

## **Title page**

**Title:** Dewatering of inorganic sludge using dual ionic thermosensitive polymers

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## Abstract

The dewatering of inorganic sludge by a novel method based on the hydrophilic/hydrophobic transition of ionic thermosensitive polymers was investigated. As an inorganic sludge, the drinking water treatment sludge was used. Cationic thermosensitive polymers, poly(NIPAM-*co*-DMPAA), which were synthesized by copolymerizing *N,N*-dimethylaminopropylacrylamide (DMPAA) as the cationic component with *N*-isopropylacrylamide (NIPAM) as the thermosensitive component, were effective in dewatering the sludge. When the dewatering was performed at room temperature, the optimum polymer dosage for the dewatering rate was observed similar to the conventional hydrophilic polymeric flocculants. On the other hand, when the dewatering was carried out above the lower critical solution temperature (LCST) of poly(NIPAM-*co*-DMPAA), the dewatering rate increased remarkably as the polymer dosage increased. Such high dewatering rates can be attributed to the hydrophobic interaction among the thermosensitive polymer molecules adsorbed on the sludge. However, the LCST of poly(NIPAM-*co*-DMPAA) increased considerably as the DMPAA content increased. In order to solve this problem, the use of dual ionic thermosensitive polymers was investigated. By using the anionic thermosensitive polymer, poly(NIPAM-*co*-AAC), which was synthesized by copolymerizing acrylic acid (AAC) with NIPAM, in combination with cationic poly(NIPAM-*co*-DMPAA), the dewatering rate was remarkably increased at relatively low temperatures. This increase was attributed to the formation of a polymer complex that decreased the LCST of the polymer molecules adsorbed on the sludge.

**Keywords:** Dewatering, Inorganic sludge, Thermosensitive polymer, Hydrophobic interaction, Dual ionic polymers, Polymer complex

## 1. Introduction

High-molecular-weight polymeric flocculants have been widely used in the flocculation of suspended particles and/or sludge dewatering. The mechanism of flocculation of suspended particles using hydrophilic polymeric flocculants is explained by the bridging of the suspended particles through the polymer molecules [1,2]. However, the flocs formed by conventional polymeric flocculants are usually bulky and contain a large amount of water, and it is difficult to remove such a large amount of water effectively by the conventional mechanical dewatering methods. In order to alleviate this problem, thermosensitive polymers have recently attracted special interest as flocculants [2,3]. Thermosensitive polymers are soluble in water at low temperatures; however, they are insoluble above the intrinsic temperature of the polymer because of transition to hydrophobicity [4,5]. The transition temperature is referred to as the lower critical solution temperature (LCST), and it depends on the side-chain structure of the polymer [4,6]. Poly(*N*-isopropylacrylamide) (poly(NIPAM)) is a representative nonionic thermosensitive polymer with an LCST of about 32°C [4].

The use of thermosensitive polymers as flocculants was reported more than ten years ago. Guillet et al. [7] reported that below the transition temperature, cationic thermosensitive polymers were effective flocculants that exhibited behaviors similar to cationic polyacrylamide, whereas above the transition temperature, the copolymers were not effective flocculants. In contrast, Deng et al. [8] found that the cationic thermosensitive polymer (poly(NIPAM-*co*-diallyldimethylammonium chloride)) induced the flocculation of a TiO<sub>2</sub> suspension even at temperatures above the transition temperature. These findings were explained by the fact that the cationic copolymer consisted of cationic colloidal particles above the transition temperature. On the other hand, recent researches are based on the hydrophilic/hydrophobic transition of polymer molecules adsorbed on the suspended particles [2,3].

The authors proposed a novel flocculation/compaction method based on the hydrophilic/hydrophobic transition of thermosensitive polymers ten years ago [9-11]. The

method is described as follows. First, by mixing the suspended particles with the thermosensitive polymer below its LCST, the surface of the particles is sufficiently covered with the adsorbed polymer molecules. Similar to the excess dosage condition in the conventional flocculation process using polymeric flocculants, these particles are stably dispersed. When this suspension is heated above the LCST, the polymer molecules adsorbed on the particles become hydrophobic. As a result, the surface of the suspended particles also becomes hydrophobic, and flocs are formed because of these hydrophobic interactions. The subsequent application of an adequate mechanical force to the flocs causes the particles in the flocs to rearrange, thereby discharging the water molecules from them; this leads to compaction. The mechanism was confirmed using kaolin-poly(NIPAM), and a compacted kaolin cake could be easily obtained on the basis of the hydrophilic/hydrophobic transition of poly(NIPAM) [9,10]. The formation mechanism of flocs by the hydrophobic interactions is basically the same as that proposed by Zhu and Napper [12], except for the fact that the rearrangement of the particles in the flocs occurs through the application of an adequate mechanical force. Recently, Burdukova et al. [13] proved the formation of flocs by the hydrophobic interaction of thermosensitive polymers.

This method was applied to the dewatering of an activated sludge which is a typical organic sludge, and a lower water content in the dewatered cake as compared to that in commercial flocculants was obtained [14]. The moisture content with a commercial flocculant was more than 78%, and that with the thermosensitive polymer decreased less than 70% under the same apparatus and the same dewatering conditions. However, it was found that the use of nonionic poly(NIPAM) has limitations, and that cationic thermosensitive polymers are more effective. In general, the LCST of ionic thermosensitive polymers is high relative to that of nonionic poly(NIPAM) [11]. However, a decrease in the moisture content in the dewatered cake was observed at temperatures relatively lower than the LCST of the cationic polymer measured in an aqueous solution. This result suggests that the LCST of the cationic polymer adsorbed on the sludge differs from that measured in an aqueous solution. It is generally accepted that the high water content in activated sludge is related to the presence of

extracellular polymeric substances that form a negatively charged polymer network [15,16]. Upon the addition of the cationic thermosensitive polymer, the extracellular polymer network forms a polymer complex with the cationic polymer. In other words, charge neutralization of the cationic polymer occurs. As a result, the LCST decreases [17], and the hydrophobic interaction occurs at temperatures relatively lower than the LCST of the cationic polymer measured in an aqueous solution.

