

# Synthesis of an Intercalated Compound of Montmorillonite and 6-Polyamide

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**Abstract.** Natural montmorillonite, fractionated from bentonite produced in Yamagata, Japan, was ion-exchanged for  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{H}^+$ . The mixtures of the ion-exchanged montmorillonite and  $\epsilon$ -caprolactam were heated at 263 °C in glass ampoules for various periods. The intercalated compounds before and after the heating were examined by X-ray powder diffraction, DSC and GPC. Although  $\epsilon$ -caprolactam was not polymerized without montmorillonite, it was polymerized at 263 °C in the presence of montmorillonite. The polymerization rate varied with the interlayer cations in the order of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH} > \text{Al}^{3+} > \text{NH}_3^+(\text{CH}_2)_5\text{COOH} > \text{H}^+ > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Co}^{2+} > \text{Li}^+ > \text{K}^+$ . After heating at 263 °C for 5 h, the mean number-average molecular weight was about  $1.5 \times 10^4$ . Although the interlayer distance of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite/ $\epsilon$ -caprolactam compound increased from 2.85 nm to 4.90 nm by heating at temperatures above the melting point of  $\epsilon$ -caprolactam, those of other compounds were not changed. After heating at 263 °C, an intercalated compound of montmorillonite and 6-polyamide, whose interlayer distance was more than 10 nm, was obtained. It is concluded that montmorillonite acts as a Brønsted acid and initiates the open ring polymerization of  $\epsilon$ -caprolactam and that the driving force of swelling is the polymerization energy.

**Key words:** Intercalation, clay mineral, montmorillonite,  $\epsilon$ -caprolactam, 6-polyamide, XRD, DSC, GPC, polymerization, catalysis, swelling.

## 1. Introduction

Intercalated compounds of clay minerals are formed by the introduction of organic and inorganic molecules between the silicate layers. Various applications of the clay/organic complexes, such as absorbents [1], additives for controlling rheological properties of organic solvents [2], separators for optically active metal complexes [3], antioxidants for rubber materials [4], curing agents for synthetic resins [5] etc., have been reported. A composite material of a clay and a polyamide might be a useful material, because the mechanical properties of a polyamide are strongly affected by inorganic additives. Although many studies on clay/organic polymer complexes [6] have been reported, clay/polyamide intercalation has not been studied extensively.

Smectite clay minerals, such as montmorillonite, saponite, nontronite, hectorite, stevensite, vermiculite and halloysite have been known to act as hosts of intercalated compounds [7] and to function as catalysts for various organic reactions [8]. The properties of smectites depend upon the interlayer cations [9], which are easily exchangeable for inorganic or organic cations.

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To understand the catalytic effect of smectites and their interlayer cations on the polymerization of amide molecules and the swelling behaviour of layered silicates by organic polymers, the intercalated compound of cation exchanged montmorillonite and  $\epsilon$ -caprolactam and the polymerization of  $\epsilon$ -caprolactam in the presence of the montmorillonite have been studied in this work.

## 2. Experimental

### 2.1. CATION EXCHANGE OF MONTMORILLONITE

The interlayer cations of high purity natural montmorillonite (particle size  $< 2 \mu\text{m}$ ) fractionated from bentonite produced in Yamagata, Japan, by suspending in water, (available from Kunimine Industries Co., Ltd.) were exchanged for  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{K}^+$ , and  $\text{H}^+$ .

One liter 1.0N aqueous solution of the nitrate of one of the inorganic cations was mixed with 200 ml of a cation-exchanged resin (DuPont 50W-X8), whose cation exchange capacity and particle sizes were 20 meq./ml and 20–50 mesh, respectively. After washing with 2.0 liters of deionized water five times, the cation exchanged resin was mixed with 3 wt % of an aqueous suspension of montmorillonite followed by settling for 24 h at 25 °C. The exchange with organic ions was accomplished by mixing 30 g of montmorillonite powder with one liter of 1.0N aqueous solutions of a chloride of one of the cations, followed by repetitive washing by deionized water and filtration until the chloride ions could not be detected by reaction with  $\text{AgNO}_3$ . The cation exchanged montmorillonites were frozen in liquid nitrogen and vacuum dried at 25 °C. The cations in the montmorillonite were analyzed by atomic absorption after extraction using 1.0N aqueous solution of ammonium acetate. The results of the analysis are shown in Table I.

