

# Intercalation Chemistry of Aluminium Dihydrogentriphosphate with Weak Bases and Polymerization of Aniline between Its Layers

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**Abstract.** Weak bases such as 2-aminopyridine, 4-aminopyridine, *o*-phenylenediamine, *p*-phenylenediamine and aniline were intercalated into aluminium dihydrogentriphosphate (ADHP) using ultrasonic wave irradiation. The interlayer spacing of ADHP increased from 8.1 Å to 12.4–20.0 Å. From the values of the layer expansions and host/guest ratios, bilayer or monolayer structures were considered. Chemical oxidation of the aniline resulted in the formation of polyaniline in the ADHP layers.

**Key words:** Intercalation, aluminium dihydrogentriphosphate, nanocomposite, polyaniline.

## 1. Introduction

Many layered solids may act as host lattices and react with a variety of guest molecules to give intercalation compounds [1–4]. If the guest are organic compounds, the intercalation compounds are nano-scale composites consisting of organic and inorganic compounds. They are candidates for electronic devices and heterogeneous catalysts. We have been interested in preparing new intercalation compounds with a combination of various organic compounds and various inorganic layer compounds [5–9].

Aluminium dihydrogentriphosphate (ADHP) is one of a number of inorganic ion exchangers with a layered structure having the composition  $H_2M(III)P_3O_{10} \cdot 2H_2O$ , where  $M(III) = Al, Ga, V, Cr, Mn, \text{ or } Fe$  [10–12]. It has been reported that ADHP can intercalate alkylamines and aniline because ADHP has an acidic hydroxyl group [13]. The driving force of intercalation into the acidic host is believed to be ion – ion interaction between acidic sites of the host and basic sites of the guest. Therefore, for many acidic hosts, guests should be strong bases. For example weak bases were not intercalated into  $[TiNbO_5^-]$  layers. We have already reported that weak bases were intercalated into  $[TiNbO_5^-]$  layers only by a multistep intercalation in which a strong base was intercalated first and a weak base

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was reacted to exchange with the strong base [7, 14]. However, ADHP is a strong acid whose  $pK_a$  is 1.5 [15], indicating the possibility of direct intercalation of weak bases. Furthermore, the effectiveness of ultrasonic wave irradiation for intercalation has been reported [16–18]. Intercalation of organic compounds into inorganic hosts is usually a heterogeneous reaction. Acceleration of heterogeneous reactions by ultrasonic wave irradiation has been well documented [19]. In this study the intercalation of weak bases into ADHP layers by irradiating with ultrasonic waves was investigated in order to get a new class of organic intercalate.

## 2. Experimental

ADHP,  $AlH_2P_3O_{10} \cdot 2H_2O$ , was prepared from phosphoric acid and aluminium hydroxide. Phosphoric acid (3 mol) and aluminium hydroxide (1 mol) were heated in a porcelain crucible. A white powder was obtained from the viscous liquid. The powder was heated at 300 °C for 20 h. After washing with distilled water, the powder was dried at 70 °C for 5 h.

Intercalation of bases were carried out by irradiating with ultrasonic waves (300 W, 20 kHz) at room temperature for 24 h. Aminopyridines and phenylenediamines were reacted with ADHP in methanol. Tetradecylamine was reacted in benzene or water. Aniline was used without any purification.

Aniline and the aniline intercalate were chemically oxidized by using potassium persulfate as the oxidizing reagent.

Powder X-ray diffraction spectra were recorded on a Rigaku powder diffractometer unit using  $CuK_\alpha$  (filtered) radiation at 40 kV and 20 mA. Thermal analyses (TG/DTA) were carried out on a SEIKO SSC5000 thermal analysis instrument using a heating rate of 10 °C/min.