However, for an inorganic sludge that does not have charged organic substrates such as extracellular polymers observed in an activated sludge, the use of ionic (cationic) thermosensitive polymers is restricted because of their high LCST. In order to solve this problem, we proposed the use of dual ionic thermosensitive polymers: cationic and anionic thermosensitive polymers [18]. The outline is as follows. First, a cationic thermosensitive polymer is added to the suspension, followed by an anionic thermosensitive polymer. By adding the latter, a polymer complex with the cationic thermosensitive polymer adsorbed on the particle is formed, and charge neutralization takes place, which decreases the transition temperature of the polymer adsorbed on the suspended particles. The hydrophobic interaction of the adsorbed polymers results in the compaction of the suspended particles at a relatively low temperature by the addition of an adequate mechanical force. In order to initiate the compaction, it is necessary to cover the surface of the particles sufficiently by the cationic thermosensitive polymer molecules. This concept was confirmed in our previous paper using a  $\text{TiO}_2$  suspension [18]. Many studies on flocculation using dual polymeric flocculants have been published, and the dual polymer system has usually been used to improve the floc strength, the sedimentation velocity of flocs, and so on [19,20]. Our concept of the use of dual ionic thermosensitive polymers is different from the numerous previous studies, as mentioned above.

In this paper, it is confirmed that the dewatering method based on the hydrophilic/hydrophobic transition of thermosensitive polymers is effective in dewatering the drinking water treatment sludge, which is a typical inorganic sludge. Furthermore, the effectiveness of the dual thermosensitive polymer method is examined.

## 2. Experimental

### 2.1. Synthesis of thermosensitive polymers

Cationic thermosensitive polymers, poly(NIPAM-*co*-DMPAA), were synthesized by copolymerizing the cationic component *N,N*-dimethylaminopropylacrylamide ( $\text{CH}_2\text{:CHCONHCH}(\text{CH}_3)_2$ ) (DMPAA) with NIPAM. These monomers were kindly supplied from Kohjin Co. Ltd. Three kinds of cationic thermosensitive polymers with different DMPAA contents (mole ratios: 0.025, 0.05, and 0.1) were prepared. Nonionic poly(NIPAM) was also prepared for use as the control. These polymers were synthesized by free radical polymerization as described in our previous paper [11]. *N,N,N',N'*-tetramethylethylenediamine (TEMED) and ammonium peroxydisulfate (APS) were used as an accelerator and an initiator, respectively. The synthesis composition are shown in Table 1. More specifically, 100 mL of aqueous solution containing NIPAM, DMPAA, and TEMED was fed into a 500 mL separable flask. The flask was stirred by a magnetic stirrer and degassed by successively purging with high-purity nitrogen for 3 h. Then 20 mL of an aqueous solution containing APS, which was also degassed, was added. The polymerization proceeded at 10°C for 3 h. After polymerization, the prepared polymer solution was diluted with deionized water and was purified by dialysis using a membrane (Cellu Sep T3, Nominal MWCO: 12000–14000, Membrane Filtration Products, Inc.) for one week. The anionic thermosensitive polymer, poly(NIPAM-*co*-AAC), was synthesized by copolymerizing acrylic acid ( $\text{CH}_2\text{:CHCOOH}$ ) (AAC) as an anionic component with NIPAM. The mole ratio of AAC was 0.1. The preparation procedure was the same as that described above.

Although the molecular weights of these copolymers were not evaluated, that of the poly(NIPAM) was estimated from the intrinsic viscosity,  $[\eta]$ , as previously reported [11]. The measurement was performed using the polymer solution dissolved in tetrahydrofuran at 27°C, and the following equation proposed by Fujishige [21] was used to calculate the

number-average molecular weight,  $\overline{Mn}$  :

$$[\eta] = 9.59 \times 10^{-6} \overline{Mn}^{0.65} \quad [\text{m}^3/\text{kg}]$$

The number-average molecular weight of poly(NIPAM) prepared was about  $7.4 \times 10^6$ .

## *2.2. Measurement of LCSTs of polymers*

The aqueous solution of the thermosensitive polymer is transparent below the LCST of the thermosensitive polymer because the polymer molecules are hydrophilic and water soluble. However, when the solution is heated above the LCST, the solution becomes milky white because the polymer molecules become hydrophobic and thus water-insoluble. Therefore, the LCST can be estimated by the change in the transmittance through the polymer solution with temperature. The transmittance through an aqueous polymer solution containing 0.5 wt% polymer was measured at 600 nm using a spectrophotometer equipped with a temperature control system (V-530, Japan Spectroscopy Co., Ltd.).

## *2.3. Dewatering apparatus and method*

The drinking water treatment sludge, which was treated by alum, was supplied from a plant in Hiroshima prefecture, and was taken out from the bottom of a thickener. The sludge concentration was about 2 wt% and remained constant during the experimental period. The dewatering test was performed using a constant pressure filtration/expression apparatus shown in Fig. 1, which was the same as that used in our previous paper [14]. The pressure was imparted using a piston (diameter: 94 mm) that was driven by an air cylinder. The displacement of the piston was measured and recorded with time using a CCD laser displacement sensor. A filter paper (Advantec #2) was used and placed on a sintered metal plate. The apparatus was covered with a jacket, and the temperature was maintained at the desired temperature. First, 450 mL of the sludge and 50 mL of the polymer solution with the

desired concentration were mixed well at room temperature in a stainless steel tank with 6 baffle plates. The agitation was performed for 5 min at 400 rpm with a paddle blade. Then, the tank was transferred to a water bath that was maintained at the desired temperature, and the agitation was continued for 30 min at 200 rpm. The temperature of the mixture in the tank reached the desired value within 30 min. The mixture was transferred to the dewatering apparatus, and a constant pressure of 0.22 MPa was applied for 1 h. Finally, the dewatered cake was taken out, and the moisture content was measured by drying at 105°C for one night.

