in the polymers, and the crosslinking density in the polymers and that the thermosensitivity of the copolymers containing both poly(NIPAAm) and charged groups depends on the content of both the poly(NIPAAm) moiety and the charged groups in the copolymers. Therefore, the various TRVB–NIPAAm–MBAAm copolymers were prepared by changing the mole ratios (a range of 1–6) of three TRVBs with different lengths of alkyl chains and the mole ratios (1–5) of MBAAm as a crosslinking

Table I Phosphonium Content of TRVB–NIPAAm–MBAAm Copolymers

Component	Mol Ratio in Feed	P Content (mmol/g)
TBVB : NIPAAm : MBAAm	1 : 100 : 1	0.14
	3 : 100 : 1	0.28
	1 : 100 : 3	0.14
	2 : 100 : 3	0.20
	3 : 100 : 3	0.28
	4 : 100 : 3	0.35
	5 : 100 : 3	0.39
	6 : 100 : 3	0.46
	1 : 100 : 5	0.13
	3 : 100 : 5	0.26
	5 : 100 : 5	0.32
	THVB : NIPAAm : MBAAm	1 : 100 : 1
3 : 100 : 1		0.25
1 : 100 : 3		0.11
2 : 100 : 3		0.20
3 : 100 : 3		0.27
4 : 100 : 3		0.31
5 : 100 : 3		0.41
6 : 100 : 3		0.47
1 : 100 : 5		0.13
3 : 100 : 5		0.25
5 : 100 : 5		0.36
TOVB : NIPAAm : MBAAm		1 : 100 : 1
	3 : 100 : 1	0.22
	1 : 100 : 3	0.14
	2 : 100 : 3	0.19
	3 : 100 : 3	0.22
	4 : 100 : 3	0.27
	5 : 100 : 3	0.32
	6 : 100 : 3	0.38
	1 : 100 : 5	0.12
	3 : 100 : 5	0.24
	5 : 100 : 5	0.33

agent, and at the constant mole ratio (100 mol ratio) of NIPAAm.

Table I shows the mole ratios of three monomers in feed and the phosphorous contents in the copolymers obtained for this study. The content of phosphonium groups in the TRVB–NIPAAm–MBAAm copolymers could be arbitrarily varied to some extent by changing the content of TRVB and at constant mole ratio of NIPAAm and MBAAm in feed.

Water Absorption Ability of TRVB–NIPAAm–MBAAm Copolymers

In general, the swelling ratio, which corresponds to water content, of hydrogels can be expressed by eq. (3)²¹

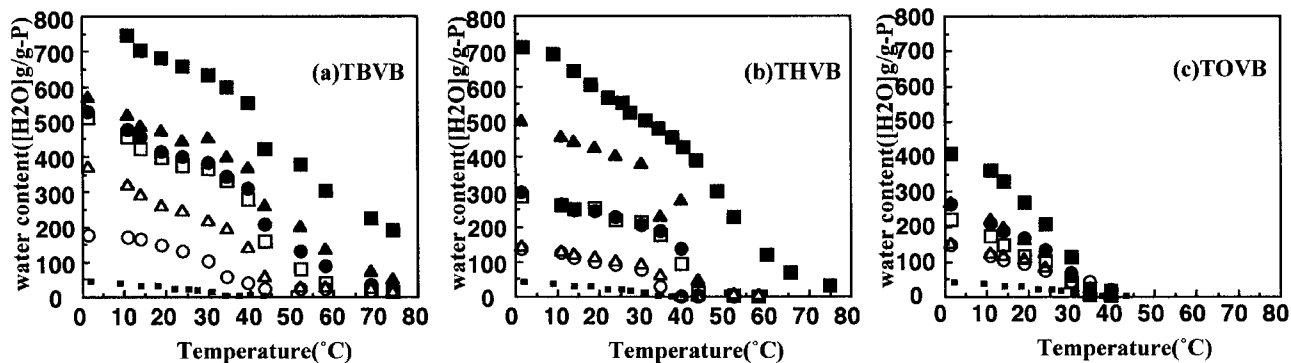


Figure 2 Temperature dependence of water content of TRVB–NIPAAm–MBAAm copolymers having different amounts of phosphonium groups. Copolymers: (a) TBVB–NIPAAm–MBAAm, (b) THVB–NIPAAm–MBAAm, (c) TOVB–NIPAAm–MBAAm; mol ratio in feed (TRVB : NIPAAm : MBAAm): (■) 0 : 100 : 3, (○) 1 : 100 : 3, (△) 2 : 100 : 3, (□) 3 : 100 : 3, (●) 4 : 100 : 3, (▲) 5 : 100 : 3, (■) 6 : 100 : 3.

