

Synthesis and Functions of Water-Soluble and Thermosensitive Copolymers Having Phosphonium Groups from Acryloyloxyethyl Trialkyl Phosphonium Chloride, *N*-Isopropylacrylamide, and without/with Butylmethacrylate

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ABSTRACT: Water-soluble thermosensitive polymers were prepared by copolymerization of acryloyloxyethyl trialkyl phosphonium chlorides (AETRs) with having varying alkyl lengths, *N*-isopropylacrylamide (NIPAAm), and without/with butyl methacrylate (BMA). The relative viscosity of the solutions of the AETR–NIPAAm copolymers increased with increasing AETR content. The thermosensitivity of the AETR–NIPAAm copolymers was affected by an introduction of hydrophobic BMA into the copolymers and the thermosensitivity of the AETR–BMA–NIPAAm copolymers increased with chain length of alkyl groups in phosphonium groups in AETR. The AETR–NIPAAm copolymers

and the AETR–BMA–NIPAAm copolymers had high flocculating ability against kaolin or bacteria such as *Escherichia coli*. The flocculating ability of the copolymers was affected with the AETR content, BMA content, and the chain length of alkyl groups in phosphonium groups. Almost 100% of the AETB–BMA–NIPAAm and AETO–BMA–NIPAAm copolymers dissolved in water could be recovered by heating the solution above 30°C in the presence of NaCl. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1139–1147, 2003

Key words: solution properties; stimuli-sensitive polymers; water-soluble polymer

INTRODUCTION

It is known that poly(*N*-isopropylacrylamide) (NIPAAm) is a thermosensitive polymer. That is, polyNIPAAm dissolves below about 32°C and does not dissolve in water above the temperature. The temperature at which this phase transition occurs thermally and reversibly is commonly referred to as the lower critical solution temperature (LCST) (see, for example, refs. 1–4). The copolymers containing NIPAAm moiety have been widely studied from fundamental and practical points of views (see, for example, refs. 5–16).

On the other hand, it has been reported that water-soluble polymers having phosphonium groups had high antibacterial activity against bacteria such as *Staphylococcus aureus* or *Escherichia coli*.^{17,18} However, other functions such as flocculating ability and so on of the polymers with phosphonium groups have not been investigated. Previously we also re-

ported that several copolymers with cationic groups such as amino or ammonium groups had high flocculating ability against kaolin suspensions^{19–21} and several water-insoluble resins or hydrogels having phosphonium groups had antibacterial activity against *S. aureus* or *E. coli*.^{22–25} Furthermore, we reported that we can prevent the residual toxicity of bactericides in water by use of these insoluble bactericides. If we can get water-soluble and thermosensitive acryloyloxyethyl trialkyl phosphonium chloride (AETR)–NIPAAm copolymers, it is considered that the copolymers exhibit high flocculating ability or antibacterial activity below the LCST and the copolymers can be recovered from an aqueous solution by raising temperature above the LCST. So we can obtain water containing no suspended particles and no polymers after treating wastewater with the copolymers.

In the previous article,²⁶ we reported the synthesis of thermosensitive hydrogels from AETR–NIPAAm–*N,N'*-methylenebisacrylamide copolymers and their temperature dependence of water absorption.

This article deals with the synthesis, solution properties, and flocculating ability of the water-soluble thermosensitive copolymers having phosphonium

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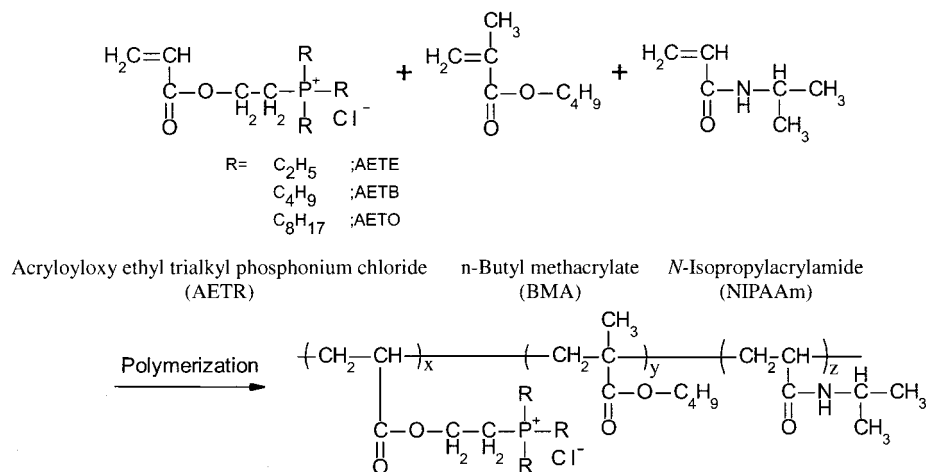


Figure 1 Synthesis of AETR–NIPAAm and AETR–BMA–NIPAAm copolymers.

groups by copolymerizing AETR, NIPAAm, and with/without butyl methacrylate (BMA).

