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Intercalation of Dendritic Polyamines by α- and γ-Zirconium Phosphates

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Tridentate polyamines, $N(CH_2CH_2NH_2)_3$ and $N(RNH_2)_3$ ($R = CH_2CH_2CONHCH_2CH_2$), react with both α- and γ-zirconium phosphates to give an intercalated phase in which the amine molecules are fully loaded as an interdigitating monolayer with their flatted molecular planes highly titles relative to the inorganic layers. On the other hand, although hexadentate polyamine, $N(RN(RNH_2)_2)_3$, forms a more expanded intercalate from its dilute solution, the longer chain amine can not be intercalated from its concentrated solution, due to the entanglement of dissolved molecules.

Much attention has been focused on the preparation of nanocomposite solids via the pillaring of inorganic layered compounds with organic or inorganic oligomeric species.[1,2] This pillaring approach has been developed based on studies concerning the structural and bonding properties of intercalation compounds containing simple-shaped, linear or ring, guest molecules. Many studies have been reported concerning the intercalation properties of alkylmono- and diamines for a wide variety of layered compounds, such as smectites,[3] tetravalent metal phosphates[4a] or phosphonates,[4b] alkali metal titanates[5] and perovskite-type niobates.[6] The arranging manner of intercalated amine molecules in the interlayer space of these host matrices has been clarified mostly from the carbon number dependence of the interlayer spacing and amine content observed in each system. Our previous study was accompanied by a side observation that the intercalation of *n*-alkylmonoamines by α-carboxylated zirconium phosphonate occurs selectively for *n*-heptylamine, leading to a new class of host–guest processes based on molecular-assembly recognition.[7] Similar extensive studies have appeared concerning the intercalation of pyridine for many layered hosts,[8—12] including a recent report on a full structure analysis of the pyridine intercalate of protonic titanate.[12] In contrast to such linear or ringed amines, however, very few data are available concerning the intercalation behavior of nonlinear polyamines containing more than three amino groups.

Previously, we observed a striking contrast between the two parent α- and γ-zirconium phosphates as host matrices for pyridine,[9] basic amino acids,[13] aminated β-cyclodextrins,[14] and crown ether.[15] These observations arouse our interest to compare the intercalation properties of polyamines for both zirconium phosphates.

Attempts were thus made to examine the intercalation of tris(2-aminoethyl)amine (**1**) and two polyamidoamines, $N(RNH_2)_3$ (**2**) and $N(RN(RNH_2)_2)_3$ (**3**) ($R = CH_2CH_2CONHCH_2CH_2$), by α- and γ-zirconium phosphates (Scheme 1).