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

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 ν/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 copolymers, and concentration of salts in the outer solution. In order to reveal the effect of TRVB on thermosensitive behavior, the water content of the TRVB–NIPAAm–MBAAm copolymer gels, which were obtained using a constant amount of the crosslinking agent and various amounts of TRVB in the feed, was measured at various temperatures (0–80°C). The results on the TRVB–NIPAAm–MBAAm (X : 100 : 3 mol ratio) copolymers are shown in Figure 2(a–c).

These figures show the temperature dependence of the water content of the TRVB–NIPAAm–MBAAm copolymers obtained at 1–6 mol % ratio of TRVB, 100 mol % ratio of NIPAAm, and 3 mol ratio of the crosslinking agent and in the feed. In Figure 2 the results on the NIPAAm–MBAAm (100 : 3) copolymer having no phosphonium groups are also shown.

In TRVB–NIPAAm–MBAAm (X : 100 : 3 mol ratio) copolymers with various amounts of different TRVBs, the water content increased with the introduction of an increasing amount of phosphonium groups. Figure 3 shows the relationship between water content and the amount of phospho-

num groups in all the TRVB–NIPAAm–MBAAm (X : 100 : 3 mol ratio) copolymers. From Figures 2 and 3 it can be seen that all the copolymers were found to have a higher water content than that of the NIPAAm–MBAAm (100 : 3) copolymer, which had no phosphonium groups. This indicates that the difference of osmotic pressure between the inner side and outer side of the copolymer hydrogels became larger as the quantity of phosphonium groups in the copolymers increased.

The order of water content of the copolymers is as follows: TBVB–NIPAAm–MBAAm > THVB–

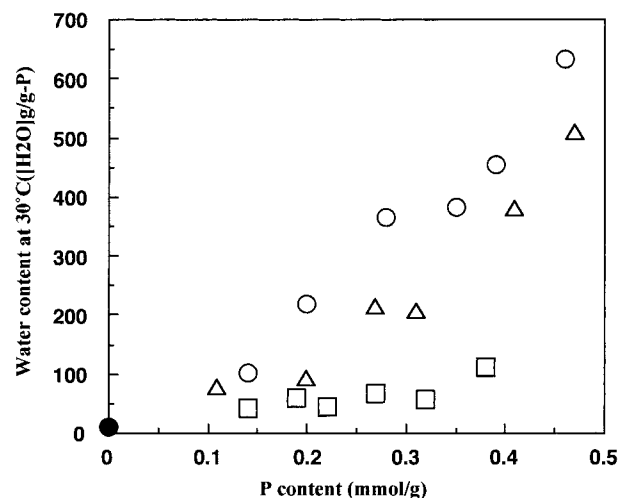


Figure 3 Water content of TRVB–NIPAAm–MBAAm copolymers containing different amounts of various phosphonium groups: (●) NIPAAm:MBAAm = 100 : 3; (○) TVBF : NIPAAm : MBAAm = X : 100 : 3; (△) THVB : NIPAAm : MBAAm = X : 100 : 3; (□) TOVB : NIPAAm : MBAAm = X : 100 : 3 (mol ratio in feed: X = 1–6).