EXPERIMENTAL

Materials

AETRs with ethyl, butyl, and octyl group in phosphonium groups were used, and these monomers are abbreviated as AETE, AETB, and AETO, respectively. AETRs and NIPAAm were kindly supplied by Nippon Kagaku Kogyo Co. (Tokyo, Japan) and Kohjin Co. (Tokyo, Japan), respectively, and used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) (Nacal tesque Co., Kyoto, Japan) was purified by recrystallization from ethanol (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Other chemical compounds were reagent grade and were used as received. Kaolin for flocculation test was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

The bacterium used in this study was *E. coli*, which was obtained commercially from the Institute for Fermentation (Osaka, Japan).

Synthesis of water-soluble copolymers

The structure of the AETR–NIPAAm and AETR–BMA–NIPAAm copolymers is shown in Figure 1.

First, AETR and NIPAAm were dissolved in 20 cm³ of dimethylsulfoxide (DMSO) in a glass vessel under a nitrogen atmosphere. Next, the copolymers were obtained by radical copolymerization using AIBN as a radical initiator at 50°C for 1 h in sealed ampoules. After polymerization, the polymer mixture was powered into hot water of 50°C to precipitate the copolymers and the copolymers obtained was redissolved in water at room temperature (about 25 °C). Then, the copolymers were purified by dialysis against deionized water. The copolymers were obtained by freeze

drying. The AETR–BMA–NIPAAm copolymers were also obtained in the same manner as the AETR–NIPAAm copolymers. BMA was used to give hydrophobicity to the water-soluble polymers obtained. 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 resulted solution was determined by phosphovanadomolybdate method.²⁷

Measurement of the relative viscosity of polymer solutions

The relative viscosity of 0.2 g/dm³ polymer aqueous solutions was measured with an Ostwald viscometer (No. 1, Sansyo, Tokyo, Japan) at various temperatures.

Measurement of flocculating ability against kaolin suspension or bacteria suspension

The clarifying ability of the polymers against kaolin suspension or bacteria suspension was estimated as the flocculating ability of the polymers as follows:

First, 500 mg/dm³ kaolin suspensions were mixed with the copolymer solutions for 2 min at 500 rpm and for subsequent 15 min at 300 rpm. Then, the clarifying ability of the copolymers against was studied by observing the optical density ($\log I_0/I$) at 660 nm of the supernatant after standing for 2 min, where I_0 and I represent the incident beam intensity and transmitted beam intensity, respectively.

TABLE I
Phosphorus Content of the AETR–NIPAAm or
AETR–BMA–NIPAAm Copolymer

Component	AETR:BMA: NIPAAm	P content (mmol/g)	
		Calcd.	Found
AETE–NIPAAm	1:0:100	0.09	0.15
	3:0:100	0.25	0.28
	5:0:100	0.40	0.33
AETB–NIPAAm	1:0:100	0.09	0.16
	3:0:100	0.24	0.24
	5:0:100	0.38	0.38
AETO–NIPAAm	1:0:100	0.08	0.17
	3:0:100	0.27	0.27
	5:0:100	0.36	0.38
AETE–BMA– NIPAAm	1:4:100	0.08	0.20
	2.5:2.5:100	0.20	0.22
	4:1:100	0.32	0.33
AETB–BMA– NIPAAm	1:4:100	0.08	0.12
	2.5:2.5:100	0.20	0.23
	4:1:100	0.31	0.28
AETO–BMA– NIPAAm	1:4:100	0.08	0.18
	2.5:2.5:100	0.19	0.31
	4:1:100	0.30	0.35

The clarifying ability against *E. coli* suspension was studied by observing the optical density at 660 nm of the supernatant after filtering the solutions with filter paper (No. 1, Advantec, Tokyo, Japan), after the copolymer solutions were mixed with about 10^7 – 10^8 cells/cm³ bacteria suspensions for 1 h by using Bio-shaker (TAITEC BR-40L) at 35°C.

Measurement of the residual copolymers in water

The polymer aqueous solution was shaken for 2 h at various temperatures and the amount of residual copolymers dissolved in aqueous solutions after shaking was determined by ultraviolet (UV) spectroscopy after filtration.

RESULTS AND DISCUSSION

Synthesis of water-soluble copolymers

Table I shows the molar ratio of each monomer in the

feed and the phosphorus content of the AETR–NIPAAm and AETR–BMA–NIPAAm copolymers obtained. The phosphonium content of the copolymers was calculated from the phosphorus content in the dried copolymers, which was determined by the phosphovanadomolybdate method.²⁷

In the AETR–NIPAAm copolymers, the NIPAAm content in the feed was held constant (100 molar ratio), while the AETR content was varied from 1 to 5 molar ratio. The AETR–BMA–NIPAAm copolymers were prepared in the same manner. In the case of the AETR–BMA–NIPAAm copolymers, the NIPAAm content in the feed was held constant (100 molar ratio), while the AETR content in feed was varied from 1 to 4 molar ratio. But the sum of AETR and BMA content in the feed was constant (5 molar ratio). The phosphonium content of the copolymers increased with increasing AETR content in the feed, although the contents were inconsistent with the values calculated.