## 3. Results and Discussion

### 3.1. INTERCALATION OF TETRADECYLAMINE AND AMINOPYRIDINES

The X-ray diffraction pattern of ADHP is shown in Figure 1. The peaks were almost identical to those reported previously [11]. The interlayer spacing of ADHP is about 8.1 Å. By the heat treatment at 140 °C for 3 h, the interlayer spacing decreased to 6.4 Å indicating the dehydration of  $AlH_2P_3O_{10} \cdot 2H_2O$  to  $AlH_2P_3O_{10}$ . To obtain information on the intercalation of ADHP, a strong base, tetradecylamine, was reacted in water. The  $pK_b$  of tetradecylamine is 3.1, as shown in Table I. As the reaction proceeded, a part of the host floated, indicating that the product was hydrophobic. The sinking part was unreacted ADHP. X-ray diffraction patterns of the floating part are shown in Figure 1. The interlayer spacing increased to 38.4 Å. From the value of the layer expansion and the length of tetradecylamine, bilayer formation of tetradecylamine with tilting was suggested. Tetradecylamine was also reacted with ADHP in benzene. The same intercalate as that obtained in water

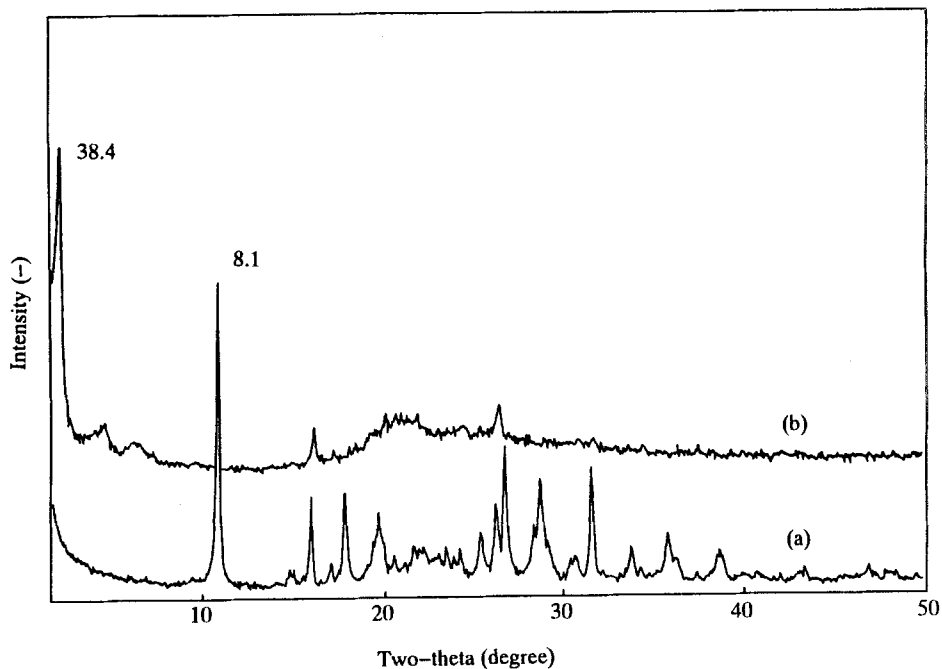


Fig. 1. X-ray diffraction patterns of (a) ADHP and (b) the tetradecylamine intercalate.

TABLE I. Organic guests reacted with ADHP.

Guest	$pK_b$
Tetradecylamine	3.1
4-Aminopyridine	5.4
2-Aminopyridine	7.2
4-Methylpyridine	7.9
Pyridine	8.8
<i>o</i> -Phenylenediamine	9.1
<i>p</i> -Phenylenediamine	9.1
Aniline	9.4

was produced more effectively than in water probably because the tetradecylamine intercalate was hydrophobic.

The  $pK_b$ s of 4-aminopyridine and 2-aminopyridine are 5.4 and 7.2, respectively. In the case of intercalation into  $HTiNbO_5$ , aliphatic amines were intercalated by direct thermal reaction. However, weak bases such as 4-aminopyridine and 2-aminopyridine were not intercalated. Irradiation with ultrasonic waves was not effective. Aminopyridine intercalates were obtained only by the multi-step method.