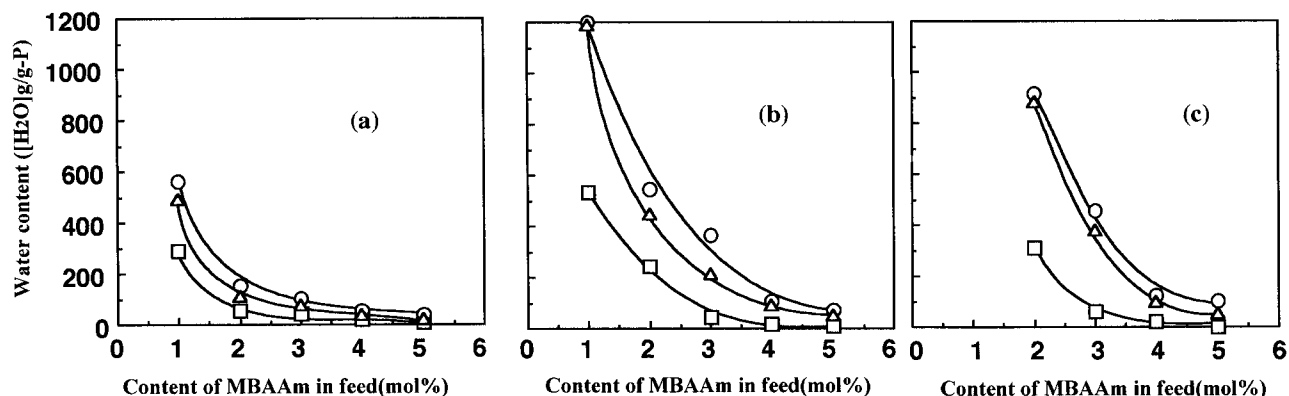


Figure 4 Water content of TRVB-NIPAAm-MBAAm copolymers with various contents of MBAAm at 30°C. TBVB-NIPAAm-MBAAm: (a) 1 : 100 : X, (b) 3 : 100 : X, (c) 5 : 100 : X (mol ratio in feed: X = 1~5); copolymers: (○) TBVB : NIPAAm : MBAAm; (△) THVB : NIPAAm : MBAAm; (□) TOVB : NIPAAm : MBAAm.

NIPAAm-MBAAm > TOVB-NIPAAm-MBAAm copolymers

In particular, the TBVB-NIPAAm-MBAAm (6 : 100 : 3) copolymer had a high water content, about 650 g of H₂O/g-polymer. F. Askali reported that acrylic-based superabsorbents had a water content of more than 900 g of H₂O/g-polymer.²²

This indicates that the TRVB-NIPAAm-MBAAm (X : 100 : 3 mol ratio) copolymers with a shorter alkyl chain have a higher affinity for water.

Figure 2 also shows that the water content of all the copolymers having different TRVB decreased with increasing temperature. In TBVB-NIPAAm-MBAAm and THVB-NIPAAm-MBAAm copolymers, the transition temperature, which is defined here as the temperature at which the water content of the copolymers decreased to half of that at room temperature (23°C), shifted clearly to higher temperatures as phosphonium content in the copolymers increased. In the TOVB-NIPAAm-MBAAm copolymer, the transition temperature became almost the same, and all the TOVB-NIPAAm-MBAAm copolymers were deswollen completely at temperatures above 40°C.

Figure 4 shows the effect of the degree of crosslinking on the water content of the TRVB-NIPAAm-MBAAm (1,3,5 : 100 : X mol ratio) copolymers at 30°C. Figure 4(a-c) shows the results of the copolymers obtained at 1, 3, and 5 mol ratio of TBVB, THVB, and TOVB, respectively. The water content of all the copolymers decreased abruptly with an increasing amount of the crosslinking agent MBAAm. In particular, the water content of the TOVB-NIPAAm-MBAAm copolymer obtained at more than 3 mol ratio of

MBAAm in feed was fairly low. In the case of TRVB-NIPAAm-MBAAm (5 : 100 : X mol ratio) copolymers [Fig. 4(c)], the water content of all the copolymers obtained at 1 mol ratio of MBAAm could not be measured because of high swelling due both to a small amount of the crosslinking agent MBAAm and a high amount of TRVB.

