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Studies of Polymeric Flocculants. XI.[1] The Preparation and Properties of Polyampholytes

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The polyampholytes were prepared by treating potassium polymethacrylate with (3-chloro-2-hydroxypropyl)-trimethylammonium chloride. The solution viscosity behavior and the potentiometric titration of the polyampholytes were studied. The flocculating ability of the polyampholytes was also investigated by the use of kaolin suspensions. The amine/acid ratio could be varied as desired to some extent by means of changing the reaction temperature. However, the polyampholytes containing more amino groups than about 46% could not be obtained. The resulting polyampholytes showed characteristic viscosity behavior. The results of the flocculation of kaolin suspensions with the polyampholytes showed that the polyampholytes can be expected to become a new type of polymeric flocculants, in which the chain expansion and the charge sign can be varied by changing the pH values of the solutions.

Some polyampholytes have been prepared and studied by a number of investigators,[2–8] but the flocculation of suspensions with polyampholytes had not been investigated. In the present paper, the preparation and properties of potassium methacrylate–[2-hydroxy-3-(methacryloyloxy)propyl]trimethylammonium chloride copolymer as a new polyampholyte were investigated. Furthermore, the flocculating ability of the polyampholytes was studied by the use of kaolin suspensions.

Experimental

Preparatoin of Potassium Polymethacrylate. The pH values of a methacrylic acid aqueous solution were adjusted to 7.0—7.2 by adding a 2-mol dm^{-3} KOH aqueous solution. Potassium methacrylate in an aqueous solution was polymerized at 40 °C for 48 h, and then the aqueous solution was poured into an excess of ethanol in order to precipitate potassium polymethacrylate. The intrinsic viscosity was measured in a 2-mol dm^{-3} $NaNO_3$ aqueous solution at 25 °C. The number-average molecular weight of the potassium polymethacrylate was calculated by means of the following equation: $[\eta]=KM^{a}$.[9]

Preparation of (3-Chloro-2-hydroxypropyl)trimethylammonium Chloride. (3-Chloro-2-hydroxypropyl)trimethylammonium chloride (**1**) was prepared by a method described previously.[10] At first, 9.6 g of trimethylammonium hydrochloride was dissolved in 10 cm^3 of water. Into this solution 9.3—14.0 g of epichlorohydrin were then stirred, drop by drop, at 40—50 °C, after which the reaction mixture was heated at the same temperature for an additional hour. The product was purified by crystallization from methanol. The total chlorine content of **1** was determined by means of a flask-combustion method.[11] The chloride-ion content was determined by means of the Mohr method.[12]

Preparation of Polyampholytes. The potassium methacrylate–[2-hydroxy-3-(methacryloyloxy)propyl]trimethylammonium chloride copolymers were prepared by treating potassium polymethacrylate with **1** at 40—120 °C for 2—10 h. The reaction mixture was poured into an excess of ethanol in order to precipitate the polyampholytes. The polyampholytes were then purified by Soxhlet extraction with ethanol for 30 h. The amine content of the polyampholytes was calculated on the basis of the nitrogen content of the polyampholytes thus obtained. The polyampholytes for an elemental analysis were obtained as follows: about 0.5 g of the polyampholytes was dissolved in 50 cm^3 of a 1-mol dm^{-3} HCl solution, after which the solution was poured into an excess of ethanol in order to precipitate the polyampholyte. The polyampholyte was purified by Soxhlet extraction with ethanol for 30 h and dried *in vacuo* at 50 °C for 5 h.

Measurement of Solution Viscosity of Polyampholytes. The viscosities were measured in an aqueous solution of various concentrations of the polyampholytes at different pH values. In order to determine the isoelectric point of the polyampholytes, the viscosities were also measured by varying the pH values of the aqueous solution of the polyampholytes. All the viscosities were measured by means of an Ostwald viscosimeter at 30 °C.

Potentiometric Titration. The polyampholytes, dissolved in 50 cm^3 of a 0.1 mol dm^{-3} KCl solution, were titrated with a 0.1 mol dm^{-3} KOH (or 0.1 mol dm^{-3} HCl)–0.1 mol dm^{-3} KCl solution. The pH values of the solution were then measured by means of a Hitachi-Horiba pH meter.