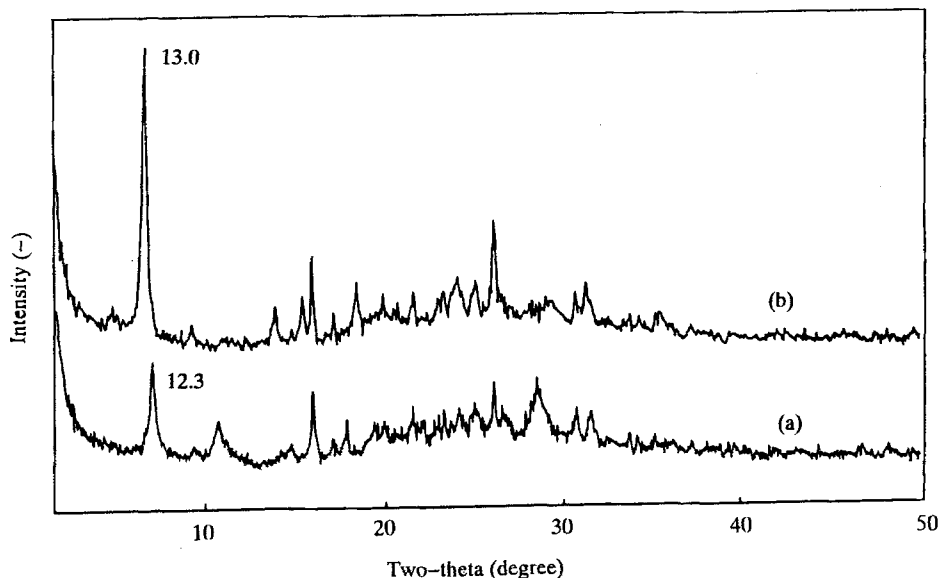
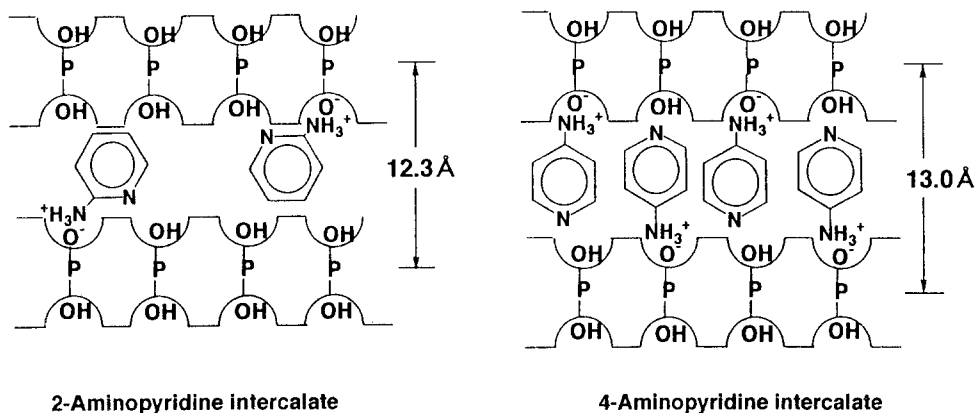


Fig. 2. X-ray diffraction patterns of (a) the 2-aminopyridine intercalate and (b) the 4-aminopyridine intercalate.

In the case of ADHP, aminopyridines were intercalated using ultrasonic wave irradiation. As shown in Figure 2, the interlayer spacing increased to 12.3 and 13.0 Å, respectively. The guest/host ratios calculated by elemental analyses were 0.23 for 2-aminopyridine and 0.48 for 4-aminopyridine. In the case of the aminopyridine intercalate in  $[\text{TiNbO}_5]$  layers, bilayer formation was suggested for the 4-aminopyridine intercalate because the interlayer spacing of the 4-aminopyridine intercalate was 23.2 Å. From the values of the layer expansions and the host/guest ratios, monolayer structures as shown in Figure 3 are suggested for the ADHP intercalate. In the case of 2-aminopyridine, pyridinium and anilinium ion may interact with the same layer surface. On the other hand in the case of 4-aminopyridine, pyridinium and anilinium ion may interact with different layer surfaces which face each other. The different results between  $\text{HTiNbO}_5$  and ADHP may result from the different configurations of acidic sites between the  $\text{HTiNbO}_5$  layers and the ADHP layers.

### 3.2. INTERCALATION OF PHENYLENEDIAMINES

Pyridine and 4-methylpyridine were reacted with ADHP using ultrasonic irradiation. No reaction occurred. Their  $pK_b$ s are 8.8 and 7.9, respectively. On the other hand the  $pK_b$ s of *o*-phenylenediamine and *p*-phenylenediamine are 9.1, as shown in Table I. They are weaker bases than aminopyridines and alkylpyridines. However, phenylenediamines were intercalated using ultrasonic wave irradiation as shown in Figure 4. The interlayer spacing increased to 20.2 Å for *o*-phenylenediamine



2-Aminopyridine intercalate

4-Aminopyridine intercalate

Fig. 3. Schematic representation of (a) the 2-aminopyridine intercalate and (b) the 4-aminopyridine intercalate.