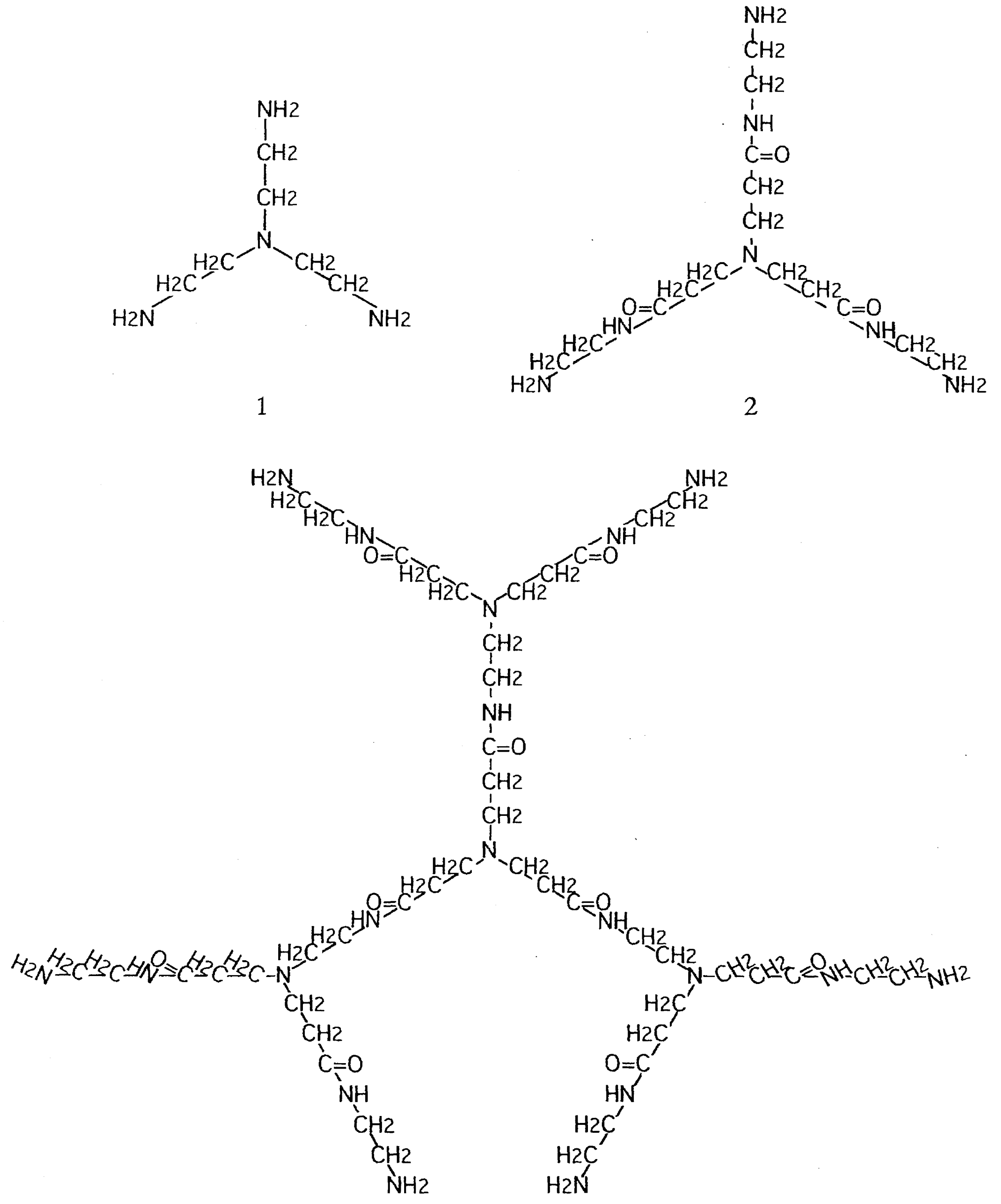
Experimental

The α- and γ-zirconium phosphate samples used were obtained similarly to those used in a previous study.[15] The polyamine 1 was reagent grade and used without further purification. The other two amidoamines were prepared in a manner reported by Tomalia and Dewald.[16] Ammonia was used as a core to obtain both dendritic amines by a stepwise Michael-type addition of methyl acrylate and an ester–amide exchange reaction with ethylenediamine at room temperature, followed by their characterization by ^1H and ^{13}C NMR. After 0.1 g of the α- or γ-zirconium phosphate sample was mixed with 4 cm^3 of an aqueous polyamine solution at varying ratios of [amine]/[Zr], stirring at 25 °C took place for 7 d. This equilibration time was selected after preliminary experiments to produce an invariant pH. The resulting mixtures were centrifuged, fully washed with water, and freeze-dried.

Thermogravimetric measurements were carried out at a heating rate of 10 $°C\,min^{-1}$ in air with a Shinku Riko TGD-5000 thermobalance. X-Ray diffraction measurements were performed on a Shimadzu XD-D1 diffractometer with Cu $K\alpha$ radiation using tetradecan-1-ol as an external standard. Infrared absorption spectra were measured by the KBr pellet method using a JASCO FTIR 3000 spectrometer.

Results and Discussion

The reaction products with **1** and **2** in the α- and γ-zirconium phosphate/amine systems were primarily characterized by their X-ray diffraction patterns, shown in Figs. 1(a) and 1(b), and by those in Figs. 2(a) and 2(b). With increasing addition of **1** or **2**, the peak at $2\theta = 11.6°$ ($d = 0.76$ nm) or $7.18°$ ($d = 1.23$ nm) due to the 002 reflection of the host phase in each system rapidly decreased in intensity, and eventually disappeared, while a new diffraction peak appeared in the lower 2θ range along with its second-order counterpart, indicating the formation of an intercalated phase. The interlayer spacings of the resulting intercalates were determined from the 002 reflection in the X-ray diffraction patterns; also, the thickness of the intercalate portion (Δ) was obtained by subtracting the thickness of the inorganic layer (0.74 nm for α-zirconium phosphate or 0.94 nm for γ-zirconium phosphate)