Temperature dependence of the viscosities of the copolymers

Figure 2 shows the relative viscosities of various AETR–NIPAAm copolymer solutions measured with an Ostwald viscometer at various temperatures.

The relative viscosities of 0.2 g/dm³ aqueous solutions of the AETR–NIPAAm copolymers increased with increasing content of phosphonium in each copolymer. It is known that the relative viscosity of usual polymers increases with increasing molecular weight of polymers. The molecular weight of the AETR–NIPAAm copolymers was not determined. Here, the AETR–NIPAAm copolymers having the same AETR and different compositions were assumed to have almost the same molecular weight, because they were copolymerized under the same conditions. Therefore, the increase in the relative viscosities of the copolymers having the same AETR and different compositions is considered to be brought about by the expansion of the polymer chains in water due to the repulsion of cationic charges introduced into the co-

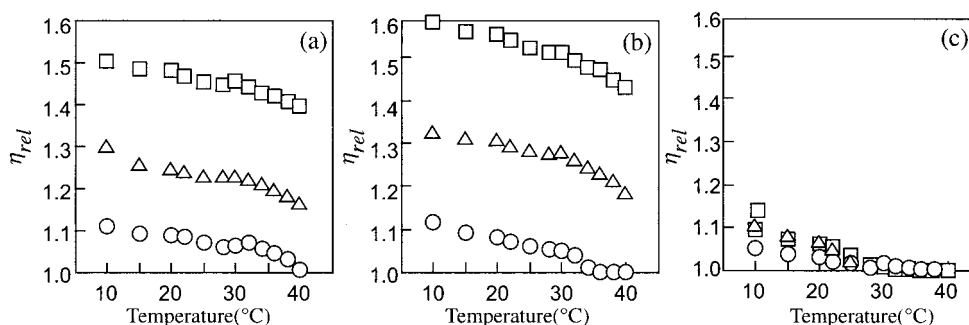


Figure 2 Temperature dependence of the relative viscosities of 0.2 g/dm³ AETR–NIPAAm copolymer solutions. Viscosity was measured with an Ostwald viscometer. Copolymers: (a) AETE–NIPAAm, (b) AETB–NIPAAm, and (c) AETO–NIPAAm. AETR–NIPAAm (X:100): (○) 1:100, (Δ) 3:100, and (□) 5:100.

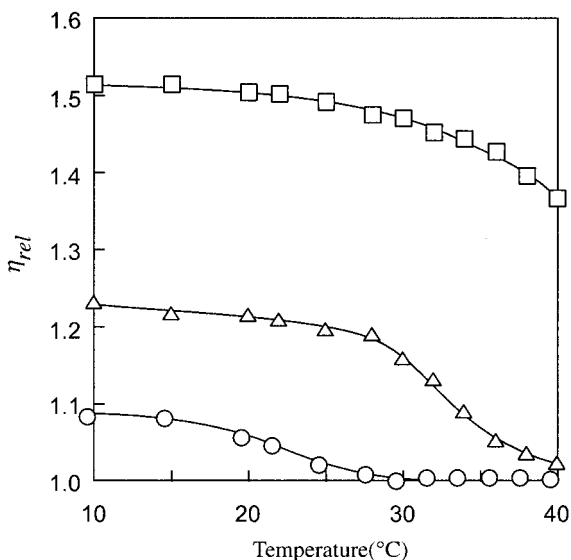


Figure 3 Temperature dependence of the relative viscosities of 0.2 g/dm³ AETB-BMA-NIPAAm copolymer aqueous solutions. AETB-BMA-NIPAAm (X:Y:100) copolymers: (○) 1:4:100, (△) 2.5:2.5:100, and (□) 4:1:100.

polymers. It is also known that the solubility of poly-NIPAAm decreases sharply at around 32°C of its LCST.⁵ Figure 2 shows that the relative viscosity of these copolymers having phosphonium groups decreased with increasing temperature in the temperature range from 10 to 40°C. In the case of the AETE-NIPAAm (1:100) and AETB-NIPAAm (1:100) copolymers, it was found that the relative viscosity of the solutions decreased sharply near the LCST of poly-NIPAAm. However, the sharp decrease near the LCST of poly-NIPAAm could not be observed with the AETE-NIPAAm (5:100) and AETB-NIPAAm (5:100) copolymer. Thus, the thermosensitivity of the AETE-NIPAAm and AETB-NIPAAm copolymers was reduced by the introduction of cationic phosphonium groups into the copolymers. This indicates that the association of poly-NIPAAm moieties due to hydrophobic interaction above the LCST became difficult because of the presence of cationic phosphonium groups.