Flocculation Tests. The flocculating ability was studied by observing the sedimentation rate and the sedimented volume by a test tube. The kaolin was supplied by the Wako Junyaku Kogyo Co. Ltd.,; its composition and particle size distribution are shown in Table 1 and Fig. 1 respectively. The pH value of a 5% suspension of this kaolin in water was 4.15. The sedimentation data were obtained at room temperature using a 25-cm^3 graduated test tube (1.7 cm

TABLE 1. COMPONENTS OF KAOLIN

Component	Weight percentage
SiO_2	78.1
Al_2O_3	13.9
Fe_2O_3	0.1
Ignition loss	3.0

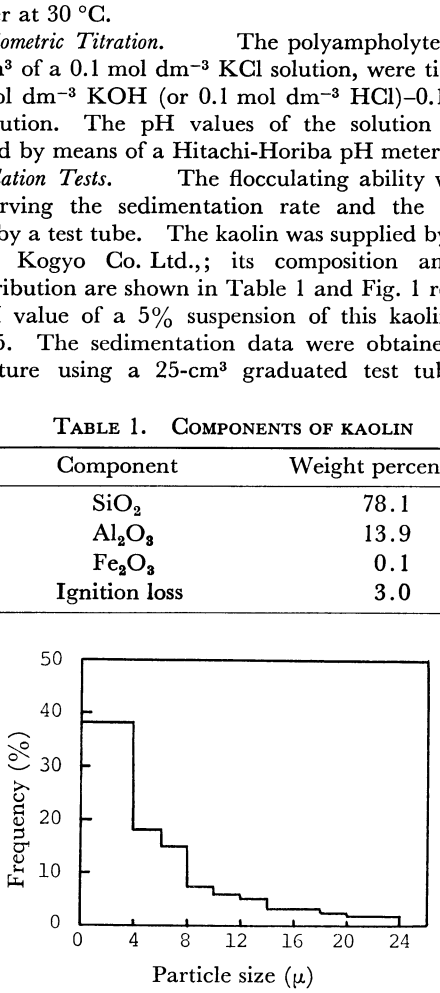


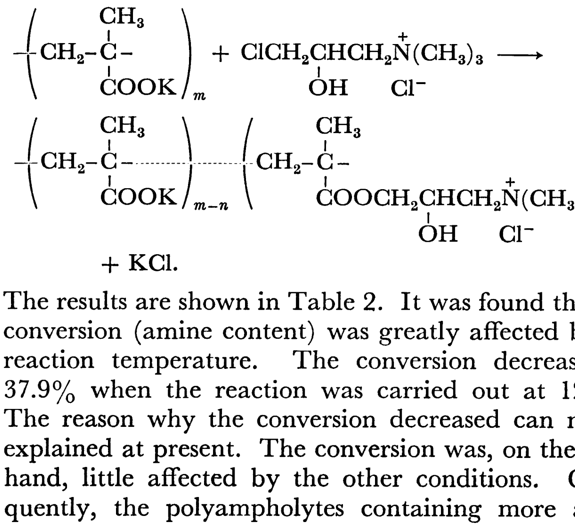
Fig. 1. Particle size distribution of kaolin.

inner diameter and 18.0 cm long). 20 cm^3 of a 6.25% (w/v) kaolin suspension was poured into the test tube. An aqueous solution of a polymer was added, and then water was added to the test tube until the total volume amounted to 25 cm^3. The contents were mixed by inverting the test tube 25 times at a speed of one time per 4 seconds. Then it was allowed to settle. The sedimentation rate was determined by plotting the height of the solid-liquid boundary as a function of the time. The sedimented volume was determined by measuring the volume of the kaolin after 24 h.