1 2 3

Scheme 1. Polyamines used.

from the observed spacing, as done previously.[9,13—15] In both phosphate systems, the interlayer spacing of the resulting intercalate with **1** or **2** increased along with the amount of amine added, and reached a constant value, as shown in Fig. 3. The X-ray diffraction patterns of the resulting solids with **1** and **2** also show a weak halo band in the 2θ range (20—25°), suggesting that their host phases are partially hydrolyzed into some amorphous phase, e.g., $ZrO(OH)_2$, as observed for the intercalation of alkyldiamines by α-zirconium (carboxyehyl)phosphonate.[17]

The FT-IR spectra of the resulting solids of α-zirconium phosphate with or without polyamines **1** and **2** are shown in Fig. 4. The typical bands for the host phosphate are present at 3593 [ν(O–H)], 3510 [ν(O–H)], 1618 [δ(H–O–H)], 1249 [ν(P=O)], 1068 [$\nu_{sym}(PO_3)$], and 964 cm^{-1} [δ(P–OH)].[18—20] The addition of polyamines gives rise to a very broad band centered near to 3000—3100 cm^{-1} due to $\nu(NH_3^+)$, the so-called ammonium absorption band, and bands at 1627—1648 and 1550—1558 cm^{-1} which are attributable to $\delta(NH_3^+)$ and/or ν(C=O) or amide I and ν(N–H) or amide II, respectively. All of those are superimposed on bands other than the 3593, 3510, and 1618 cm^{-1} bands associated with the structural water observed for the host phosphate. A similar observation was made for the intercalates of γ-zirconium phosphate with polyamines **1** and **2**. It is thus most likely that the intercalated polyamine molecules are ionically bonded through their ammonated termini to the PO$^-$ sites in both systems.

The thermogravimetric curves for the resulting solids with **1** and **2** showed three or four steps at temperatures of up to