Table I. The results of the atomic absorption analysis of interlayer inorganic cations of cation exchanged montmorillonite

Type of montmorillonite	$\text{Al}^{3+}$	$\text{Cu}^{2+}$	$\text{Mg}^{2+}$	$\text{Co}^{2+}$	$\text{Li}^+$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	Total
	(meq./100 g clay)								
$\text{Al}^{3+}$	31.8	0	1.4	0	0	0.2	4.4	0	37.9
$\text{H}^+$	7.2	0.4	5.0	0	0	0.3	8.0	4.0	24.9
$\text{Cu}^{2+}$	0	53.6	9.0	0	0	11.9	8.9	0.6	84.0
$\text{Mg}^{2+}$	0	1.8	88.8	0	0	0.8	8.1	0.4	99.5
$\text{Co}^{2+}$	0	0.8	19.2	72.0	0	0.6	11.4	1.8	105.8
$\text{Li}^+$	0	0.2	1.8	5.4	90.0	0.4	7.0	0	104.9
$\text{K}^+$	0	0	20.8	0	0	52.9	13.6	0	80.5
$\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$	0	0	1.0	0	0	0.1	0.4	0	1.5

### 2.2. PREPARATION OF INTERCALATED COMPOUNDS

Mixtures of 2.0 g of the cation exchanged montmorillonite powders and 8.0 g of  $\epsilon$ -caprolactam were heat treated for 2 h in air at 80 °C, which is about 10 °C higher than the melting point of  $\epsilon$ -caprolactam. These mixtures were vacuum dried at

25 °C for 2 h followed by sealing in glass ampoules, and were heat treated at 263 °C for 1, 2, 3 and 5 h. The amount of 6-polyamide was estimated by the heat of fusion of  $\epsilon$ -caprolactam, which was measured by DSC on a Seiko DSC-10, using a 15 ml sealed capsule made of aluminum, and an aluminum metal disk as a reference sample. About 10 mg of the sample was used for the DSC measurement, and the heating rate was 5 °C/minute.  $\epsilon$ -Caprolactam without montmorillonite was dried, heated and analyzed by DSC in a similar manner.

### 2.3. MEASUREMENT OF MOLECULAR WEIGHT OF POLYAMIDE

The molecular weight of the organic components in the mixtures of  $\text{Cu}^{2+}$ ,  $\text{NH}_3^+$ — $(\text{CH}_2)_{11}$ — $\text{COOH}$ ,  $\text{H}^+$  or  $\text{Mg}^{2+}$  type montmorillonites and  $\epsilon$ -caprolactam heat treated at 263 °C for 5 h were analyzed by gel permeation chromatography (GPC).

The organic components were extracted with *m*-cresol at 100 °C for 1 h. The molecular weights of the extracted molecules were analyzed using a Waters 150-C GPC and a column of polystyrene gel (Shodex AD-20  $\mu$ /s from Showadenko Co., Ltd.) heated at 100 °C, and at a 1.0 ml/minute flow of the 0.25 wt/vol % *m*-cresol solution. The molecular weight of common 6-polyamide (Amilan CM1017 from Toray Co. Ltd.) was analyzed in a similar manner.

### 2.4. X-RAY POWDER DIFFRACTION (XRD) STUDY

XRD data on powdered samples were taken using a conventional Bragg-Brentano type diffractometer, where Fe-filtered  $\text{Co-}K_\alpha$  ( $\lambda = 0.1789$  nm) was used as the X-ray source, the tube voltage was 30 kV, the tube current was 20 mA,  $1^\circ$ - $0.15$  mm- $1^\circ$  ( $2^\circ < 2\theta < 10^\circ$ ) or  $0.167^\circ$ - $0.15$  mm- $0.167^\circ$  ( $1^\circ < 2\theta < 3^\circ$ ) slits were used and the scanning speed was  $2^\circ(2\theta)$ /minute.