Results and Discussion

*Potassium Polymethacrylate and **1**.* Potassium polymethacrylate with a different degree of polymerization was obtained by an aqueous-solution polymerization of potassium methacrylate using a different amount of the initiator (ammonium persulfate). **1** was prepared by the method described previously.[10)] When **1** was prepared by treating 1.2 mol of epichlorohydrin with 1 mol of trimethylamine hydrochloride, the values of the elemental analysis of the products were in good agreement with the values calculated for $C_6H_{15}NOCl_2$. Found: C, 38.43; H, 7.97; N, 7.42; Cl, 37.70%. Calcd for $C_6H_{15}NOCl_2$: C, 38.29; H, 7.98; N, 7.45; Cl, 37.70%. The chloride-ion content was 50.19 per cent of the total chlorine of the product.

Preparation of Polyampholytes. In order to prepare polyampholytes containing both amino groups and carbonyl groups in the desired ratio, the reaction of potassium polymethacrylate with **1** was carried out under a variety of conditions. The reaction equation was as follows:



$$\left(\mathrm{CH_2}-\underset{\mathrm{COOK}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\right)_m + \mathrm{ClCH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2}\overset{+}{\mathrm{N}}(\mathrm{CH_3})_3\ \mathrm{Cl^-} \longrightarrow$$

$$\left(\mathrm{CH_2}-\underset{\mathrm{COOK}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\right)_{m-n}\cdots\left(\mathrm{CH_2}-\underset{\mathrm{COOCH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2}\overset{+}{\mathrm{N}}(\mathrm{CH_3})_3\ \mathrm{Cl^-}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\right)_n + \mathrm{KCl}. \qquad (1\text{-}1)$$

The results are shown in Table 2. It was found that the conversion (amine content) was greatly affected by the reaction temperature. The conversion decreased to 37.9% when the reaction was carried out at 120 °C. The reason why the conversion decreased can not be explained at present. The conversion was, on the other hand, little affected by the other conditions. Consequently, the polyampholytes containing more amino groups than about 46% could not be obtained. This is probably due to the steric hindrance of the bulky amine compound to be introduced into potassium polymethacrylate.

The reaction of potassium polyacylate with **1** was carried out under the same conditions as those used for potassium polymethacrylate. Some results are shown in Table 2. In this case, it was found that the conversion was also affected by the reaction temperature. The polyampholytes obtained at temperatures above 80 °C were insoluble in water. Therefore, a more detailed investigation was not carried out with this polyampholyte.

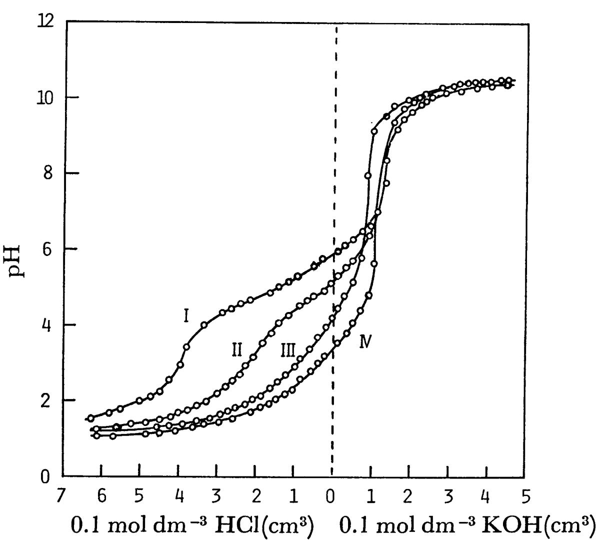


Fig. 2. The pH titration curves of the polyampholytes. Polymer concentration: *ca.* 0.16 g/100 cm^3.

		I	II	III	IV
Polyampholyte		**A**	**B**	**C**	**D**
$\frac{\text{Amine}}{\text{Acid}}$	mole ratio	$\frac{8.1}{91.8}$	$\frac{29.2}{70.8}$	$\frac{37.6}{62.4}$	$\frac{45.5}{54.5}$

pH *Titration Curves of the Polyampholytes.* The pH titration curves of the polyampholytes obtained are shown in Fig. 2. The pH titration curves show that each potassium methacrylate–[2-hydroxy-3-(methacryloyloxy)propyl]trimethylammonium chloride copolymer contained about 0.56 meq/g of the acid form of carboxyl groups. An obvious inflection point in the titration curves can be observed with the polyampholyte **A** (amine/acid mole ratio=8.1/91.9) obtained at 40 °C and the polyampholyte **B** (amine/acid mole ratio=29.2/70.8) obtained at 60 °C in the low pH region. These points probably correspond to the completed change from potassium salt to the acid form of carboxyl groups in the polyampholytes. However, such an obvious inflection point in the titration curves can not