In this experiment, although the agitation condition was constant (30 min and 200 rpm), the agitation speed was relatively high and the agitation period was quite long. It is well known that such a prolonged shear treatment makes flocs denser [22–28]. However, such a long agitation period was required to adjust the temperature of the sludge in the tank to the desired value.

### 3. Results and Discussion

#### 3.1. Dewatering performance of sludge by cationic thermosensitive polymers

Previously, the dewatering rates of the drinking water treatment sludge were examined by using poly(NIPAM-*co*-DMPAA) (10 mol% DMPAA), poly(NIPAM-*co*-AAC) (10 mol% AAC) and poly(NIPAM). The dewatering rate obtained with poly(NIPAM-*co*-DMPAA) was larger compared with those obtained with other polymers.

Fig. 2 shows the change in the piston height from the filter paper with time during the dewatering process of the sludge using three kinds of cationic thermosensitive polymers, poly(NIPAM-*co*-DMPAA) with three different DMPAA contents. The polymer dosage was 1 wt% for the dry sludge weight, and the dewatering temperature was 30°C, which is lower than the LCSTs of these polymers. The experiment was also performed without the polymer, which served as the control. The piston height decreased rapidly when the pressure was applied by the piston. Then, the height decreased gradually with time, abruptly decreased at a certain time, and decreased gradually again. This rapid decrease by the application of



pressure at the initial stage was due to the compression of air between the piston and sludge. The subsequent decrease was due to the progress of filtration by the air pressure in the space above the sludge. At the end of the filtration period, air passed through the cake. As a result, the piston height decreased abruptly again, and the piston came into contact with the filtered cake. Thereafter, the expression started. As the copolymerizing ratio of DMAPAA increased, the dewatering rate increased, which suggests that the cationic polymer is more effective in dewatering the water treatment sludge.

Fig. 3 shows the temperature dependence of the transmittance through the aqueous solutions of three kinds of cationic thermosensitive polymers with different DMAPAA content. The pH values of these solutions were almost neutral. The data for poly(NIPAM) is also shown for comparison. The transmittance through the poly(NIPAM) solution changed drastically around 32°C, which is the LCST of poly(NIPAM). On the other hand, for solutions containing poly(NIPAM-*co*-DMAPAA), as the DMAPAA content in the copolymer increased, the temperature at which the decrease in the transmittance started, i.e., the LCST, shifted to a higher temperature. In the case of the polymer copolymerized DMAPAA of 10 mol%, a decrease in the transmittance was not observed in the experimental range of temperature.

The LCST of poly(NIPAM-*co*-AAC) copolymerized AAC of 10 mol% was also measured. The transition of this polymer was also not observed in the experimental range of temperature under the neutral pH condition, although the data were not shown here.

The LCSTs of these cationic and anionic thermosensitive polymers largely depended on the pH of the solution. The LCST of poly(NIPAM-*co*-DMAPAA) decreased with an increase in the pH of the solution. The data are discussed in the following section. On the other hand, the LCST of poly(NIPAM-*co*-AAC) decreased with a decrease in the pH of the solution.

### *3.2. Effect of hydrophilic/hydrophobic transition of polymer on dewatering performance*

The LCST of the polymer copolymerized DMAPAA of 2.5 mol% is relatively low, around 40°C, as shown in Fig. 2. By using this polymer, the effect of the hydrophilic/hydrophobic

transition of the polymer on the dewatering performance was examined. Fig. 4 shows the change in the piston height with time, i.e., the dewatering rate at 30°C (Fig. 4(a)) and at 60°C (Fig. 4(b)). These temperatures are below and above the LCST of the polymer, respectively. The examined polymer dosages were more than 1 wt%. At 30°C, the polymer is hydrophilic and the dewatering rate decreased as the polymer dosage increased, which implies that the polymer dosages are in the so-called excess dosage region. In other words, the dispersion of the suspended particles is promoted by the increase in the amount of the polymer molecules adsorbed on the surface of the suspended particles. On the other hand, at 60°C, the polymer adsorbed on the suspended particles became hydrophobic and the dewatering rate increased as the polymer dosage increased. This implies that the hydrophobic transition of the polymer molecules adsorbed on the suspended particles promotes the aggregation of particles through the hydrophobic interaction and improves the dewatering rate. Incidentally, the prolonged shear treatment affects the density of the flocs. Therefore, it is considered that the agitation conditions in this experiment also affect the high dewatering rate, as shown in Fig. 4(b). This needs to be investigated further.

The moisture content of the dewatered cake was measured after the dewatering operation was carried out for 90 min. Table 2 lists the moisture contents of the dewatered cakes. In the case of the dewatering at 30°C, the moisture contents were largely depended on the polymer dosage, as expected from Fig. 4(a). The moisture content of the dewatered cake obtained without adding the polymer was 84%, and it is lowest in these experimental conditions. On the other hand, in the case of the dewatering at 60°C, the moisture content scarcely depended on the polymer dosage: 71% (without polymer) and 68% (polymer dosage: 1 to 5 wt%).