It was also found that the relative viscosities of the aqueous solutions of the AETO-NIPAAm copolymers were considerably low compared to those of other AETE-NIPAAm and AETB-NIPAAm copolymers. This is because of higher hydrophobicity of the octyl group in phosphonium groups in AETO compared to the ethyl or butyl group in phosphonium groups in AETE or AETB.

Figure 3 shows the temperature dependence of the relative viscosities of the aqueous solutions of the AETB-BMA-NIPAAm (X:Y:100, X+Y=5) copolymers with different compositions. Here, the copolymers containing AETB were selected for this experiment,

because high relative viscosity of the copolymer solutions was observed with the AETB-NIPAAm copolymer as shown in Figure 2. BMA was introduced to give hydrophobicity to the AETB-NIPAAm copolymers.

The relative viscosities of the aqueous solutions of the AETB-BMA-NIPAAm (X:Y:100) copolymers increased with increasing AETB content and decreasing BMA content. It has been reported that the introduction of hydrophilic or hydrophobic moiety to poly-NIPAAm shifted its LCST (ca. 32°C) to higher or lower temperature, respectively.^{28,29} The temperature at which the relative viscosity of the AETB-BMA-NIPAAm copolymer solutions decreased sharply shifted to lower temperature with decreasing AETB content and increasing BMA content than the LCST of poly-NIPAAm. This means that the introduction of BMA into the AETB-NIPAAm copolymers increased the hydrophobicity of the copolymers.

Next, the relative viscosity of various AETR-BMA-NIPAAm (4:1:100) copolymer solutions was measured at various temperatures. The results are shown in Figure 4.

The relative viscosities of the aqueous solutions of the AETR-BMA-NIPAAm (4:1:100) copolymers decreased with increasing chain length of alkyl groups in phosphonium groups. In particular, the relative viscosity of the aqueous solutions of the AETO-BMA-NIPAAm (4:1:100) copolymer was significantly low compared with that of other copolymers containing AETE or AETB. The viscosity of the solutions of copolymers containing AETE or AETB decreased gradually with increasing temperature in the temperature range from 10 to 40°C studied. However, the relative

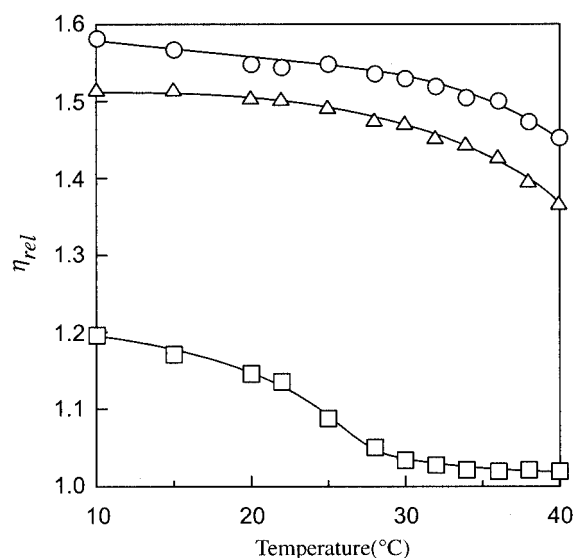


Figure 4 Temperature dependence of the relative viscosities of 0.2 g/dm³ copolymer aqueous solutions. AETR-BMA-NIPAAm (4:1:100) copolymers. AETR: (○) AETE, (△) AETB, and (□) AETO.

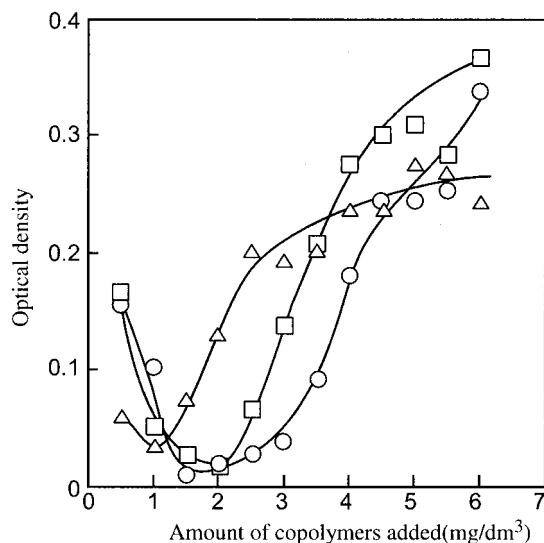


Figure 5 Optical density at 660 nm of kaolin suspension after addition of copolymers at 22°C. Kaolin suspension (500 mg/dm³): 300 cm³. AETR-NIPAAm (5:100). AETR: (○) AETE, (△) AETB, and (□) AETO.

viscosity of the aqueous solution of the copolymer containing AETO decreased more sharply above 20°C than that of other copolymers and it reached a certain constant value above 30°C. Thus, the copolymer containing AETO exhibited the highest thermosensitivity in the three copolymers in the temperature range studied. This is due to the highest hydrophobicity of octyl group in three alkyl groups in phosphonium groups.