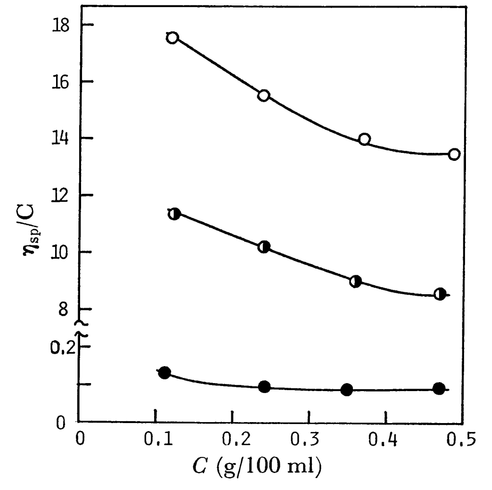


Fig. 3. Relation between the reduced viscosity and the polymer concentration at different pH values. Polymer: Polyampholyte **A**; pH, ●: 4, ◑: 7, ○: 10.

TABLE 2. PREPARATION OF POLYAMPHOLYTES

Expt. No.	PMAK[a) g	1[b) g	H_2O cm^3	Temp °C	Time h	Yield g	Amine[c)/Acid mole ratio
1	1.24	1.88	40	40	6	0.80	8.1/91.9
2	1.24	1.88	40	60	6	1.13	29.2/70.8
3	1.24	1.88	40	80	6	1.17	37.6/62.4
4	1.24	1.88	40	100	6	1.63	45.5/54.5
5	1.24	1.88	40	80	2	1.08	32.9/67.1
6	1.24	1.88	40	80	4	1.09	37.6/62.4
7	1.24	1.88	40	80	6	1.17	37.6/62.4
8	1.24	1.88	40	80	10	1.34	37.7/62.3
9	1.24	1.88	40	80	6		37.6/62.4
10	1.24	3.76	40	80	6		38.5/61.5
11	1.24	1.88	20	80	6		41.8/58.2
12	1.24	1.88	40	80	6		37.6/62.4
13	1.24	1.88	80	80	6		33.5/66.5
	PAK[d)						
14	1.10	1.88	30	40	6	1.15	4.4/95.6
15	1.10	1.88	30	60	6	1.15	21.6/78.4
16	1.10	1.88	30	80	6	1.15	34.4/65.6
17	1.10	1.88	30	100	6	1.45	41.4/58.6

a) Potassium polymethacrylate with the degree of polymerization of 600. b) (3-Chloro-2-hydroxypropyl)trimethylammonium chloride. c) The amine content was calculated on the basis of the nitrogen content of the polyampholytes. d) Potassium polyacrylate.

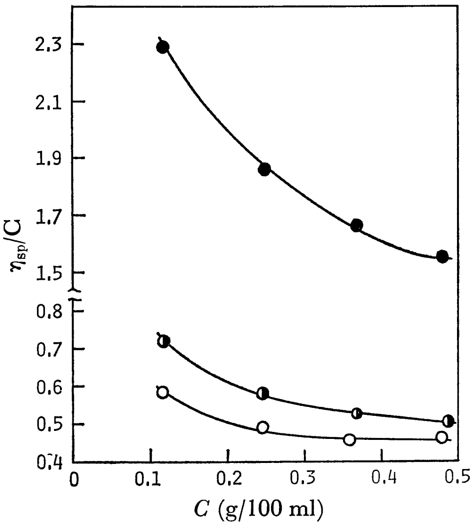


Fig. 4. Relation between the reduced viscosity and the polymer concentration at different pH values.
Polymer: Polyampholyte **D**; pH; ●: 4, ◑: 7, ○: 10.

be observed with the polyampholyte **C** (amine/acid mole ratio=37.6/62.4) obtained at 80 °C and the polyampholyte **D** (amine/acid mole ratio=45.5/54.5) obtained at 100 °C.