Fig. 5 shows the effect of the temperature on the dewatering rate. Figs. 5(a) and (b) show the results obtained without polymer and with the polymer dosage of 1 wt%, respectively. In both cases, the dewatering rate increased with temperature. From these results, the times of the filtration by air pressure (the filtration time) were read, and the relationship between the filtration time and the temperature is shown in Fig. 5(c). Below the LCST of the polymer (around 40°C), the filtration time of the sludge with the added polymer was longer than that

of the sludge without the polymer, whereas above the LCST of the polymer, the opposite result was obtained. In other words, the dewatering rate of the sludge with the added polymer was lower than that of sludge without the polymer below the LCST, and was larger above the LCST. This result is attributed to the fact that the polymer dosage of 1 wt% is in excess for the dewatering of the sludge under the hydrophilic condition, and above the LCST, the polymer dosage promotes the aggregation of the suspended particles through the hydrophobic interaction.

However, the improvement of the dewatering rate obtained with the polymer copolymerized DMAPAA of 2.5 mol% was not sufficient. From the result shown in Fig. 2, it is expected that the polymers copolymerized DMAPAA of 5 mol% or 10 mol% would be more effective although the LCST of these polymers are significantly high. It is well known that the LCST of cationic thermosensitive polymers depends on the pH of the solution, and that the LCST decreases as the pH increases, as mentioned above. Fig. 6 shows the comparison of the temperature dependence of the transmittance through the aqueous solutions containing the polymer copolymerized DMAPAA of 10 mol% at pH 6.5 and pH 9. Although at pH 6.5 the decrease in the transmittance was not observed in the experimental range of temperature, at pH 9 the transmittance decreased from about 45°C. In other words, the LCST shifted to the lower temperature, around 45°C.

Fig. 7 shows the effect of pH on the dewatering rate. Figs. 7(a) and (b) show the results obtained at pH 6.5 and pH 9, respectively. The dewatering temperature was 50°C. At pH 6.5 (Fig. 7(a)), the dewatering rate increased as the polymer dosage increased. However, as the dosage increased further, the dewatering rate decreased. These results are attributed to the fact that the polymer is hydrophilic at pH 6.5 even though the temperature is relatively high, 60°C. On the other hand, at pH 9 (Fig. 7(b)), the polymer is hydrophobic, and the dewatering rate increased as the polymer dosage increased. From these results, it is clear that the hydrophobic transition of the polymer molecules adsorbed on the surface of suspended particles improves the dewatering rate of the drinking water treatment sludge. However, the moisture contents of the dewatered cakes shown in Table 3 are about 69% and do not depend much on the polymer

dosage.

### *3.3. Dewatering of the sludge by dual thermosensitive polymers*

Although the ionic thermosensitive polymers were effective in dewatering the sludge, the LCSTs of the polymers were too high in the neutral pH region as mentioned above. In order to alleviate this problem, in our previous paper we proposed the use of the dual thermosensitive polymers: cationic and anionic thermosensitive polymers [18]. The use of the anionic thermosensitive polymer in combination with the cationic thermosensitive polymer results in the formation of a polymer complex. In other words, charge neutralization occurs. As a result, the LCST of the polymer adsorbed on the suspended particles decreases, and the hydrophobic interaction appears at temperatures relatively lower than the LCST of the cationic thermosensitive polymer.

Fig. 8 shows the dewatering rate caused by the addition of the anionic thermosensitive polymer (copolymerization ratio of AAC: 10 mol%) in combination with the cationic thermosensitive polymer (copolymerization ratio of DMAPAA: 10 mol%). The experimental procedure was as follows: First, 450 mL of the sludge and 25 mL of the cationic polymer solution were mixed well in a stainless steel tank for 5 min at room temperature as mentioned in the experimental section, and then 25 mL of the anionic polymer solution was added, and the solution was mixed well for 5 min. Then, the tank was transferred to a water bath. The subsequent procedure was the same as that mentioned in the experimental section. The polymer dosage of the cationic polymer was fixed at 1 wt%, and that of the anionic polymer varied from 0 to 1.5 wt%. The experiments were carried out at 60°C. The dewatering rate drastically increased as the dosage of the anionic polymer increased in the experimental range of the polymer dosage. These results are attributed to the fact that the LCST of the cationic polymer adsorbed on the suspended particles decreases with the addition of the anionic polymer. However, when the anionic polymer dosage was higher than 1 wt%, the dewatering rate did not increase any further. The moisture content of the dewatered cakes (shown in

Table 4) is approximately 68%, and this does not appear to depend on the polymer dosage.

Fig. 9 shows the effect of the temperature on the dewatering rate using the dual thermosensitive polymers. The dewatering rates between 30°C and 60°C were almost the same. This implies that the LCST of the adsorbed polymer considerably decreases by adding the anionic thermosensitive polymer in combination with the cationic thermosensitive polymer, and that the dewatering rates are considerably large, and are probably controlled by the resistance of the filter.

#### **4. Conclusion**

The dewatering method based on the hydrophilic/hydrophobic transition of thermosensitive polymers was effective in dewatering the drinking water treatment sludge, which is a typical inorganic sludge. Although the cationic thermosensitive polymers are effective, the LCST of the polymers increases with an increase in the amount of the cationic component. In order to solve this problem, the method based on the dual ionic thermosensitive polymers proposed by the author was found to be effective. The use of the anionic thermosensitive polymer in combination with the cationic thermosensitive polymer resulted in a remarkable increase in the dewatering rate at relatively low temperatures. This increase was attributed to the formation of a polymer complex that decreased the LCST.