Flocculation of kaolin with AETR-NIPAAm copolymers

It is known that the cationic polymers bearing amino or ammonium groups exert as polymeric flocculants against suspended particles with anionic charges in aqueous solution such as kaolin. We have also reported the synthesis of various cationic polymers by chemical modification of several vinyl polymers such as polyvinylalcohol,¹⁹ polyvinylchloride,²⁰ and poly(3-chloro-2-hydroxypropyl methacrylate),²¹ and their flocculating ability against kaolin suspension.

The clarifying ability of the AETR-NIPAAm copolymers against 500 mg/dm³ kaolin suspension was studied by observing the optical density at 660 nm of the supernatant after standing for 2 min after mixing the copolymer solutions with the kaolin suspensions. Figure 5 shows the relationship between the optical density of kaolin suspensions and the amount of copolymers added to kaolin suspensions. The decrease in the optical density of the solutions means the decrease in the concentration of suspended kaolin particles in the solutions. The concentration of the copolymers added at which the lowest optical density was obtained is defined as the optimum dosage of the

copolymer for the clarification against kaolin suspensions.

As shown in Figure 5, first the optical density decreased with increasing amounts of the copolymers added, then increased. All the AETR-NIPAAm copolymers exhibited high clarifying ability against 500 mg/dm³ kaolin suspensions at the optimum dosage.

It has been reported that, in the case of polymer flocculants with the same cationic charges, the optimum dosage of the polymer flocculants against kaolin suspensions decreases with increasing content of cationic groups in the polymer flocculants.¹⁹⁻²¹ This result means that the flocculation of kaolin particles is mainly brought about by neutralization of anionic charges on the surface of kaolin particles with cationic copolymers, followed by bridging kaolin particles. Figure 5 shows that the optimum dosage of the AETE-NIPAAm (5:100) copolymer is higher than that of the AETB-NIPAAm copolymer. This is due to smaller content of phosphonium groups in the AETE-NIPAAm (5:100) copolymer than the AETB-NIPAAm (5:100) copolymer (Table I). However, the optimum dosage of the AETO-NIPAAm copolymer was almost the same as that of the AETE-NIPAAm copolymer, although the phosphonium content of the AETO-NIPAAm copolymer was higher than that of the AETE-NIPAAm copolymer. This is probably due to a slight reduction of the net charges of the AETO-NIPAAm copolymer, which exerts as a cationic poly-flocculant.

Above the optimum dosage of the copolymers, the remarkable increase in the optical density was also observed with all the copolymers in Figure 5. These phenomena were also reported in the previous articles.¹⁹⁻²¹ These phenomena are due to the dispersion of the kaolin particles by the electrostatic repulsion because of excess adsorption of cationic polymers on the surface of kaolin particles. Furthermore, in the case of the AETB-NIPAAm and AETO-NIPAAm copolymer, it was found that the degree in the increase in optical density above the optimum dosage with increasing amounts of the copolymers added was different from each other, although the both copolymers had almost the same phosphonium content. These phenomena are probably due to the difference of alkyl group in phosphonium groups of AETRs. However, the exact reason for these phenomena is not obvious at present. This result indicates that not only the content of phosphonium groups but also alkyl groups in phosphonium groups affect the flocculating ability of the copolymers.

Flocculation of kaolin with the AETR-BMA-NIPAAm copolymers

The clarifying ability of the AETB-BMA-NIPAAm copolymers with different compositions against 500 mg/

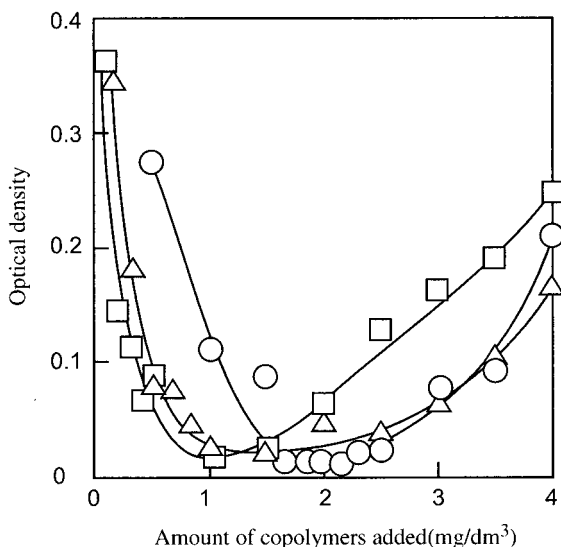


Figure 6 Optical density at 660 nm of kaolin suspension after addition of polymers at 22°C. Kaolin suspension (500 mg/dm³): 300 cm³. AETB-BMA-NIPAAm (X:Y:100) copolymers (○): 1:4:100, (△) 2.5:2.5:100, and (□) 4:1:100.

dm³ kaolin suspension was studied at 22°C. Figure 6 shows the relationship between the optical density of kaolin suspensions after an addition of the copolymers and the amount of copolymers added to kaolin suspensions.