To study the effect of neutral salt on the water absorption of the copolymers, the water content of the TRVB-NIPAAm-MBAAm (X : 100 : 3 mol ratio) copolymers was measured in 0.09% and 0.9% NaCl solutions at 20°C and 35°C. Figure 5(a-c) shows the results on the copolymers containing TBVB, THVB, and TOVB, respectively. In all cases, the water content was depressed significantly by the addition of NaCl. In the case of the copolymers containing TBVB and THVB [Fig. 5(a,b)], the water content in 0.09% NaCl solution at 20°C increased with an increasing content of phosphonium groups. But the water content of the TOVB-NIPAAm-MBAAm copolymers under the same conditions decreased with increasing TOVB content [Fig. 5(c)]. This decrease in the water content of the TOVB-NIPAAm-MBAAm copolymers with an increasing TOVB content in 0.09% NaCl solution is a result of a higher number of hydrophobic octyl groups in TOVB compared to the number of alkyl groups in TBVB or THVB. The water content of all the copolymers in 0.9% NaCl at 20°C was lower than those in a 0.09% NaCl solution and decreased with an increasing TRVB content.

On the other hand, the water contents of the TBVB-NIPAAm-MBAAm copolymer in 0.09% NaCl solution at 35°C increased with increasing

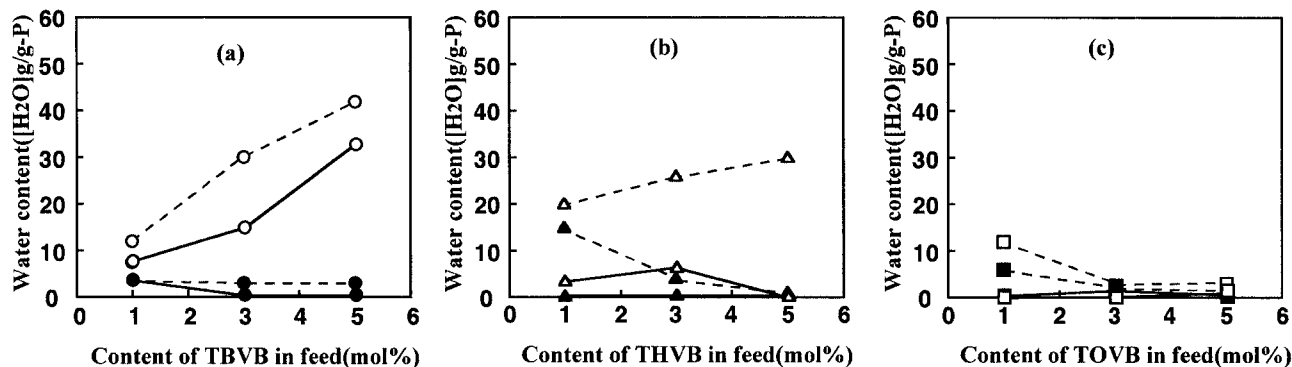


Figure 5 Water content of TRVB-NIPAAm-MBAAm copolymers in 0.09% and 0.9% NaCl solution at 30°C. Copolymers: (a) TBVB-NIPAAm-MBAAm, (b) THVB-NIPAAm-MBAAm, (c) TOVB-NIPAAm-MBAAm; NaCl concentration (wt %): (○, △, □) 0.09; (●, ▲, ■) 0.9.

TBVB content. But the water contents of THVB-NIPAAm-MBAAm copolymers in 0.09% NaCl solution at 35°C increased slightly increasing THVB contents, then decreased as shown in Fig. 5(b). The water contents of the TOVB-NIPAAm-MBAAm copolymer in a 0.09% NaCl solution at 35°C was nearly zero. Furthermore, the water content of all the copolymers in a 0.9% NaCl solution at 35°C was nearly zero. The decrease in water content of the copolymers in NaCl solutions is because there is very little difference in osmotic pressure between the inner side and outer side of the copolymer hydrogels because of the addition of NaCl into the outer solution. The larger reduction of water content of the copolymers containing a larger number of hydrophobic alkyl groups indicates the dehydration effect of NaCl is larger for these copolymers.

Thus, it was found that in a NaCl solution the water content of the copolymers containing phosphonium groups was greatly affected by the content of the phosphonium groups, the length of the alkyl chains in the phosphonium groups, the concentration of NaCl, and the temperature.

Antibacterial Activity of TRVB-NIPAAm-MBAAm Copolymers

The antibacterial activity of TRVB-NIPAAm-MBAAm copolymers against *S. aureus* was investigated at 20, 30, and 35°C.