The Solution Viscosity and the Isoelectric Point of the Polyampholytes. The relation between the reduced viscosities and the concentrations of the polyampholytes **A** and **D** are shown at different pH values in Figs. 3 and 4 respectively. It was found that the polyampholytes showed viscosity vehavior typical of common polyelectrolytes. A difference in the order of the reduced viscosities at different pH values was observed with the polyampholytes with different amine/acid mole ratios. In the cases of the polyampholytes **A** and **B**, the reduced viscosities at different pH values increased in the order of pH 10>pH 7>pH 4. In the cases of the polyampholytes **C** and **D**, the reduced viscosities increased in the order of pH 4>pH 7>pH 10. These phenomena are characteristic of polyampholytes. The relation between the reduced viscosities of these polyampholytes and the pH values are shown in Fig. 5. Figure 5 shows that the reduced viscosities of the polyampholytes **A** and **B** increased with an increase in the pH values in the pH region from 5.3 to 8.2. This viscosity increase is ascribed to the chain expansion caused by the repulsion of the negatively charged carboxyl groups. On the other hand, the reduced viscosities increased a little with a decrease in the pH values in the pH region from

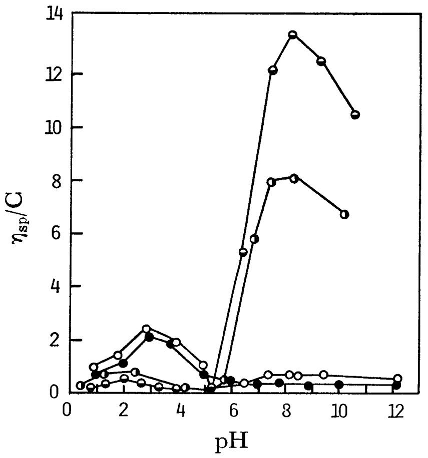


Fig. 5. Relation between the reduced viscosities of the polyampholytes with the different amine/acid ratio and pH values.
Polyampholyte; ◒: **A**, ◑: **B**, ○: **C**, ●: **D**.

5.3 to 2.0. This viscosity increase is ascribed to the chain expansion caused by the repulsion of a small amount of the positively charged amino groups in the polyampholytes. The reduced viscosities decreased at pH values above 8.2 and below 2.0. This viscosity decrease is ascribed to the chain contraction of the polyampholytes caused by the increase in the ionic strength by the addition of KOH or HCl to adjust the pH values of the solution. The reduced viscosities of the polyampholytes **C** and **D** scarcely increased at pH values above 5.3. As the amino groups in the polyampholytes obtained are quaternary amino groups, they dissociate even in an aqueous solution with the pH values above 7. Therefore, the viscosity decrease is ascribed to the chain contraction of the polyampholytes caused by the formation of the polyioncomplexes by means of interaction between the amino groups and carboxyl groups in the polyampholytes in the high pH region.

The isoelectric point, characterized by a minimum in the solution viscosity, of the polyampholytes **A** and **B** was obvious, but the isoelectric point of the polyampholytes **C** and **D** could not be obviously observed.