Figure 6 shows that the optical density decreased first with increasing amounts of the copolymers added, then increased. All the AETB-BMA-NIPAAm copolymers exhibited almost the same clarifying ability against 500 mg/dm³ kaolin suspension at the optimum dosage. The optimum dosage of the AETB-BMA-NIPAAm copolymers increased slightly with decreasing AETB content in the copolymers. Furthermore, it was found that the degree of the increase in the optical density above the optimum dosage of the AETB-BMA-NIPAAm (2.5:2.5:100) copolymer was almost the same as that of the AETB-BMA-NIPAAm (1:4:100) copolymer, although the AETB-BMA-NIPAAm (2.5:2.5:100) copolymer had higher phosphonium groups than the AETB-BMA-NIPAAm (1:4:100) copolymer. This means that the dispersion of kaolin particles due to the electrostatic repulsion because of excess adsorption of polymers on kaolin particles was depressed by the presence of higher content of BMA moiety in the AETB-BMA-NIPAAm (2.5:2.5:100) copolymer than the AETB-BMA-NIPAAm (4:1:100) copolymer. In other words, this result indicates that the BMA moiety strengthened the flocculating ability of the copolymers for kaolin particles.

Flocculation of kaolin with the AETB-BMA-NIPAAm copolymers in the presence of NaCl

We mentioned that the flocculation of kaolin particles with polymers with cationic groups was mainly

brought about by neutralization of anionic charges on the surface of kaolin particles with cationic copolymers, followed by bridging kaolin particles.

Figure 7 shows the effect of NaCl on the clarification of kaolin suspensions with the AETB-BMA-NIPAAm (X:Y:100) copolymers at the optimum dosage.

In all cases, the optical density of kaolin suspensions increased sharply above the concentration of about 5×10^{-3} mol/dm³ NaCl. The degree of increase in the optical density decreased with increasing phosphonium content and decreasing BMA content. In particular, the sharpest increase in the optical density was observed with the AETR-BMA-NIPAAm (1:4:100) copolymers, which has the smallest phosphonium content and the highest BMA content. It is known that an addition of NaCl shields the charges of polymers in water. This means that NaCl depressed the electrostatic interaction between the kaolin particles and the copolymers. The decrease in the charges of the polymers also results in the decrease of the expansion of cationic polymers in water. The decrease in the expansion of the polymers in water also results in the decrease in flocculating ability of the polymers, as the bridging between kaolin particles with polymers becomes unfavorable.

These results also indicate that the flocculation of kaolin particles with cationic polymers was mainly brought about by neutralization of anionic charges on the surface of kaolin particles with cationic copolymers, followed by bridging kaolin particles.

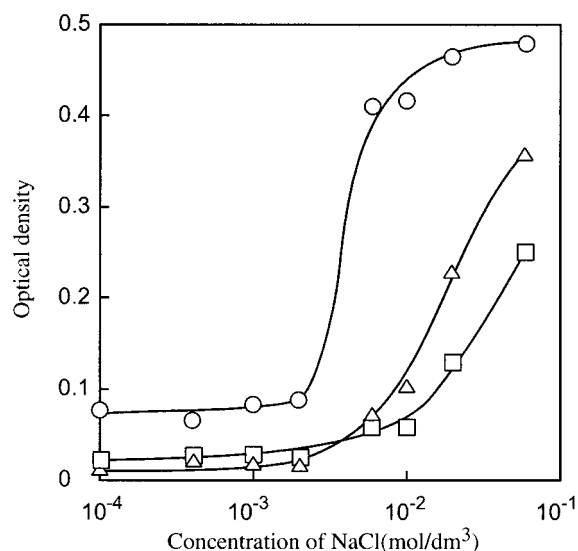


Figure 7 Optical density at 660 nm of kaolin suspension at the optimum dosage of copolymers in the presence of NaCl at 22°C. Kaolin suspension (500 mg/dm³): 300 cm³. AETB-BMA-NIPAAm (X:Y:100) copolymers: (○) 1:4:100, (△) 2.5:2.5:100, and (□) 4:1:100.

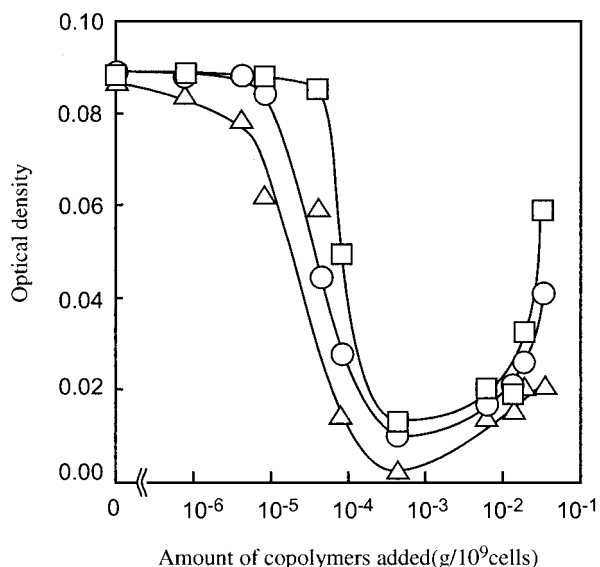


Figure 8 Changes in optical density of *E. coli* suspension at 660 nm after contacting with the AETR-BMA-NIPAAm copolymers at 35°C. *E. coli* suspension in deionized water (10^8 cells/cm³; 10 cm³. Shaking rate: 220/min. Shaking time: 1 h. AETR-BMA-NIPAAm (4:1:100) copolymers. AETR: (○) AETE, (△) AETB, and (□) AETO.