XRD data of the mixtures of liquid  $\epsilon$ -caprolactam and  $\text{NH}_3^+$ — $(\text{CH}_2)_{11}$ — $\text{COOH}$ ,  $\text{NH}_3^+$ — $(\text{CH}_2)_5$ — $\text{COOH}$ ,  $\text{Mg}^{2+}$  or  $\text{Cu}^{2+}$  type montmorillonites were taken at 80 °C using a diffractometer designed for the examination of liquids and an aluminum sample holder with a silicone plate heater, a thermocouple and an aluminum foil cover. The conditions of the XRD for liquid samples were as follows; Ni-filtered  $\text{Cu-}K_\alpha$  ( $\lambda = 0.1542$  nm) was used. Tube voltage was 30 kV, tube current was 20 mA,  $0.5^\circ$ - $0.15$  mm- $0.5^\circ$  slits were used and scanning speed was  $1.0^\circ(2\theta)$ /minute.

The diffractometers were calibrated by using a standard reference fluorophlogopite mica powder [10] from NBS for the XRD *d*-spacing.

## 3. Results

### 3.1. MOLECULAR WEIGHT OF POLYAMIDE

The results of the GPC analyses are listed in Table II, which shows that  $\epsilon$ -caprolactam was polymerized to 6-polyamide, whose mean number-average molecular weight;  $\overline{M}_w(N)$ , was about  $1.5 \times 10^4$ . The molecular weight, however, was smaller than those of common 6-polyamide, whose  $\overline{M}_w(N)$  is about  $2 \times 10^4$ . A small peak or shoulder, which suggests the existence of oligomers, whose  $\overline{M}_w(W) \approx 800$ , was also observed.

Table II. Mean number-average molecular weight;  $\overline{Mw}(N)$ , mean weight-average molecular weight;  $\overline{Mw}(W)$  and distribution of molecular weight;  $\overline{Mw}(W)/\overline{Mw}(N)$  of the 6-polyamide, polymerized at 263 °C for 5 h in the presence of montmorillonites

Type of montmorillonite	$\overline{Mw}(N)$	$\overline{Mw}(W)$	$\overline{Mw}(W)/\overline{Mw}(N)$
$NH_3^+(CH_2)_{11}COOH$	$1.4 \times 10^4$	$1.1 \times 10^5$	7.9
$H^+$	$1.4 \times 10^4$	$1.2 \times 10^5$	8.6
$Cu^{2+}$	$1.0 \times 10^4$	$1.0 \times 10^5$	10.0
$Mg^{2+}$	$1.8 \times 10^4$	$1.0 \times 10^5$	5.5

### 3.2. POLYMERIZATION RATE OF $\epsilon$ -CAPROLACTAM

DSC curves for the mixture of  $\epsilon$ -caprolactam and the  $Al^{3+}$  type montmorillonite after various periods of treatment at 263 °C are shown in Figure 1. The area of the endothermic peak between 40 and 80 °C, corresponding to melting of  $\epsilon$ -caprolactam, decreased and that between 150 and 180 °C, corresponding to melting of 6-polyamide, increased with increasing reaction time. These results also suggest the polymerization of  $\epsilon$ -caprolactam.