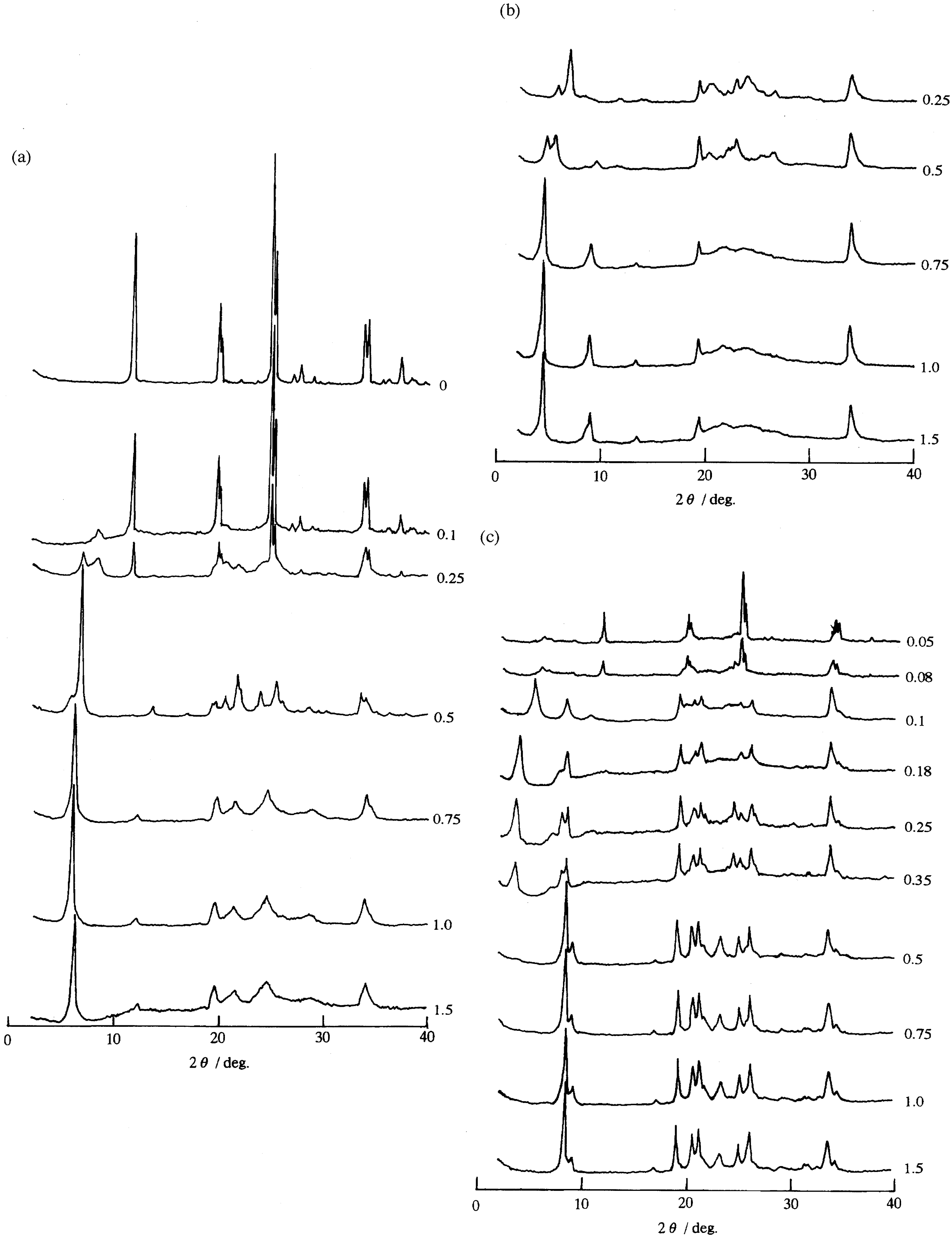


Fig. 1. X-Ray diffraction patterns of α-zirconium phosphate and its reaction products with **1** (a), **2** (b), and **3** (c) at their addition levels indicated in mol per mol of host phosphate.