#### **References**

1. S. Sakohara, H. Unno, T. Akehata, Removal of turbidity by the use of an organic, polymeric flocculant. Analysis using a simple bridging model, *Int. Chem. Eng.* (1982) 652–658.
2. H. Li, J. Long, Z. Xu, J.H. Masliyah, Flocculation of kaolinite clay suspensions using a temperature-sensitive polymer, *AIChE J.*, 53 (2007) 479–488.
3. J.P. O'Shea, G.G. Qiao, G.V. Franks, Solid-liquid separations with a temperature-responsive polymeric flocculant: Effect of temperature and molecular weight on polymer adsorption and

- desorption, *J. Colloid & Interface Sci.*, 348 (2010) 9–23.
4. S. Ito, Phase transition of aqueous solution of poly(*N*-alkylamide) derivatives—effects of side chain structure, *Kobunshi Ronbunshu (Jpn.)* 46 (1989) 437–443.
  5. H.G. Schild, Poly(*N*-isopropylacrylamide): experiment, theory and application, *Prog. Polym. Sci.* 17 (1992) 163–249.
  6. T. Mori, M. Hamada, T. Kobayashi, H. Okamura, K. Minagawa, S. Masuda, M. Tanaka, Effect of alkyl substituents structures and added ions, *Prog. Polym. Sci. Part A: Polym. Chem.* 43 (2005) 4942–4952.
  7. J.E. Guillet, M. Heskins, Polymeric flocculants, US Patent no. 4,536,294 (1985).
  8. Y. Deng, R. Pelton, Synthesis and solution properties of poly(*N*-isopropylacrylamide-co-diallyldimethylammonium chloride), *Macromolecules* 28 (1995) 4617–4621.
  9. S. Sakohara, K. Nishikawa, Flocculation and compaction of highly concentrated suspension by using thermosensitive polymers, *Kagakukougaku Ronbunshu (Jpn.)* 26 (2000) 298–304.
  10. S. Sakohara, T. Kimura, K. Nishikawa, Flocculation mechanism of suspended particles using the hydrophilic/hydrophobic transition of a thermosensitive polymer, *KONA Powder Particle* 20 (2002) 246–250.
  11. S. Sakohara, K. Nishikawa, Compaction of TiO<sub>2</sub> suspension utilizing hydrophilic/hydrophobic transition of cationic thermosensitive polymers, *J. Colloid Interface Sci.* 278 (2004) 304–309.
  12. P.W. Zhu, D.H. Napper, Studies of aggregation kinetics of polystyrene lattices sterically stabilized by poly (*N*-isopropylacrylamide), *Phys. Rev. E* 50 (1994) 1360–1366.
  13. E. Burdukova, H. Li, N. Ishida, J.-P. O'Shea, G.V. Franks, Temperature controlled surface hydrophobicity and interaction forces induced by poly(*N*-isopropylacrylamide), *J. Colloid Interface Sci.* 342 (2010) 586–592.
  14. S. Sakohara, E. Ochiai, T. Kusaka, Dewatering of activated sludge by thermosensitive polymers, *Sep. Purif. Technol.* 56 (2007) 296–302.
  15. K. Keiding, L. Wybrandt, P.H. Nielsen, Remember the water—a comment on EPS

colligative properties, *Water Sci. Technol.* 43 (2001) 17–23.

16. L.H. Mikkelsen, K. Keiding, Physico-chemical characteristics of full scale sewage sludges with implications to dewatering, *Water Res.* 36 (2002) 2451–2462.

17. M.K. Yoo, Y.K. Sung, Y.M. Lee, C.S. Cho, Effect of polymer complex formation on the cloud-point of poly(*N*-isopropylacrylamide) (PNIPAAm) in the poly(NIPAAm-*co*-acrylic acid): polyelectrolyte complex between poly(acrylic acid) and poly(L-lysine), *Polymer* 39 (1998) 3703–3708.

18. S. Sakohara, R. Hinago, H. Ueda, Compaction of TiO<sub>2</sub> suspension by using dual ionic thermosensitive polymers, *Sep. Purif. Technol.* 63 (2008) 319–323.

19. G. Petzold, A. Nebel, H.-M. Buchhammer, K. Lunkwitz, Preparation and characterization of different polyelectrolyte complexes and their application as flocculants, *Colloid Polym. Sci.* 276 (1998) 125–130

20. M.R. Wu, T.G.M. van de Ven, Flocculation and reflocculation: Interplay between the adsorption behavior of the components of a dual flocculant, *Colloids Surfaces A: Physicochem. Eng. Aspects* 341 (2009) 40–45.

21. S. Fujishige, Intrinsic viscosity-molecular weight relationships for poly(*N*-isopropylacrylamide) solutions, *Polym. J.* 19 (1987) 297–300.

22. R.C. Sonntag, W.B. Russel, Structure and breakup of flocs subjected to fluid stresses I. Shear experiments, *J. Colloid Interface Sci.* 113 (1986) 399–413.

23. R.C. Sonntag, W.B. Russel, Structure and breakup of flocs subjected to fluid stresses II. Theory, *J. Colloid Interface Sci.* 115 (1987) 378–389.