TABLE II. Interlayer spacing and composition of intercalation compounds.

Guest	$d(\text{\AA})$	$\Delta d(\text{\AA})$	$x, y$ in ADHP (guest) <sub>x</sub> (H <sub>2</sub> O) <sub>y</sub>	
			$x$	$y$
—	8.1	—	—	—
4-aminopyridine	13.0	4.9	0.48	0.12
2-aminopyridine	12.3	4.2	0.23	0.07
<i>o</i> -phenylenediamine	20.0	11.9	0.51	0.56
<i>p</i> -phenylenediamine	14.6	6.5	0.50	0.89
aniline	15.5	7.4	0.51	0.71
	19.9	11.8	0.79	0.26

and 14.6 Å for *p*-phenylenediamine. The guest/host ratios were 0.51 and 0.50. From the values of the layer expansions and host/guest ratios, a bilayer structure for *o*-phenylenediamine and a monolayer structure for *p*-phenylenediamine were suggested, as shown in Figure 5. The interlayer spacing for *p*-phenylenediamine was 14.6 Å, larger than the value of 13.0 Å for 4-aminopyridine. The amounts of included water in the layer were larger in the phenylenediamine intercalates than in the aminopyridine intercalates. This indicates that the phenylenediamine intercalates have more space to include water than the aminopyridine intercalates.

### 3.3. INTERCALATION OF ANILINE

Aniline is a weak base with a  $pK_b$  value of 9.42. It has already been reported that aniline was intercalated into ADHP under ultrasonic wave irradiation although the detail was not reported [13]. X-ray diffraction patterns of aniline intercalates are shown in Figure 6. As the reaction proceeded, swelling occurred. Therefore, we could not prevent the presence of unreacted ADHP because some portion of the

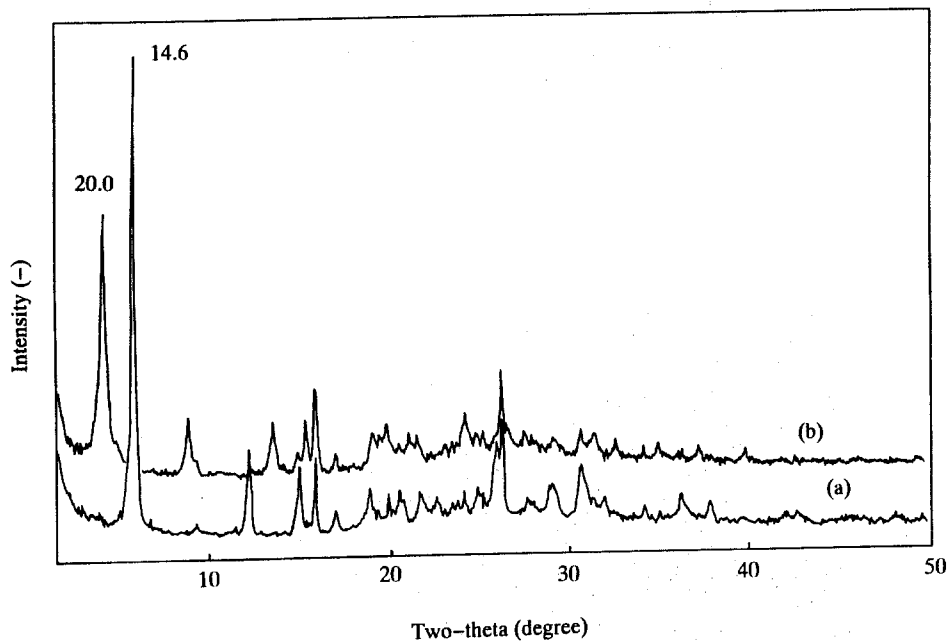


Fig. 4. X-ray diffraction patterns of (a) the *p*-phenylenediamine intercalate and (b) the *o*-phenylenediamine intercalate.