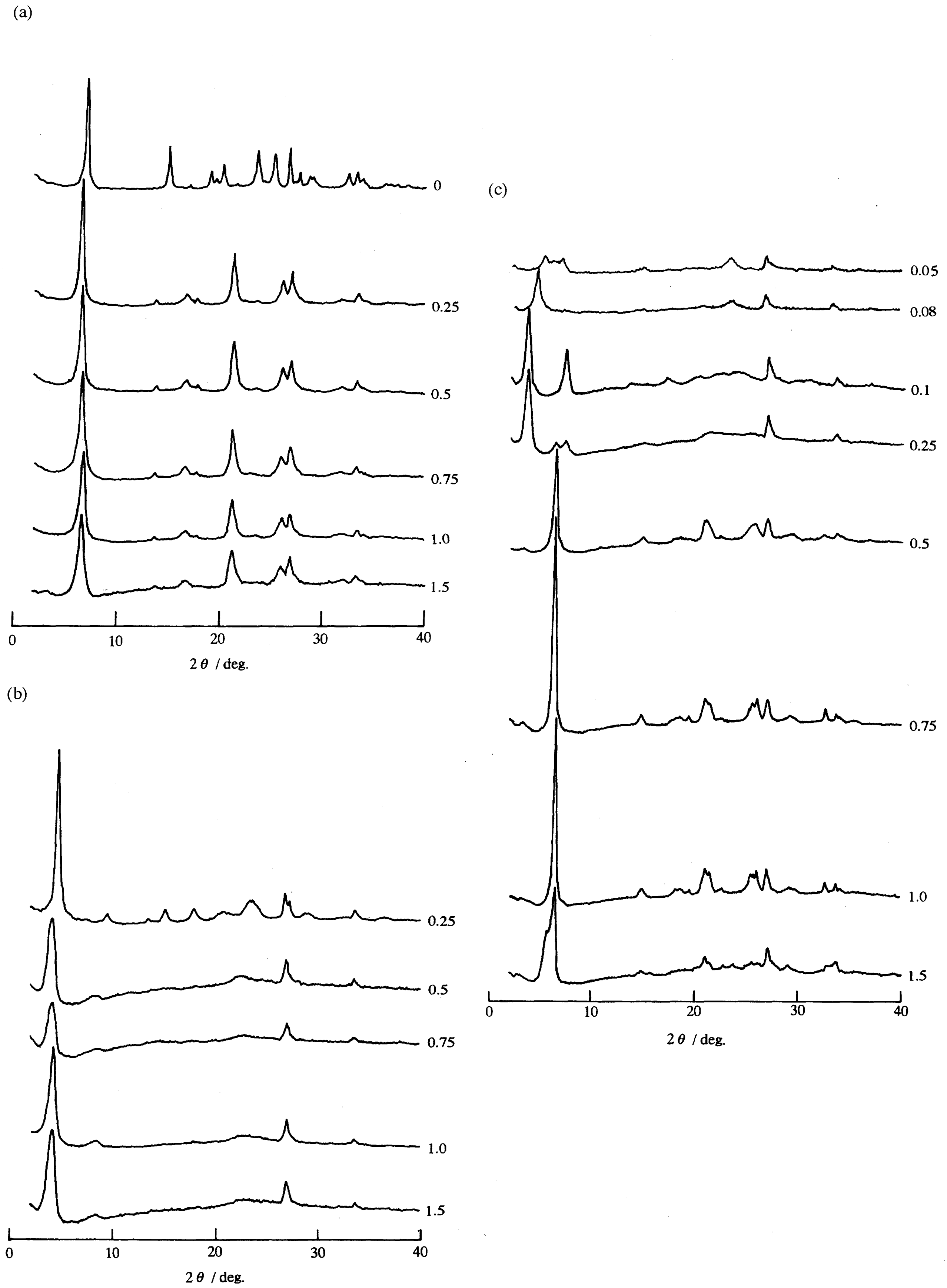


Fig. 2. X-Ray diffraction pattern of γ-zirconium phosphate and its reaction products with **1** (a), **2** (b), and **3** (c) at their addition levels indicated in mol per mol of host phosphate.

1000 °C, as shown for two selected systems in Fig. 5. The first weight loss at below 100 °C is due to the desorption of interlayer water; the second in the temperature range of 100—300 °C is assignable to partial desorption of the organic moiety. The third and/or fourth weight loss at above 300 °C is primarily due to desorption of the residual organic moiety and partly to condensation of the hydrogen phosphate groups, which occurs in one step near to 400 °C for the α form and in two steps at 300 and 800 °C for the γ form. The amine uptakes in moles (x) per formula weight of α- or γ-zirconium phosphate were determined by the combined use of thermogravimetric data for both of the resulting solids and their host phosphates. The uptakes of **1** and **2** by either α- or γ-zirconium phosphate increased up to a constant value, as shown in Fig. 6. Table 1 lists the intercalation parameters for the resulting intercalates with **1** and **2** at their full loadings.

In striking contrast to the uptakes of **1** and **2**, the uptake processes in the α- and γ-zirconium phosphates/**3** systems showed two different stages, depending on the amount of amine added. At the first uptake stage, the α-system yielded an intercalated phase with an interlayer spacing of 2.49 nm along with a minor phase with that of 1.04 nm; the γ-system gave only an intercalated phase with an interlayer spacing of 2.36 nm, as shown in Figs. 1(c), 2(c), and 3. The IR spectra of the resulting solids for both systems exhibited the same $\delta(\mathrm{NH}_3^+)$ bands at 1637—1654 and 1540—1558 cm^{-1}, overlapped with ν(C=O) and ν(N–H) bands, respectively, as those observed for the intercalated solids with **1** and **2**, as exemplified for the α-system in Fig. 4. With a further addition of the amine, however, the major phases in the α- and γ-systems were changed into the 1.04 nm phase and an intercalated phase with an interlayer spacing of 1.37 nm, respectively (Figs. 1(a), 1(b), and 3). By comparing the observed d values of the resulting solids with those in the literature,[21,22] the 1.04 and 1.37 nm phases were assigned to the ethylenediamine intercalates of α- and γ-zirconium phosphates, respectively. This assignment is not incompatible with the IR data (Fig. 4). The molar uptake of amine reduced to that of the polyamine **3** per mol of phosphate decreased rapidly from 0.11 to 0.03 for the α-system or from 0.08 to 0.04 for the γ-system (Fig. 6). No high spacing phases were also observed to occur as an intermediate product during the reaction at high addition levels. When the reaction mixture with **3** at a level of 0.5 in amine-to-Zr ratio or 0.04 mol dm^{-3} in concentration was diluted five times with water in each system, a small portion (α-system), or nearly half (γ-system) of the ethylenediamine intercalate formed before dilution, was converted into the same high spacing phases as those formed directly at low addition levels. These facts suggest that the material of polyamine **3** used is contaminated by a small amount of ethylenediamine, and that the contaminant was selectively taken up by both host phosphates in concentrated solutions of **3**. A broad halo band, indicative of the partial hydrolysis of the host phosphate by polyamines,