24. Y. Adachi, Dynamic aspects of coagulation and flocculation, *Adv. Colloid Interface Sci.* 56 (1995) 1–31.

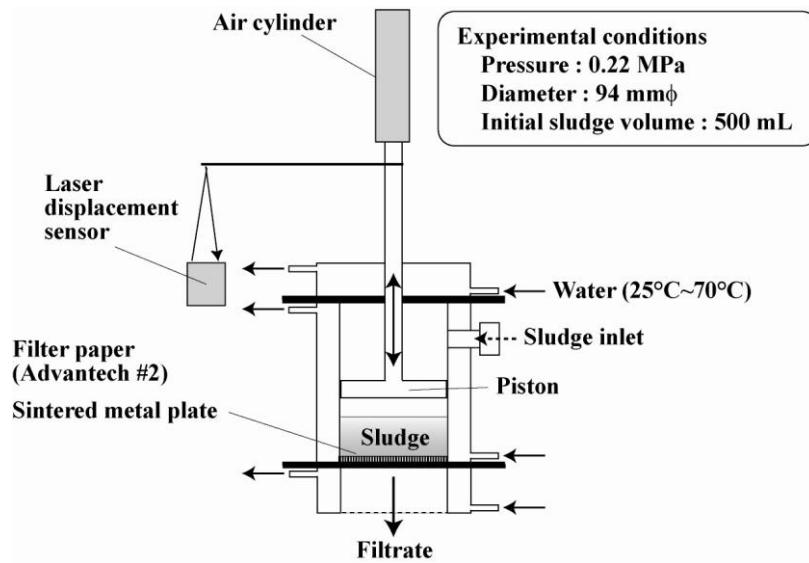
25. M. Kobayashi, Y. Adachi, S. Ooi, Breakup of fractal flocs in a turbulent flow, *Langmuir* 15 (1999) 4351–4356.

26. M. Kobayashi, Strength of natural soil flocs, *Water Res.* 39 (2005) 3273–3278.

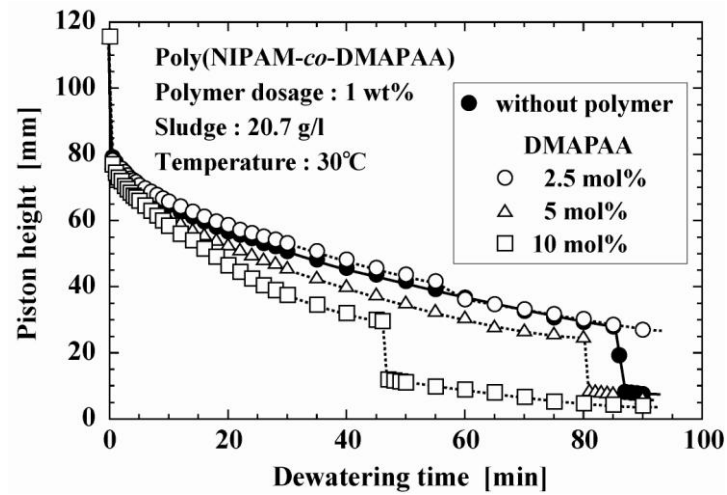
27. Y. Adachi, K. Aoki, Restructuring of small flocs of polystyrene latex with polyelectrolyte, *Colloids Surf. A: Physicochem. Eng. Aspects* 342 (2009) 24–29.

28. M.L. Eggersdorfer, D. Kadau, H.J. Herrmann, S.E. Pratsinis, Fragmentation and restructuring of soft-agglomerates under shear, *J. Colloid Interface Sci.* 342 (2010) 261–268.

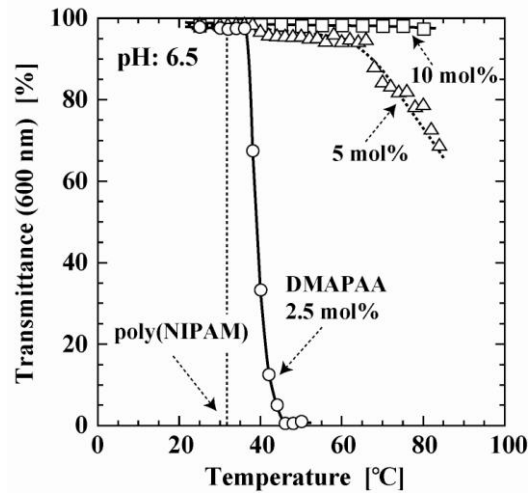




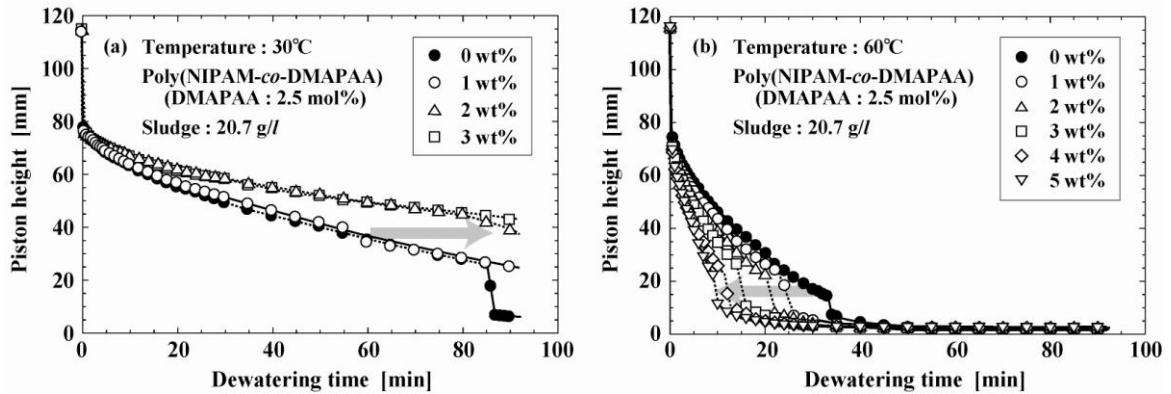
**Fig. 1** Experimental apparatus used for dewatering sludge.