Flocculation of *E. coli* with the AETR-BMA-NIPAAm copolymers

It is known that many bacteria have negative charges on their surface in water.^{17,28} Therefore, such bacteria must be flocculated with cationic polymers having phosphonium groups.

The flocculating ability of the AETR-BMA-NIPAAm copolymers against *E. coli* suspensions was evaluated by measuring the optical density at 660 nm of the supernatant after mixing the copolymers with bacteria suspensions at 35°C. The decrease in the optical density means the decrease in the concentration of bacteria in an aqueous solution. The results are shown in Figure 8.

The optical density decreased sharply above 1×10^{-5} or 8×10^{-5} g / 10^9 cells of the copolymers and reached to the minimum, then increased with increasing the amount of the copolymers added. The lowest optical density was observed at the amount of about 5×10^{-4} g/ 10^9 cells for all the copolymers. This means that the flocculating ability of the copolymers against the bacteria (*E. coli*) suspension increased with increasing amount of copolymers up to the optimum dosage, then decreased. This result indicates that the mechanism of the flocculation of *E. coli* suspension with the copolymers is similar as that of kaolin particles, because it is known that bacteria such as *E. coli* have the same negative charges on the surface as kaolin particles in water. The lowest optical density was observed with the AETB-BMA-NIPAAm copolymer and the highest optical density was observed with the AETO-

BMA-NIPAAm copolymer. This indicates that the highest flocculating ability of the copolymers against *E. coli* suspension was obtained with the AETB-BMA-NIPAAm copolymer. This result indicates that butyl groups in phosphonium groups in AETB also participate effectively in the flocculating ability against bacteria. It is considered that the lowest flocculating ability of the AETO-BMA-NIPAAm copolymer is due to high hydrophobicity or steric hindrance of three octyl groups in phosphonium groups in AETO.

Effect of temperature on the flocculation of *E. coli* suspension with the AETO-BMA-NIPAAm copolymers

We mentioned before that the AETO-BMA-NIPAAm copolymer had the highest thermosensitivity, although the relative viscosity of the copolymer solutions was fairly low compared to that of other AETE-BMA-NIPAAm and AETB-BMA-NIPAAm copolymers (Figure 4). Therefore, the flocculating ability of the copolymers against *E. coli* suspension was investigated by use of the AETO-BMA-NIPAAm (4:1:100) copolymer at 22, 30, and 35°C. The results are shown in Figure 9.

All the AETO-BMA-NIPAAm copolymers exhibited high flocculating ability against *E. coli* suspension at the same optimum dosage in the temperature range from 22 to 35°C. Furthermore, it was found that the rapid increase in the optical density above the optimum dosage was observed at 22 and 30°C. However, the degree of increase in the optical density above the

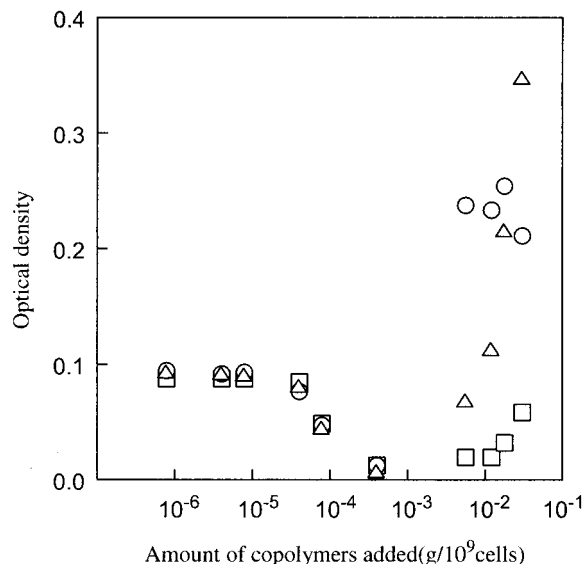


Figure 9 Changes in optical density of *E. coli* suspension at 660 nm after contacting with the AETO-BMA-NIPAAm (4:1:100) copolymers at different temperatures. *E. coli* suspension in deionized water (10^8 cells/cm³; 110 cm³. Shaking rate: 220/min. Shaking time: 1 h. Temperature: (○) 22°C, (△) 30°C, and (□) 35°C.