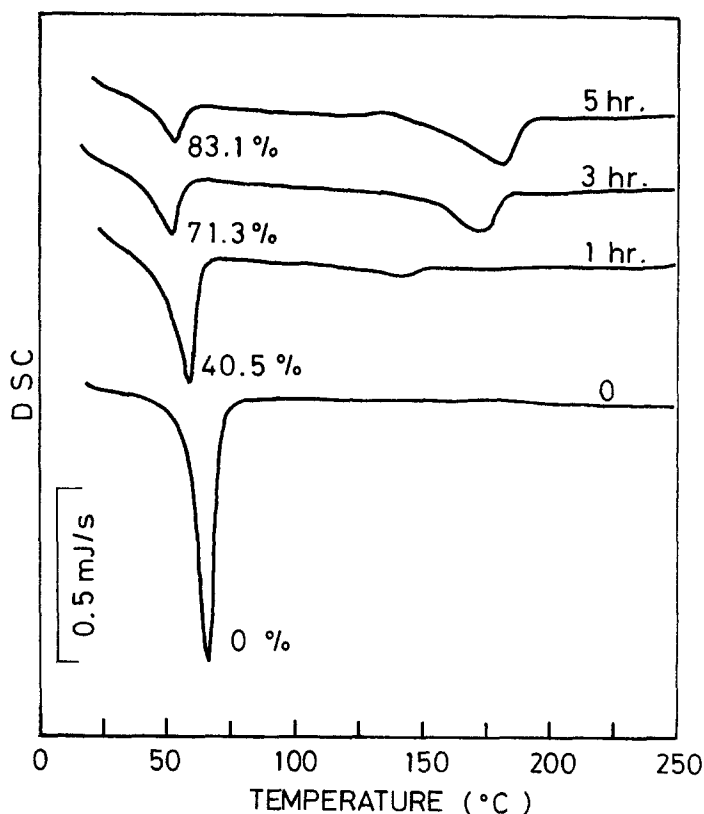


Fig. 1. DSC curves for the mixture of  $\epsilon$ -caprolactam and  $Al^{3+}$  type montmorillonite after the various periods of treatment at 263 °C.

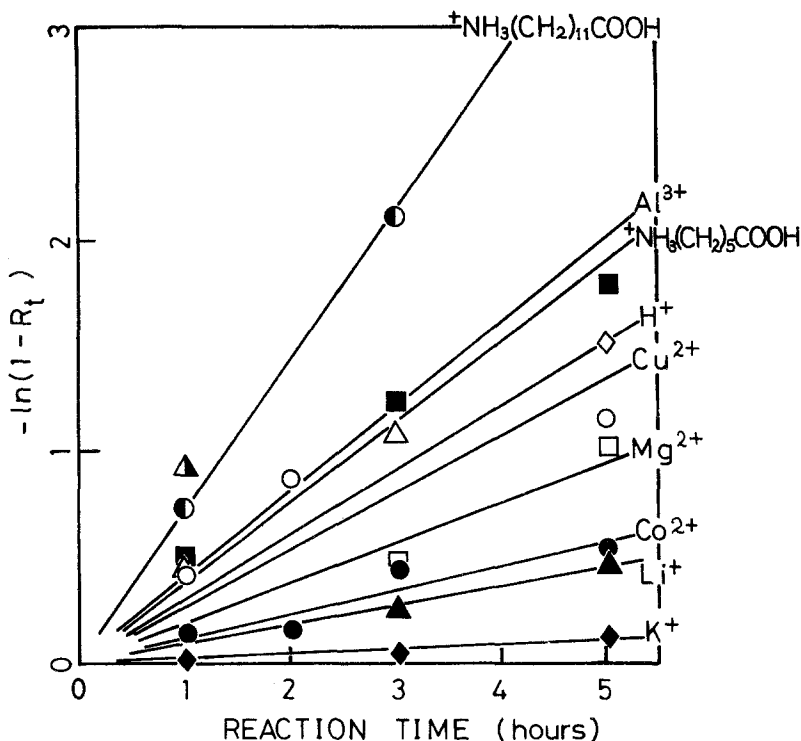


Fig. 2. First order reaction plot for the polymerization of polyamide in the presence of various types of montmorillonite.  $R_t$  is the degree of polymerization estimated by Eq. (1).

The degree of polymerization after  $t$  hours of treatment at 263 °C,  $R_t$ , was estimated using the heat of fusion of  $\epsilon$ -caprolactam, according to the equation,

$$R_t = \left(1 - \frac{\Delta H_t}{\Delta H_0}\right), \quad (1)$$

where  $\Delta H_t$  and  $\Delta H_0$  are enthalpy changes calculated by using the endothermic peak between 40 and 80 °C after and before the heat treatment, respectively. The  $R_t$  values for the polymerization are shown in Figure 2. The polymerization rate decreased with the interlayer cations of montmorillonite in the order of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH} > \text{Al}^{3+} \geq \text{NH}_3^+(\text{CH}_2)_5\text{COOH} > \text{H}^+ > \text{Cu}^{2+} > \text{Mg}^{2+} > \text{Co}^{2+} > \text{Li}^+ > \text{K}^+$ . However,  $\epsilon$ -caprolactam was not polymerized in the absence of montmorillonite and the DSC curve was not altered after 5 h treatment at 263 °C. Even in the presence of montmorillonite, no changes in DSC curves were observed by treatment at a temperature less than 100 °C.