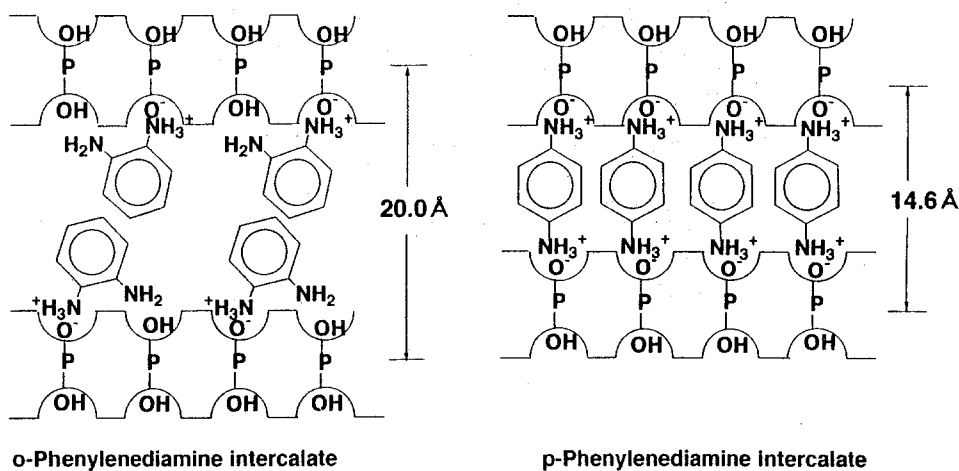


Fig. 5. Schematic representation of (a) the *o*-phenylenediamine intercalate and (b) the *p*-phenylenediamine intercalate.

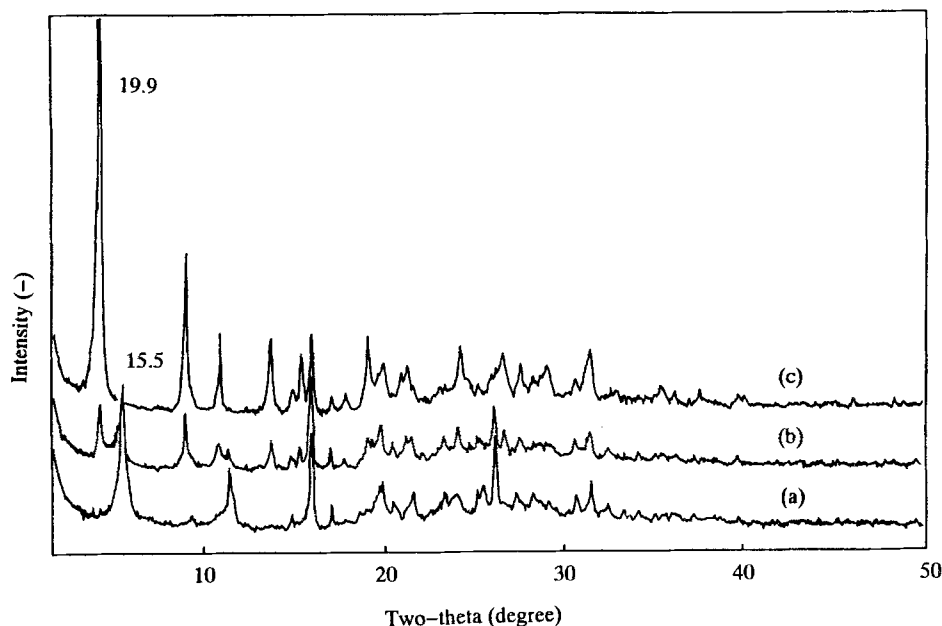


Fig. 6. X-ray diffraction patterns of aniline intercalates.

swelling reactant did not mix effectively, although the amount of unreacted host was small. The peak at 8.1 Å corresponds to unreacted ADHP. Three types of aniline intercalates were obtained. The interlayer spacing of the first type (type I) and the second type (type II) were 15.5 and 19.9 Å. The last type was the mixture of type I and II. The guest/host ratios of type I and II were 0.51 and 0.79, respectively. From the value of the layer expansion, a bilayer structure was suggested in the case of type II.

#### 3.4. POLYMERIZATION OF ANILINE BETWEEN ADHP LAYERS

Conducting polymers – inorganic hybrid materials have been the object of intense investigation because they can possess novel electrical and structural properties [20–22].