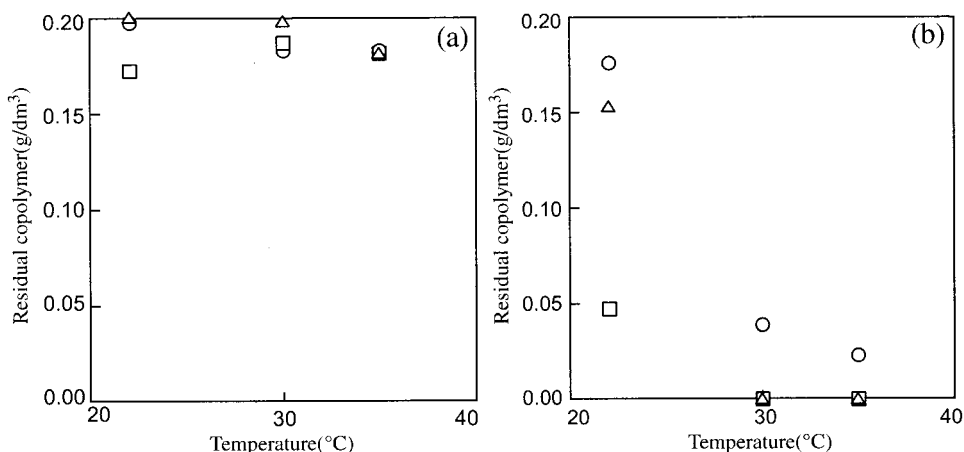


Figure 10 Effect of temperature on the recovery of copolymers from aqueous solutions (a) in the absence of NaCl, and (b) in the presence of NaCl (0.15 mol/dm³). Initial concentration of copolymer: 0.2 g/dm³. Shaking rate: 220/min. Shaking time: 2 h. AETR: (○) AETE, (△) AETB, and (□) AETO.

optimum dosage at 35°C was small. This result indicates that the dispersion of bacteria (*E. coli*) due to the electrostatic repulsion because of excess adsorption of polymers on *E. coli* cells was reduced at 35°C. The AETO–BMA–NIPAAm (4:1:100) copolymer is considered to become more hydrophobic in water at 35°C, because the relative viscosity of the copolymer solution became very low below 30°C (Fig. 4). This means that the flocculating ability of the copolymers against bacteria suspension is affected by not only the charges of the copolymers and alkyl groups in phosphonium groups but also the whole hydrophobicity of the copolymers at the temperature measured. Figure 9 also shows that the optical density above the concentration of 10⁻² g/10⁹ cells of the copolymers at 22 and 30°C became sharply higher than that below the concentration of 10⁻⁵ g/10⁹ cells. The reason for this phenomenon is not clear at present.

The antibacterial activity of the AETR–NIPAAm and AETR–BMA–NIPAAm copolymers against *E. coli* was also investigated. The antibacterial activity of the copolymers was very low. This is due to the low content of phosphonium groups of these copolymers used for this study.

Recovery of water-soluble copolymers from their aqueous solutions

Water-soluble AETE–NIPAAm and AETR–BMA–NIPAAm copolymers were found to have high flocculating ability against kaolin or bacteria suspensions. But an excess of the copolymers, which did not participate in the flocculation against kaolin or bacteria suspension, must remain in water. Therefore, the residual copolymer dissolved in water should be recovered and reused. Therefore, the recovery of the AETR–BMA–NIPAAm copolymers from their aqueous solutions was studied by changing the temperature of the

solutions in the absence or the presence of NaCl. The results are shown in Figure 10.

The amount of the residual copolymers after heating the aqueous solutions at various temperatures, followed by filtration, was determined by UV spectroscopy.

All the AETR–BMA–NIPAAm copolymers dissolved in deionized water could not be recovered, even when the solutions were heated at the temperature above 30°C. However, the AETB–BMA–NIPAAm and AETO–BMA–NIPAAm copolymers dissolved in 0.9 wt % NaCl solution were recovered completely from its solution by heating above 30°C. This result indicates that the presence of NaCl accelerates the association of the copolymers due to hydrophobic interaction in water because of its dehydration effect. Thus, the AETB–BMA–NIPAAm and AETO–BMA–NIPAAm copolymers could be recovered by heating above 30°C in the presence of NaCl.

CONCLUSIONS

1. Water-soluble and thermosensitive polymers having phosphonium groups were prepared by copolymerization of AETR, NIPAAm, and without/with BMA.
2. The relative viscosities of the solutions of the AETR–NIPAAm copolymers increased with increasing AETR content and decreased slightly with increasing temperature.
3. The thermosensitivity of the AETR–NIPAAm copolymers was affected by the kind of AETR and introduction of hydrophobic BMA into the copolymers.
4. The AETR–NIPAAm and the AETR–BMA–NIPAAm copolymers had high flocculating ability against kaolin or bacteria suspension.

5. Almost 100% of the AETB–BMA–NIPAAm and AETO–BMA–NIPAAm copolymers dissolved in water could be recovered by heating the solution above 30°C in the presence of NaCl.

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