### 3.3. RESULTS OF XRD

The XRD patterns in the low angle region of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  type montmorillonites and the mixture with  $\epsilon$ -caprolactam before and after 5 h treatment at 263 °C are shown in Figure 3. Although the (001) peak of  $\text{Mg}^{2+}$  type montmorillonite with  $\epsilon$ -caprolactam was

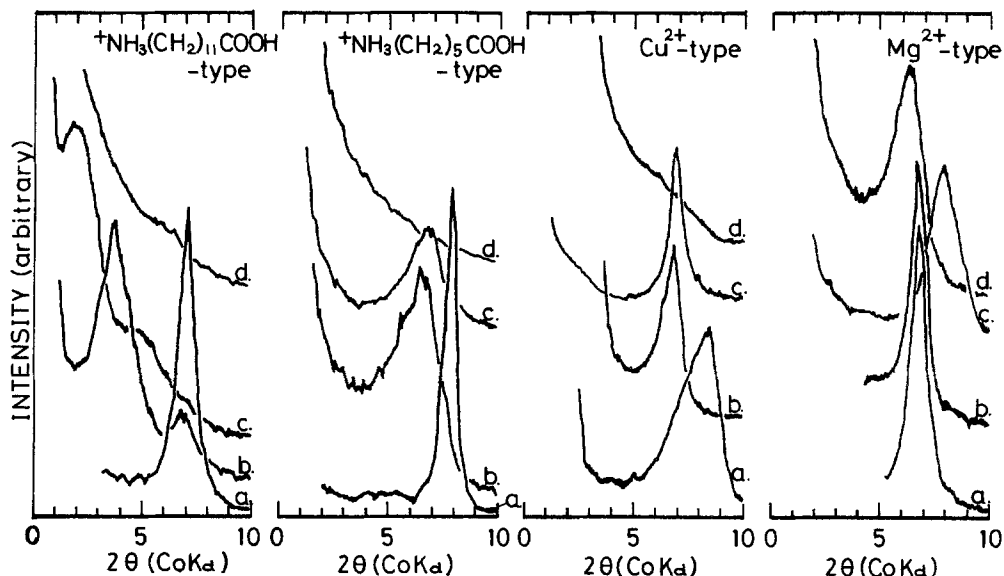


Fig. 3. XRD patterns of (a)  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mg}^{2+}$  type montmorillonite, and the mixtures with  $\epsilon$ -Caprolactam taken at (b) 25 °C and (c) 80 °C and (d) those after 5 h treatment at 263 °C. (Although XRD at 80 °C were taken using  $\text{CuK}\alpha$ , the abscissa was normalized as if  $\text{CoK}\alpha$  was used.)

still observed after 5 h treatment at 263 °C, no distinct peaks could be observed but only an increase of the background level was observed for the  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$  and  $\text{Cu}^{2+}$  type montmorillonites with  $\epsilon$ -caprolactam. Changes in XRD patterns of the  $\text{Cu}^{2+}$ -montmorillonite with  $\epsilon$ -caprolactam after various periods of treatment at 263 °C are shown in Figure 4. Increasing the heating time, that is increasing the polymerization rate, the (001) peak of montmorillonite was decreased and the background in small angle regions was increased. In Figure 5, XRD patterns of the complexes with various 6-polyamide/ $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite ratios are shown. With an increase in the 6-polyamide content, peaks in the low angle region,  $d \approx 2.0$  nm, 5.4 nm and 8.4 nm and an increased background level in small angle regions were observed. This result shows that the increase in the background in small angle regions for the mixture of 2 g of montmorillonite and 8 g of  $\epsilon$ -caprolactam, which was shown in Figure 3, suggests that the stacking of silicate layers became disordered and/or the mean interlayer distances in these mixtures were more than 10 nm. The mean interlayer distances of montmorillonites, estimated by (001) peak positions are listed in Table III. The interlayer distances increased with the intercalation with  $\epsilon$ -caprolactam and the interlayer distances were not changed by heating at temperatures above the melting point of  $\epsilon$ -caprolactam, except for the mixture of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite and  $\epsilon$ -caprolactam. For the mixture of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite and  $\epsilon$ -caprolactam, the interlayer distance was increased from 2.85 nm to 4.90 nm by heating to 80 °C and decreased to 2.85 nm with solidification of  $\epsilon$ -caprolactam by cooling. After the polymerization, the interlayer distances of  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$ ,  $\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$ ,  $\text{Al}^{3+}$ ,  $\text{H}^+$ , and  $\text{Cu}^{2+}$  type montmorillonites with  $\epsilon$ -caprolactam were increased beyond 10 nm. However, those of the  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Li}^+$  and  $\text{K}^+$  type montmorillonite were not changed by the 5 h treatment at 263 °C.