Figure 6(a-c) shows the changes in viable cell numbers of three kinds of TRVB-NIPAAm-MBAAm (1,3 : 100 : 3 mol ratio) copolymers—containing TBVB, THVB, and TOVB, respec-

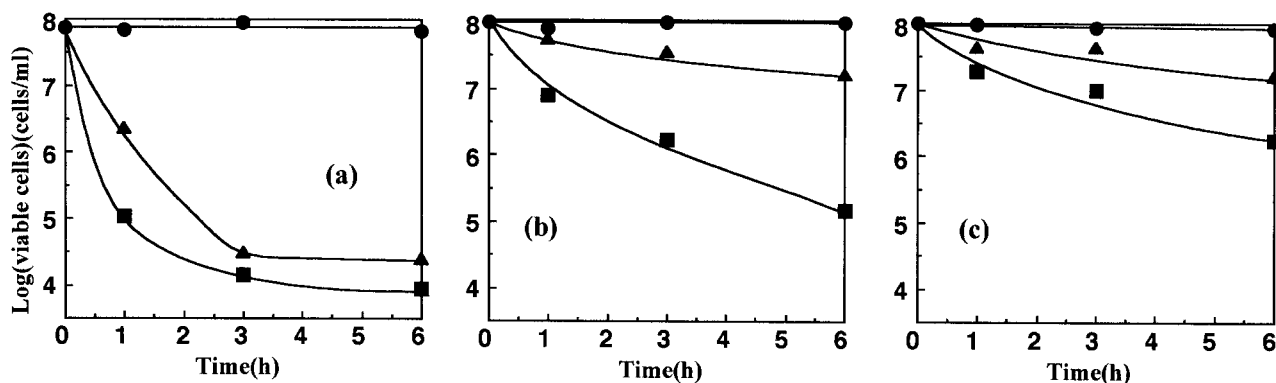


Figure 6 Change in number of viable cells after contact with TRVB-NIPAAm-MBAAm at 30°C. Copolymers: (a) TBVB-NIPAAm-MBAAm, (b) THVB-NIPAAm-MBAAm, (c) TOVB-NIPAAm-MBAAm; Mol ratio in feed (TRVB-NIPAAm-MBAAm): (●) Blank, (▲) 1 : 100 : 3, (■) 3 : 100 : 3. Shaking at 30°C; weight of copolymers: 0.05 g; suspension of *S. aureus* in 60 mL of deionized water.

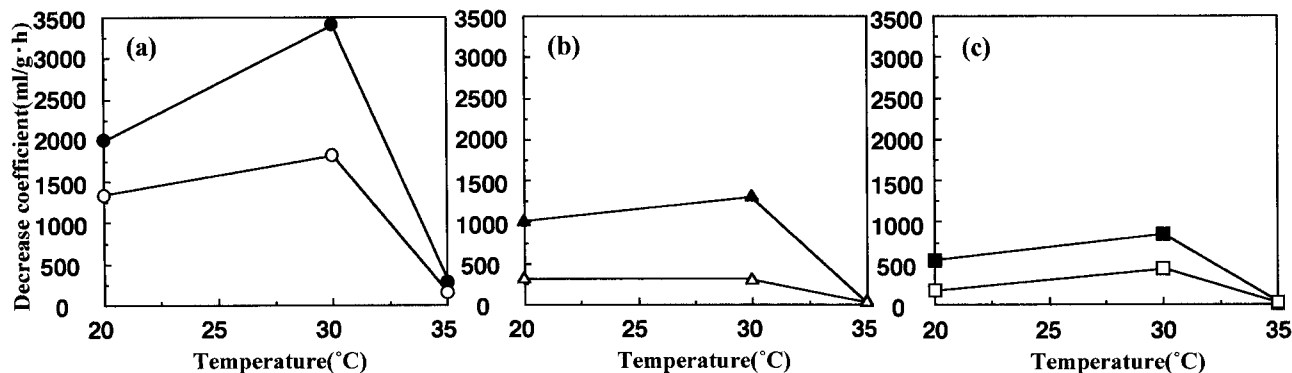


Figure 7 Temperature dependence of decrease coefficient for *S. aureus* of TRVB-NIPAAm-MBAAm copolymers. Copolymers: (a) TBVB-NIPAAm-MBAAm, (b) THVB-NIPAAm-MBAAm, (c) TOVB-NIPAAm-MBAAm; mol ratio in feed (TRVB : NIPAAm : MBAAm): (○, △, □) 1 : 100 : 3; (●, ▲, ■) 3 : 100 : 3.