It has been reported that the redox intercalative polymerization of pyrrole, thiophene and aniline to the corresponding conjugated polymers in  $V_2O_5 \cdot nH_2O$  and  $FeOCl$  produce well-ordered compounds [23–25]. The process works with suitably oxidizing hosts. Recently, one-dimensional polypyrrole, polyfuran and polyaniline were obtained by intercalative polymerization in zeolite [26]. Furthermore, encapsulation of polyaniline followed by the chemical oxidation of aniline in zirconium phosphates [27] and polyaniline itself in  $MoS_2$  [28] were reported. Polyaniline is black; however, the aniline intercalates obtained in this study were not black, indicating that aniline in the ADHP layer did not polymerize in the course of intercalation.

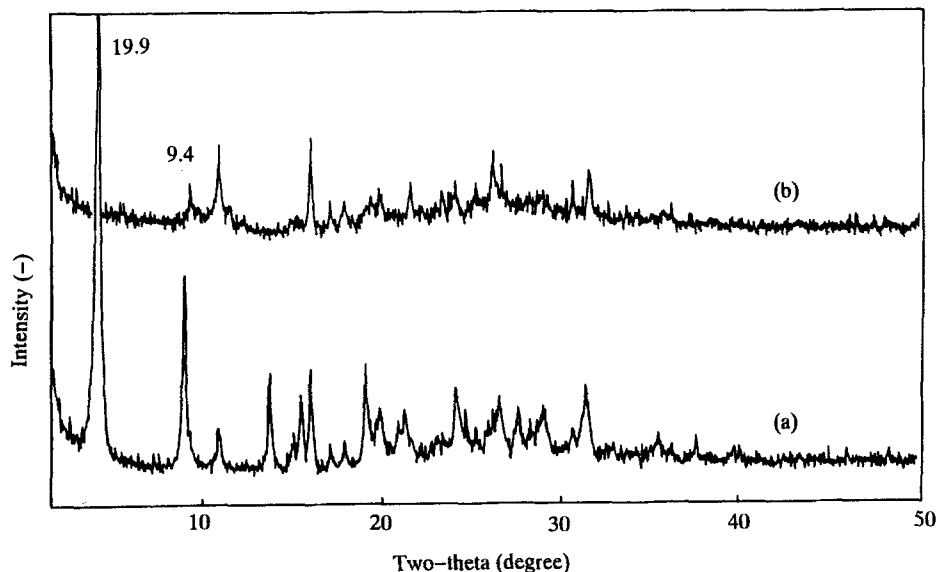


Fig. 7. X-ray diffraction patterns of (a) the aniline intercalate and (b) the oxidation product of the aniline intercalate.

It is well known that aniline is readily oxidized chemically, giving polymerization products [29, 30]. Due to the oxidation reaction, the white powder gradually changed to black, indicating the occurrence of a polymerization reaction. After the chemical oxidation of the type I intercalate, the intense peak at  $19.9 \text{ \AA}$  in the XRD trace disappeared, as shown in Figure 7. The peak of unreacted ADHP and a small peak corresponding to an interlayer spacing of  $9.4 \text{ \AA}$  were observed. By the chemical oxidation of the type II intercalate, the same peaks were observed. There was a possibility of an exchange reaction of aniline with ammonium ion which was used as a counter ion of the oxidizing agent. However, the interlayer spacing of the ammonium ion intercalate was near  $8.8 \text{ \AA}$  [11]. In the case of zirconium phosphate, the layer spacing increased from  $7.6 \text{ \AA}$  to  $10.4 \text{ \AA}$ , indicating an expansion of  $2.8 \text{ \AA}$  [27]. The interlayer spacing of dehydrated ADHP is  $6.4 \text{ \AA}$ , as already described. It indicates that the value of the layer expansion in this study was about  $3 \text{ \AA}$ . However, the peak at  $9.4 \text{ \AA}$  was not large indicating the possibility of the formation of an amorphous type compound.