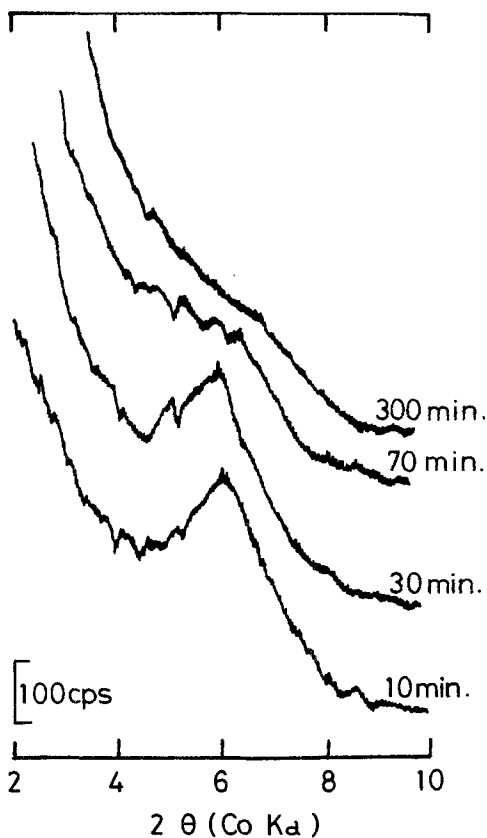


Fig. 4. XRD patterns of  $\text{Cu}^{2+}$  type montmorillonite/ $\epsilon$ -caprolactam mixture after various periods of treatment at  $263^\circ\text{C}$ .

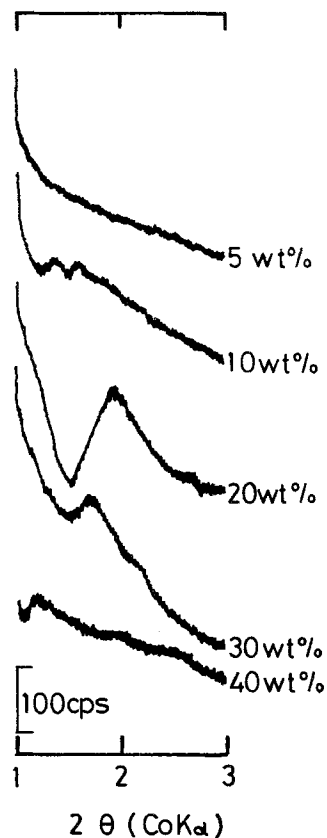


Fig. 5. XRD patterns of complexes with various 6-polyamide/ $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite ratio.

Table III. Interlayer distances of montmorillonites and that of the montmorillonite/ $\epsilon$ -caprolactam and montmorillonite/6-polyamide complexes

Type of montmorillonite	Interlayer distance (nm)			
		With $\epsilon$ -caprolactam		
		25 °C	80 °C	after $\times$ 5 h
$\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$	1.65	2.85	4.9	Ind.
$\text{Al}^{3+}$	1.59	1.71	1.7	Ind.
$\text{NH}_3^+(\text{CH}_2)_5\text{COOH}$	1.32	1.47	1.5	Ind.
$\text{H}^+$	1.32	1.51	—	Ind.
$\text{Cu}^{2+}$	1.22	1.51	1.5	Ind.
$\text{Mg}^{2+}$	1.51	1.51	1.5	1.60
$\text{Co}^{2+}$	1.49	1.51	—	1.86
$\text{Li}^+$	1.21	2.00	—	2.00
$\text{K}^+$	1.22	1.51	—	1.53

Ind. = Tendency to indefinite swelling.