tively—after they were contacted with different amounts of phosphonium groups at 30°C. In each TRVB-NIPAAm-MBAAm copolymer, the copolymer with a higher phosphonium content exhibited higher antibacterial activity against *S. aureus*. Similar results were obtained at both 20°C and 35°C, although the magnitude of antibacterial activity of the TRVB-NIPAAm-MBAAm copolymers was different at each temperature. The NIPAAm-MBAAm copolymers, which had no phosphonium groups, exhibited no antibacterial activity at 20°C, 30°C, and 35°C.

The decrease coefficients of these TRVB-NIPAAm-MBAAm copolymers for *S. aureus* were calculated by eq. (4):

$$D \text{ (cm}^3 \text{ g}^{-1} \text{ h}^{-1}) = (V/W \cdot t) \log(N_0/N_t) \quad (4)$$

where V is the volume of cell suspension (cm^3), W is the weight of dry copolymers (g), t is the contact time (h), N_0 is the initial number of viable cells (cells/cm^3), and N_t is the number of viable cells after contact time t (cells/cm^3).

The temperature dependence of the decrease coefficients of these TRVB-NIPAAm-MBAAm copolymers for *S. aureus* is shown in Figure 7. With each copolymer, the maximum decrease coefficient was obtained at 30°C and the order of antibacterial activity of the TRVB-NIPAAm-MBAAm copolymers is as follows: TBVB-NIPAAm-MBAAm > THVB-NIPAAm-MBAAm > TOVB-NIPAAm-MBAAm. That is, the TRVB-NIPAAm-MBAAm copolymers with shorter alkyl chains had higher antibacterial activity than

those with longer alkyl chains in the phosphonium groups.

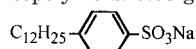
To clarify the reason for the temperature dependence of the activity of the copolymers and the highest antibacterial activity of the TBVB-NIPAAm-MBAAm copolymer, the adsorption capacity of the copolymers with different phosphonium groups for SBS and SDBS was measured at 20°C, 30°C, and 35°C because it is known that most bacteria have negative charges on their surfaces in water. Table II shows that copolymer gels with a higher phosphonium content adsorbed more SDBS or SBS than copolymer gels with a lower phosphonium content, although the adsorption capacity of those copolymer gels for SDBS was a fair amount higher than that for SBS. In addition, the maximum adsorption capacity for SDBS was at 35°C. These results indicate that dodecyl groups in SDBS contribute a great deal to the adsorption of SDBS on copolymer gels in water.

It has been reported that the antibacterial activity of water-insoluble polymers containing cationic groups such as quaternary ammonium groups or phosphonium groups is affected by both electrostatic interaction and hydrophobic interaction between the surface of water-insoluble polymers and bacteria.¹⁵⁻¹⁸ So far, the surface charges on polymer hydrogels have not been reported. In general, ζ potential is used as the surface charge of particles such as colloids. However, the ζ potential of highly swollen polymer hydrogels is difficult by conventional methods such as a ζ potential meter. On the other hand, colloidal titration is used to determine the charges in poly-

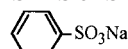
Table II Adsorption of SDBS or SBS with TRVB–NIPAAm–MBAAm Copolymers

Component	Mol Ratio in Feed	Amount of Adsorbed SDBS (mmol/g)			Amount of Adsorbed SBS (mmol/g)		
		20°C	30°C	35°C	20°C	30°C	35°C
TBVB : NIPAAm : MBAAm = 1 : 100 : 3		0.75	0.75	0.93	0.02	0.02	0.04
	= 3 : 100 : 3	1.00	1.02	1.11	0.09	0.08	0.11
THVB : NIPAAm : MBAAm = 1 : 100 : 3		0.76	0.76	0.86	0.03	0.01	0.06
	= 3 : 100 : 3	0.96	0.96	1.10	0.15	0.14	0.20
TOVB : NIPAAm : MBAAm = 1 : 100 : 3		0.82	0.80	0.92	0.02	0.03	0.05
	= 3 : 100 : 3	0.99	0.92	1.07	0.13	0.12	0.17

Weight of TRVB–NIPAAm–MBAAm copolymers: 0.05 g. Concentration of SDBS or SBS: 4.0×10^{-3} mol/dm³.