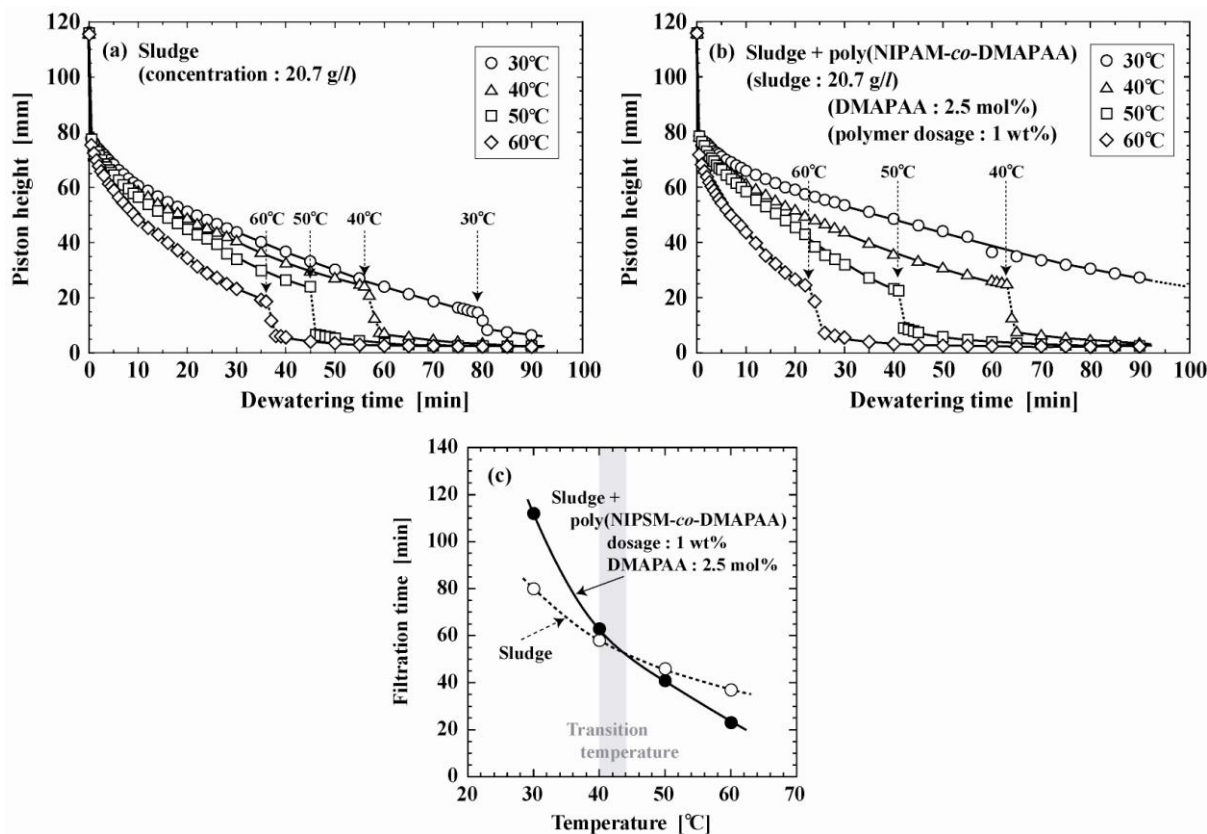
**Fig. 2** Time course of the piston height during filtration and the expression of sludge with poly(NIPAM-co-DMAPAA) having different DMAPAA contents.



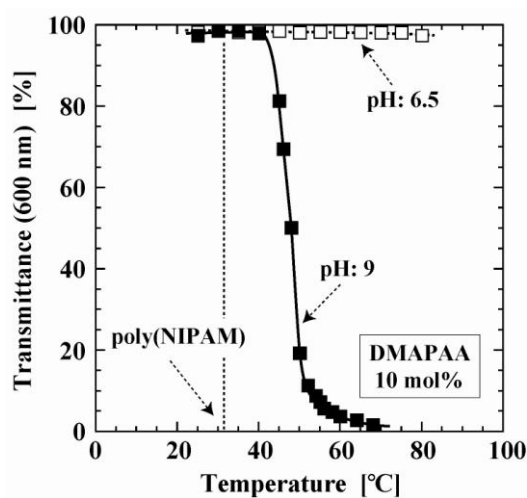
**Fig. 3** Change in transmittance with temperature through solutions of poly(NIPAM) and poly(NIPAM-*co*-DMAPAA) with different DMAPAA contents.



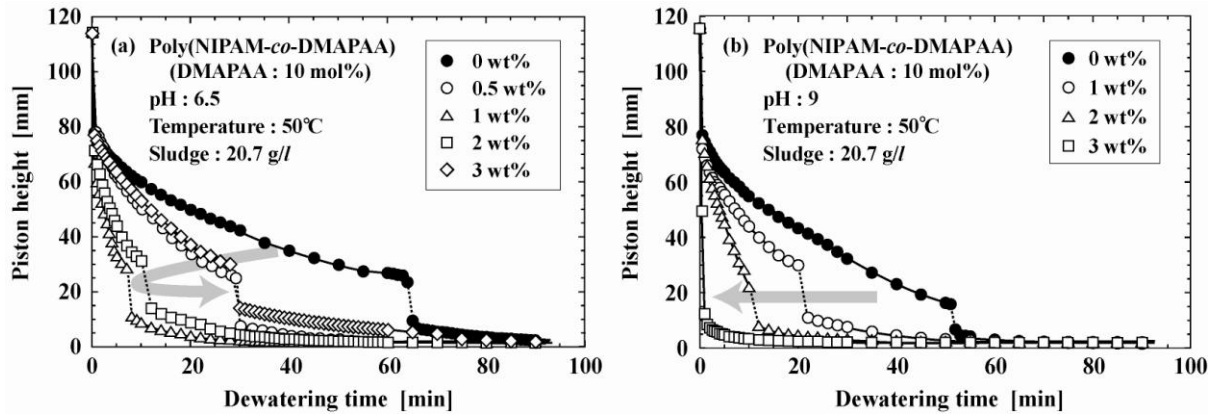
**Fig. 4** Time course of piston height during filtration and expression of sludge with poly(NIPAM-*co*-DMAPAA). Filtration temperatures were (a) 30°C and (b) 60°C.