## 4. Discussion

### 4.1. ROLE OF MONTMORILLONITE IN THE POLYMERIZATION

It is well known that the smectite clays such as montmorillonite act as Brønsted or Lewis acids and the acidity varies with the interlayer cation. The polymerization rate constant,  $k$ , was calculated by using the formula for first order reactions,

$$-\ln(1 - R_t) = kt. \quad (2)$$

As shown in Figure 6, the polymerization rate is dependent on the strength of the electric field around the interlayer cations. An EXAFS study on the  $\text{Cu}^{2+}$  type montmorillonite and its intercalated compound with  $\epsilon$ -caprolactam [11] suggests that  $\text{Cu}^{2+}$  in these compounds coordinated with water molecules even after vacuum drying at room temperature. Besides, the polymerization rate was increased by the addition of water molecules. These facts suggest that the polarized water molecules in the interlayer region of montmorillonite act as a Brønsted acid and opens the  $\epsilon$ -caprolactam rings to initiate the polymerization.

The results of the previous EXAFS study [11] and of this work suggest that the ring-opening polymerization of  $\epsilon$ -caprolactam is initiated by the cations existing in the interlayer region of layered silicates. The polymerization would be controlled not only by the acidity of the cations, but also by the swelling behaviour of the layered silicate by monomers of polymer molecules.

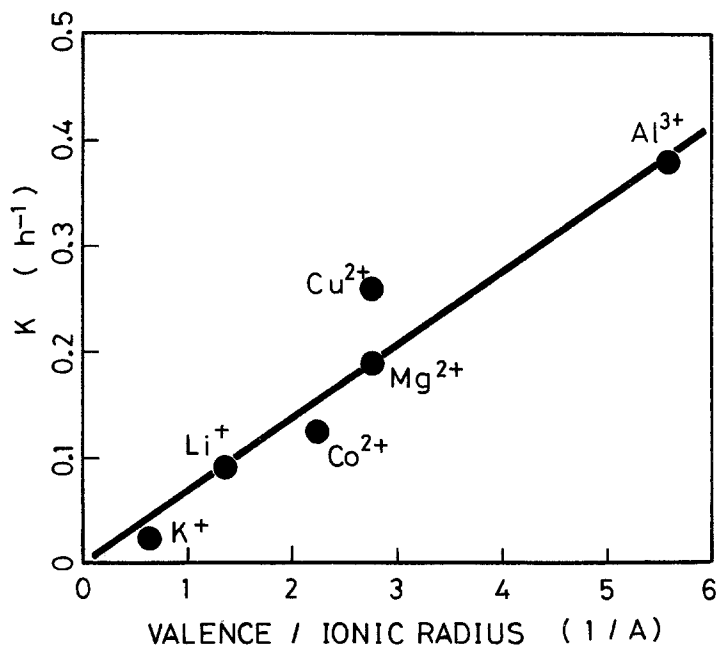


Fig. 6. Relationship between the polymerization rate constant,  $k$ , defined in Eq. (2) and the electric field strength around the cations.



## 4.2. SWELLING BEHAVIOUR OF MONTMORILLONITE

The swelling phenomena of montmorillonites are considered to be a result of a balance between the interlayer cohesive force and the force required to increase the interlayer distance. The latter force in this system would be the attractive force between interlayer cations and  $\epsilon$ -caprolactam molecules, which would be increased with the strength of the electric field around the cations, as discussed in the previous section. Since the cohesive force would be the van der Waals or ionic interaction, the cohesive force is expected to decrease with increasing interlayer distance.

As the attractive force between  $\epsilon$ -caprolactam molecules and polarized water molecules or cations would be strong enough to increase the interlayer distance, the intercalated compound of montmorillonites and  $\epsilon$ -caprolactam was formed. By heating at 80 °C, the attractive force would be enough to increase the interlayer distance of the  $\text{NH}_3^+(\text{CH}_2)_{11}\text{COOH}$  type montmorillonite from 2.85 nm to 4.90 nm, because of the weak interlayer cohesive force due to the large interlayer distance. However, in other montmorillonites, the interlayer cohesive force is strong enough to prevent further swelling. These results correspond well to the result of the study on the swelling behaviour of  $\text{CH}_3\cdot(\text{CH}_2)_{n-1}\text{N}^+(\text{CH}_3)_3$  type montmorillonite by liquid toluene, where only the montmorillonites with  $n \geq 12$  were swollen by toluene [12].

When the mixtures of montmorillonites and  $\epsilon$ -caprolactam are heated at 263 °C in ampoules, the driving force of swelling may be the polymerization energy of  $\epsilon$ -caprolactam. Since the polymerization energy was enough to increase the interlayer distance, the interlayer distance was increased remarkably in the system in which a high polymerization rate could be obtained.

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