Sodium *n*-dodecylbenzenesulfonate (SDBS)



Sodium benzenesulfonate (SBS)

electrolytes such as alginic acid.²³ Potassium poly(vinyl sulfate) (PVSK), one of the reagents for colloidal titration, has negative charges and a molecular weight of about 320,000. Therefore, we considered PVSK difficult to penetrate into polymer hydrogels because it is adsorbed on the surface of polymer hydrogels. Based on this consideration, we used the values obtained by colloidal titration as the surface charges on polymer hydrogels.

Table III shows the positive charges on the surface of copolymer hydrogels with different phosphonium groups, measured by a colloidal titration at 20°C, 30°C, and 35°C. The values are considerably smaller than the phosphonium content in dried polymers, determined by a method mentioned in the Experimental section. This indicates that a part of the positive charges in the copolymers appears on the sur-

face of copolymer hydrogels. The copolymers with a higher phosphonium content had higher positive charges on the surface than those with a lower phosphonium content. Furthermore, positive charges on the surface of each copolymer hydrogel increased with decreasing temperature in the temperature range studied except for the TOVB–NIPAAm–MBAAm copolymers. This increase in the positive charges with decreasing temperature results from the larger swelling of the polymer gels at lower temperatures.

An assessment of this study's results indicates that antibacterial activity of all the TRVB–NIPAAm–MBAAm copolymer hydrogels became highest at 30°C because antibacterial activity of copolymers is affected by both electrostatic interaction and hydrophobic interaction between polymer gels and bacteria.

Table III Positive Charge on Surface of TRVB–NIPAAm–MBAAm Copolymers

Component	Mol Ratio in Feed	Phosphonium Content (mmol/g)	Positive Charge ^a on Surface (meq/g)		
			20°C	30°C	35°C
TBVB : NIPAAm : MBAAm = 1 : 100 : 3		0.14	0.066	0.045	0.019
	= 3 : 100 : 3	0.28	0.102	0.090	0.077
THVB : NIPAAm : MBAAm = 1 : 100 : 3		0.11	0.063	0.028	0.028
	= 3 : 100 : 3	0.27	0.115	0.054	0.041
TOVB : NIPAAm : MBAAm = 1 : 100 : 3		0.14	0.059	0.059	0.065
	= 3 : 100 : 3	0.22	0.087	0.105	0.027

Weight of TRVB–NIPAAm–MBAAm copolymers: 0.05 g.

^a These values were determined by colloidal titration.

CONCLUSIONS

Thermosensitive and superabsorbent polymer hydrogels could be obtained from TRVB–NIPAAm–MBAAm copolymers.

The water content of TRVB–NIPAAm–MBAAm copolymers increased with increasing phosphonium groups in the copolymers, while it decreased with increasing chain length of the alkyl groups in the phosphonium groups as well as with an increasing degree of crosslinking in the copolymers.

The water content of the copolymers in NaCl solutions decreased with an increasing concentration of NaCl. The longer the chain length of alkyl groups in the phosphonium groups, the stronger the effect of adding NaCl on the water content of the copolymers.

The TRVB–NIPAAm–MBAAm copolymers with a higher phosphonium content exhibited higher antibacterial activity against *S. aureus* than did the copolymers with a lower phosphonium content, but this activity decreased with increasing chain length of the alkyl groups in phosphonium groups. In 30°C deionized water, the TRVB–NIPAAm–MBAAm copolymers exhibited the highest antibacterial activity against *S. aureus*.

It was also found that both electrostatic interaction and hydrophobic interaction between polymer hydrogels and bacteria brought about the high antibacterial activity of the TRVB–NIPAAm–MBAAm copolymers.

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