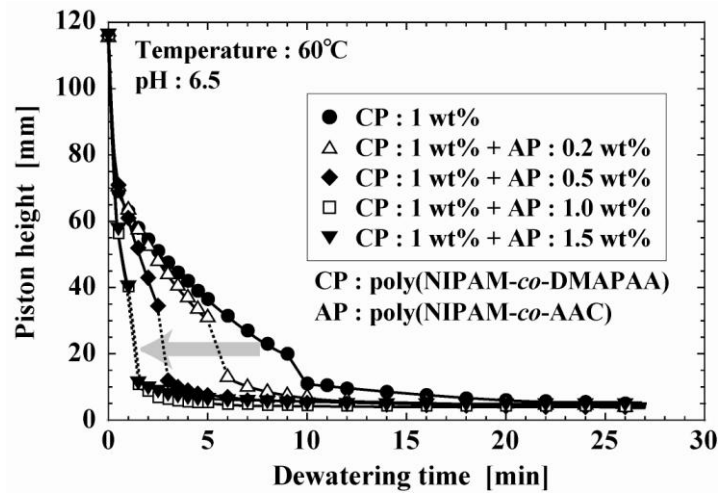
**Fig. 5** Time course of piston height during filtration and expression sludge at various temperatures: (a) no addition of polymer, (b) addition of poly(NIPAM-*co*-DMApAA) with DMApAA content of 2.5 mol%; and (c) relationship between filtration time and temperature.



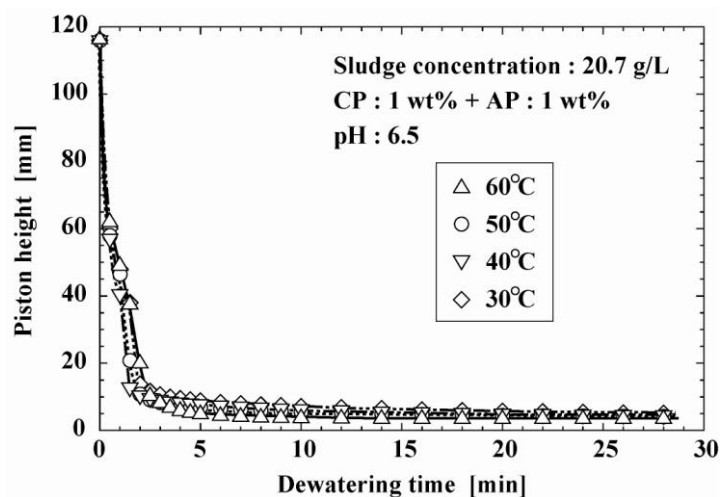
**Fig. 6** Change in transmittance with temperature through solutions of poly(NIPAM) and poly(NIPAM-*co*-DMApAA) with DMApAA content of 10 mol% at pH 6.5 and 9.



**Fig. 7** Time course of piston height during filtration and expression of sludge with poly(NIPAM-co-DMAPAA) having DMAPAA content of 10 mol% at (a) pH 6.5 and (b) pH 9.



**Fig. 8** Time course of piston height during filtration and expression of sludge with poly(NIPAM-co-AAC) and poly(NIPAM-co-DMAPAA). The contents of AAC and DMAPAA are both 10 mol%. The dosage of poly(NIPAM-co-DMAPAA) was fixed at 1 wt%, and the dosage of poly(NIPAM-co-AAC) was varied from 0 to 1 wt%.



**Fig. 9** Time course of piston height during filtration and expression of sludge with poly(NIPAM-*co*-AAC) and poly(NIPAM-*co*-DMPAA). The experiments were performed at various temperatures.

**Table 1**

Synthesis composition of polymers

		Poly(NIPAM)	* <sup>a</sup> CP-2.5	* <sup>b</sup> CP-5	* <sup>c</sup> CP-10	* <sup>d</sup> AP
Monomer	: <i>N</i> -Isopropylacrylamide (NIPAM)	1500	750	750	750	750
Co-monomer	: <i>N,N</i> -Dimethylaminopropylacrylamide (DMPAA)	—	19.2	39.5	83.3	—
	Acrylic acid (AAC)	—	—	—	—	83.3
Accelerator	: <i>N,N,N',N'</i> -Tetramethylethylenediamine (TEMED)	6	6	6	6	6
Initiator	: Ammonium peroxodisulfate (APS)	2	2	2	2	2

Values are in mol/m<sup>3</sup>\*<sup>a</sup>CP-2.5: poly(NIPAM-*co*-DMPAA), DMPAA: 2.5 mol%\*<sup>b</sup>CP-5: poly(NIPAM-*co*-DMPAA), DMPAA: 5 mol%\*<sup>c</sup>CP-10: poly(NIPAM-*co*-DMPAA), DMPAA: 10 mol%\*<sup>d</sup>AP: poly(NIPAM-*co*-AAC), AAC: 10 mol%**Table 2**

Moisture contents of dewatered cakes shown in Fig. 4

	[wt%]					
Temperature [°C]	Polymer dosage [wt%]					
	0	1	2	3	4	5
30	82.3	83.9	86.7	88.1	—	—
60	71.4	68.3	67.7	68.6	68.5	68.2

**Table 3**

Moisture contents of dewatered cakes shown in Fig. 7

pH	[wt%]				
	Polymer dosage [wt%]				
	0	0.5	1	2	3
6.5	77.1	70.8	69.5	69.4	73.6
9.0	71.0	–	–	71.6	68.8

**Table 4**

Moisture contents of dewatered cakes shown in Fig. 8

[wt%]				
AP dosage [wt%]				
0	0.2	0.5	1.0	1.5
69.1	69.3	68.9	68.3	68.1
CP dosage: 1 wt%				