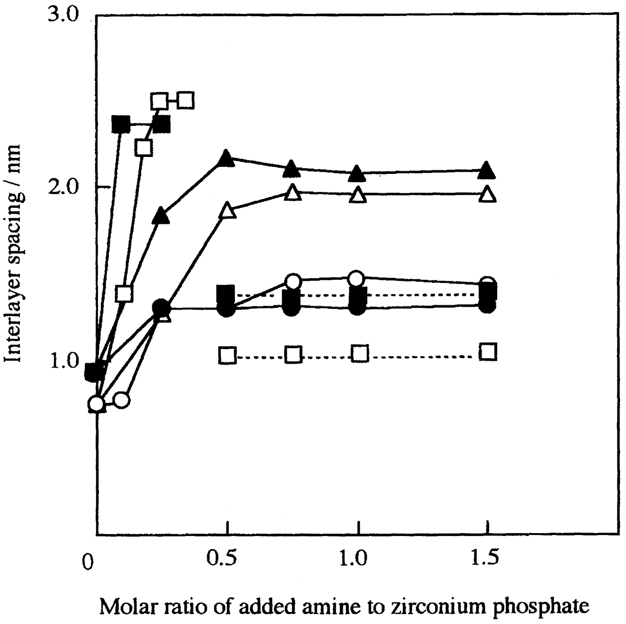


Fig. 3. Interlayer spacing as a function of polyamine added for the resulting intercalates of α- and γ-zirconium phosphates with **1** (○, ●), **2** (△, ▲), and **3** (□, ■). Open and solid symbols refer to the α- and γ-systems, respectively. See text for the keyes ---□--- and ---■---.

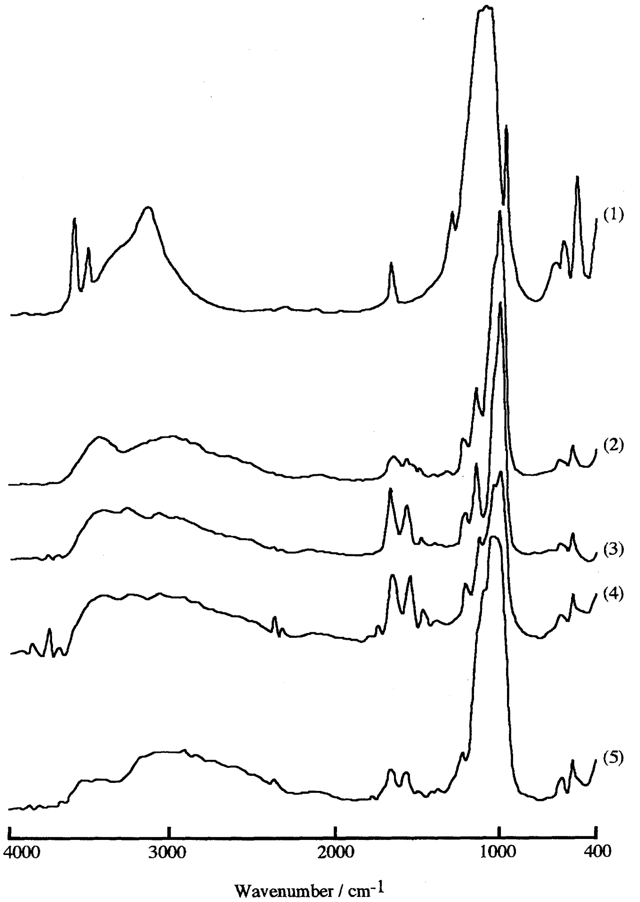


Fig. 4. FT-IR spectra of α-zirconium phosphates (1) and their reaction products with **1** (2), **2** (3), and **3** (4,5). Amount of **1**, **2** or **3** added (mol per mol of host phosphate): (2—3) 1.0, (4) 0.25, and (5) 1.0.