Thermal analysis of ADHP (Figure 8) shows that water within the interlayer was evolved at a temperature from  $70$  to  $150 \text{ }^\circ\text{C}$ , and the weight loss was about  $11\%$ , close to the calculated value of  $11.3\%$ . The weight loss of the aniline intercalate was stepwise. Weight losses from  $70$  to  $154 \text{ }^\circ\text{C}$ , and from  $154$  to  $224 \text{ }^\circ\text{C}$ , were  $11.1$  and  $12.5\%$ , respectively. From the composition, water was included with the intercalation of aniline. Therefore, evolution of adsorbed aniline and water occurred at  $154$  to  $224 \text{ }^\circ\text{C}$ . In the case of the oxidation product, the weight decrease from  $70$  to  $154 \text{ }^\circ\text{C}$  was  $11\%$ , the same as that of ADHP itself. However, a weight decrease



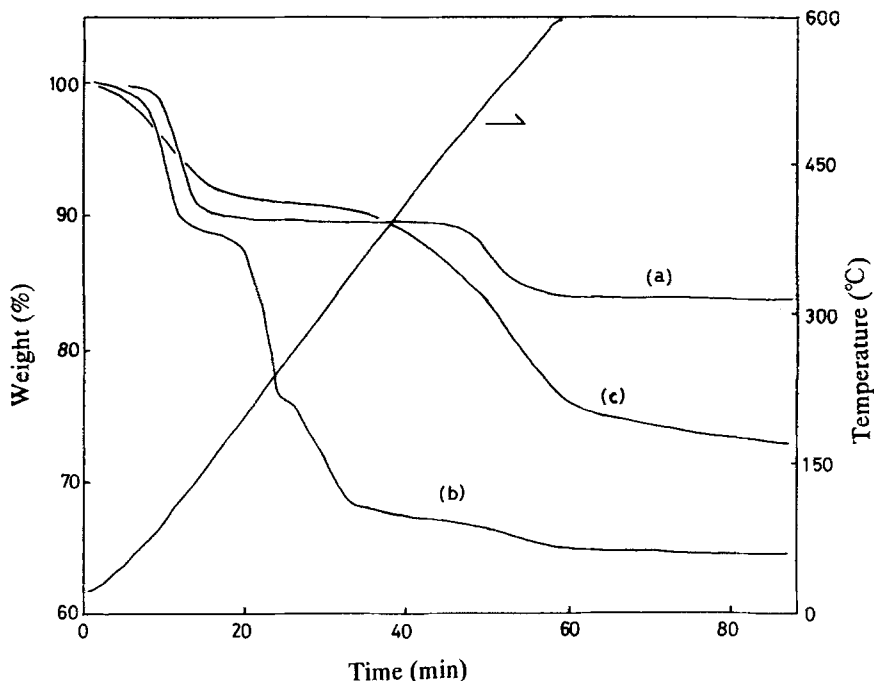


Fig. 8. Thermal analyses of (a) ADHP, (b) the aniline intercalate and (c) the chemical oxidation product of the aniline intercalate.

from 154 to 224 °C was not observed. It indicated that water adsorbed with aniline and some aniline were desorbed in the course of polymerization. The random polymerization may cause various shrinkage of the interlayer spacing resulting in an amorphous type compound. Also the weight decrease from 224 to 424 °C was small. It shows that almost all the monomeric aniline had already reacted to give polyaniline.

A SEM micrograph of ADHP shows plate-like pieces with sharp edges; even on intercalation of aniline the sharp edges did not change. The chemical oxidation products are slightly round, however, we could recognize ADHP pieces clearly, as shown in Figure 9 (b). Figure 9 (a) shows the polyaniline alone, which was made under the same oxidation conditions as the aniline intercalate. Block and spherical polymer particles were clearly observed. These results indicate that aniline was intercalated in the ADHP layers and chemically polymerized mainly in the layers.