The Flocculation of Kaolin Suspension with the Polyampholytes. We have previously reported the preparation of cationic polymers and their flocculating ability.[13-15] The flocculation of suspensions with polyampholytes has not, however, been reported. The polyampholytes are expected to become a new type of flocculants, as the chain expansion and the charge sign of the polyampholytes can be varied by changing the pH values of the solution. Therefore, the flocculating ability of the polyampholytes was investigated by the use of kaolin suspensions at different pH values (3, 5.5, and 8). These pH values correspond, respectively, to the pH values at which the maximum, minimum, and maximum in the reduced viscosities of the polyampholytes were observed (Fig. 5). The polymers used are the polyampholytes **A**, **B**, **C**, and **D**. The results are shown in Figs. 6, 7, and 8. Figure 6 shows that the sedimentation rate of kaolin at pH 3 with the polyampholytes increased in the order of the polyampholytes **A**>**B**>**C**>**D** when more than 0.02% of the polyampholytes were added to kaolin. This order of the sedimentation rate was not in agreement with the order of the reduced viscoisities of the polyampholytes in pH 3. The sedimentation rate and the sedimented volume of kaolin with potassium polymethacrylate with the same degree of polymerization (600) as the polyampholytes are also shown in Fig. 6. The sedimentation rate of kaolin with potassium polymethacrylate increased slightly with an increase in the amount of the polymers added, but the sedimented volume of kaolin was almost the same as that in the case of no addition of a polymer. It is said that the flocculation of kaolin with sodium polyacrylate in a low pH region was brought about by a hydrogen bonding between the polymers and kaolin particles.[16] In the flocculation of kaolin with the polyampholytes at pH 3, it is considered that the flocculation was brought about with both amino groups and carboxyl groups in the polyampholytes.

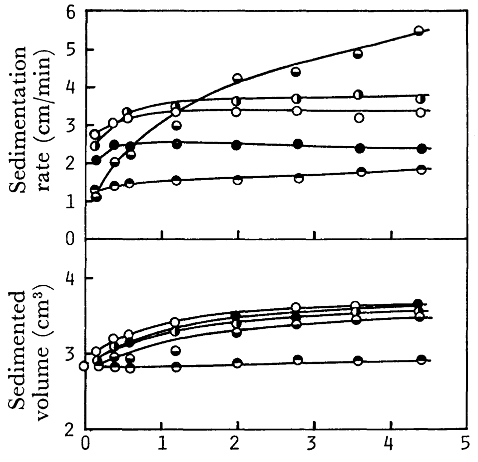


Fig. 6. Relation between sedimentation rate (or sedimented volume) and the amount of the polymer added at pH 3.

Polyampholyte; ◒: **A**, ◑: **B**, ○: **C**, ●: **D**, ◓: PMAK (potassium polymethacrylate).

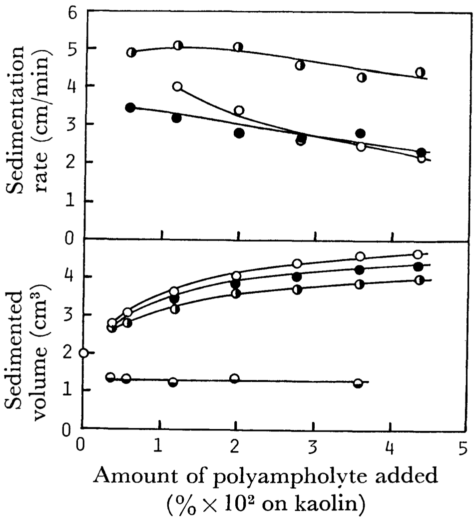


Fig. 7. Relation between sedimentation rate (or sedimented volume) and the amount of the polymer added at pH 5.5.

Polyampholyte; ◒; **A**, ◑: **B**, ○: **C**, ●: **D**.

Figure 7 shows that the highest sedimentation rate, at pH 5.5, was observed with the polyampholyte **B**. At pH 5.5, the kaolin suspension was not flocculated with the polyampholyte **A** and potassium polymethacrylate. The sedimented volume of kaolin with the polyampholyte **A** was smaller than that in the case of the addition of no polymer. These data show that the polyampholyte **A** acted as a dispersing agent of the negatively charged kaolin particles.