We have previously reported that a method of exfoliation followed by its restacking was effective for the intercalation of non-donor and weak donors into MoS<sub>2</sub> layers [31]. Both polyaniline [28] and aniline were intercalated into MoS<sub>2</sub> layers by using the exfoliation – restacking method. On intercalation of aniline the host layer expanded from 6.2 to 12.1 Å. The layer distance of the polyaniline intercalate was 10.4 Å. However, even during the treatment of the aniline intercalate into MoS<sub>2</sub>

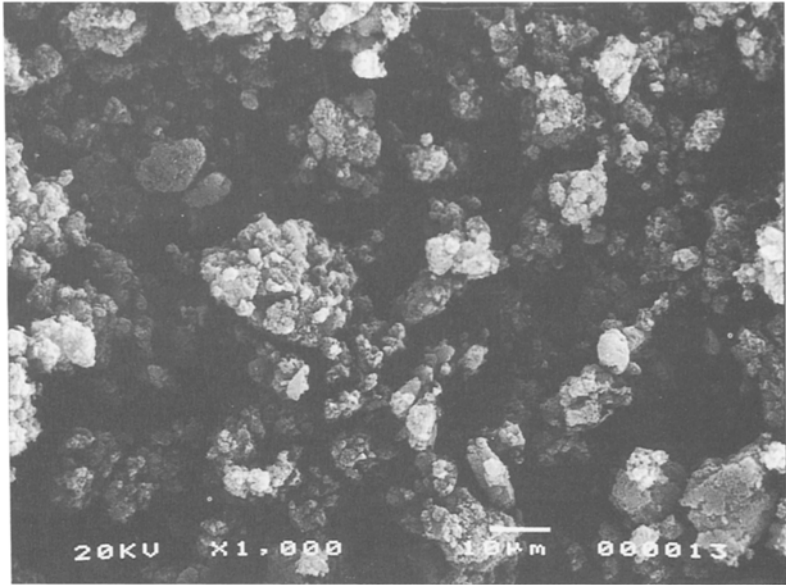
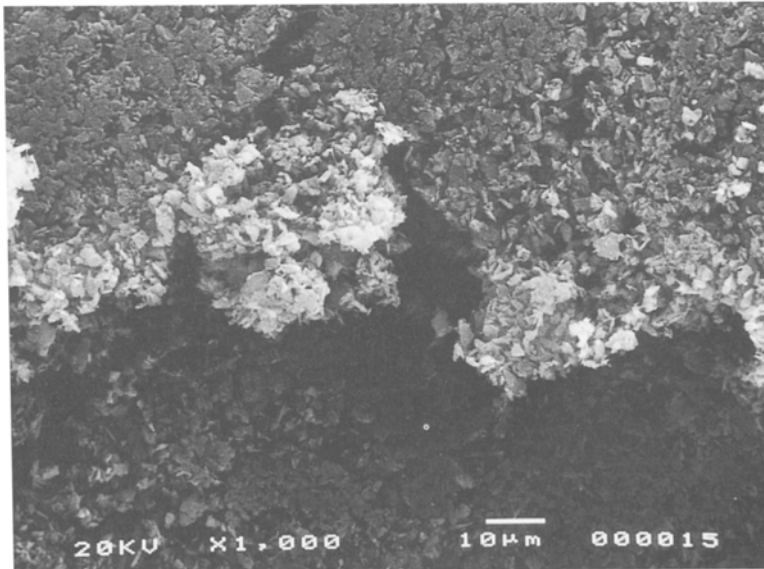
**(a)****(b)**

Fig. 9. SEM photograph of (a) polyaniline and (b) the chemical oxidation product of the aniline intercalate.

TABLE III. Electronic conductivity of ADHP and the intercalation compound.

compound	electronic conductivity (S/cm)
ADHP	$2.29 \times 10^{-6}$
polyaniline	$2.90 \times 10^{-1}$
aniline intercalate <sup>a</sup>	$1.91 \times 10^{-3}$

<sup>a</sup> Aniline intercalate after oxidative polymerization.

by a chemical oxidizing agent, a change of the layer distance was not observed. It indicated that no polymerization of aniline occurred in the host in the case of a host with electronic conductivity such as MoS<sub>2</sub>.

The conductivities of polyaniline and ADHP themselves are 0.29 and  $2.3 \times 10^{-6}$  S/cm, respectively, as shown in Table III. The conductivity of polyaniline intercalated in MoS<sub>2</sub> was reported as 0.4 S/cm because MoS<sub>2</sub> is a host with electronic conductivity [28]. However, the conductivity of polyaniline intercalated in ADHP was as small as  $1.9 \times 10^{-3}$  S/cm because ADHP is an insulator host.

The high polarization of polyaniline is well known. Polyaniline intercalated in ADHP gives interesting materials of high polarization materials coated by an insulator compound.

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