Figure 8 shows that, at pH 8, the kaolin suspension was not flocculated with the polyampholytes **A** and **B**, but was flocculated with the polyampholytes **C** and **D**, when a large amount of the polyampholytes was added. It is considered that, at pH 8, the polyampholytes (**A** and **B**) containing many carboxyl groups acted as dispersing agents of the negatively charged kaolin particles. This consideration was also confirmed by the

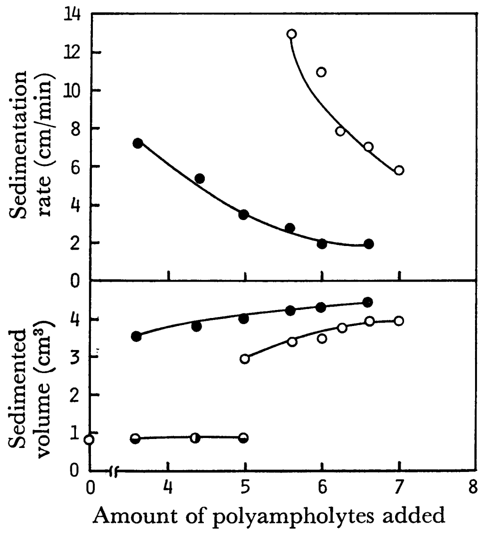


Fig. 8. Relation between sedimentation rate (or sedimented volume) and the amount of the polymer added at pH 8.

Polyampholyte; ◒: **A**, ◑: **B**, ○: **C**, ●: **D**.

small sedimented volume of kaolin with the polyampholytes **A** and **B**. Consequently, the polyampholytes **A** and **B** may be said to be excellent polymeric flocculants for positively charged particles in a high pH region, although the flocculation of positively charged particles with the polyampholytes was not investigated in this paper.

The sedimentation rate of kaolin with the polyampholyte **C** was higher than that with the polyampholyte **D**. On the other hand, the sedimented volume of kaolin with the polyampholyte **C** was smaller than that with the polyampholyte **D**. In the flocculation of kaolin with the polyampholytes, no definite relation between the sedimentation rate and the sedimented volume was observed.

Effect of the Degree of Polymerization of the Polyampholytes on the Flocculation. Many investigators have reported that the flocculating ability increased with an increase in the degree of polymerization of polymeric flocculants.[13,14,17,18] The flocculation of the kaolin suspension was investigated with polyampholytes with different degrees of polymerization at pH 3. The results are shown in Fig. 9. Figure 9 shows that the flocculating ability of the polyampholytes increased with an increase in the degree of polymerization of the polymers, in the same manner as with cationic[13,14] or nonionic[17,18] polymeric flocculants. For comparison, the sedimentation rate and the sedimented volume of kaolin with Primafloc C-7,[19,20] which is a commercial cationic polymeric flocculant, *i.e.*, a polyvinylimidazoline with the molecular weight of more than a million, prepared by Rohm and Haas Co., America, are also shown in Fig. 9.

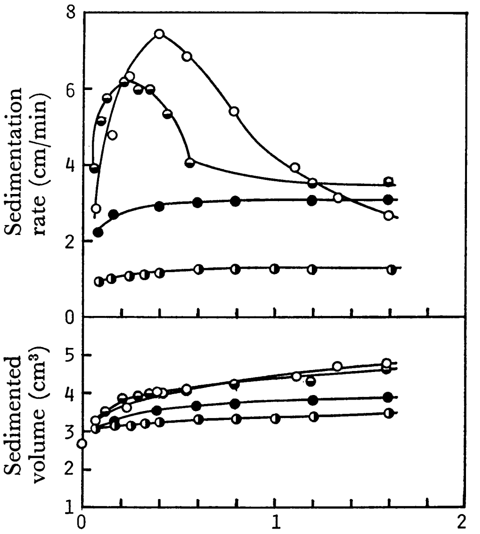


Fig. 9. Effect of the degree of polymerization of the polyampholytes on the flocculation of kaolin.

	◓	●	◑	○
$\bar{P}$n	1960	600	310	Primafloc C-7
$\frac{\text{Amine}}{\text{Acid}}$ mole ratio	$\frac{44.3}{55.7}$	$\frac{41.1}{58.9}$	$\frac{35.6}{64.4}$	(Rohm and Haas Co.)

As has been mentioned above, the polyampholytes could be prepared by treating potassium polymethacrylate with **1** and the amine/acid ratio could be varied as desired to some extent by means of changing the reaction temperature. The polyampholytes can be expected to become a new type of polymeric flocculant, in which the chain expansion and the charge sign can be varied by changing the pH values of the solution.

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