Table 1. Interlayer Spacing and Composition of Intercalates of α- and γ-Zirconium Phosphates with **1**, **2**, and **3**

		α-Zirconium phosphate			γ-Zirconium phosphate		
Amine	Amine added mol/mol Zr	Interlayer spacing/nm	Δ/nm	Composition[a]	Interlayer spacing/nm	Δ/nm	Composition[a]
1	1.5	1.46	0.72	0.41	1.30	0.36	0.18
2	1.5	1.96	1.22	0.38	2.10	1.16	0.26
3	0.25	2.49	1.75	0.11	2.36	1.42	0.08
	1.5	1.04	0.30	0.03[b]	1.37	0.43	0.04[b]

a) In molar ratio of amine to Zr, or x in $Zr(HPO_4)_2(amine)_x \cdot yH_2O$ for the α system or $ZrPO_4(H_2PO_4)(amine)_x \cdot yH_2O$ for the γ system. b) The value refers to the ethylenediamine content reduced to that of **3**.

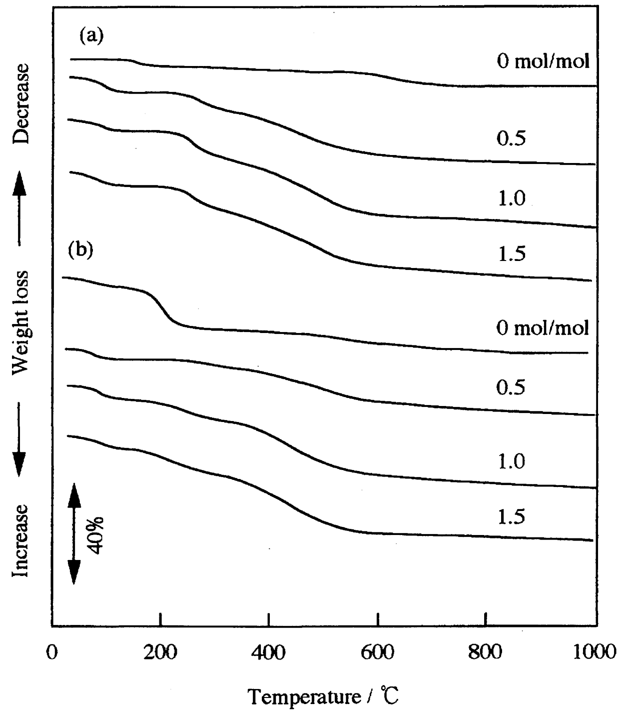


Fig. 5. TG curves for the host and the intercalated phases in (a) α-zirconium phosphate/**1** and (b) γ-zirconium phosphates/**2** systems. Amount of amine added is indicated in mol per mol of host phosphate.

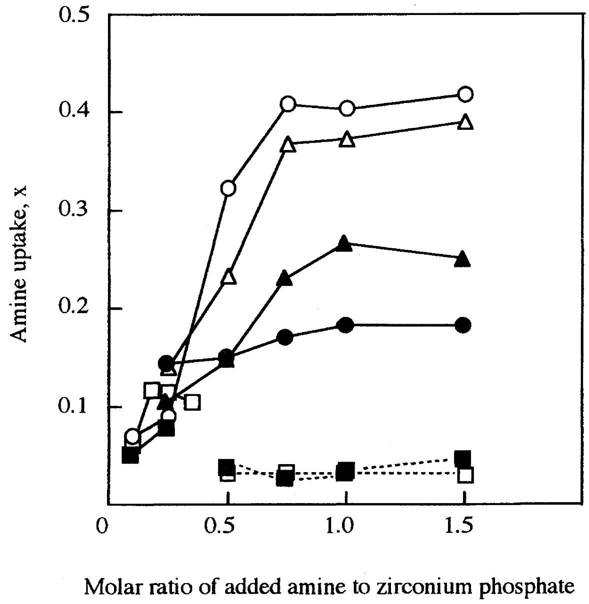
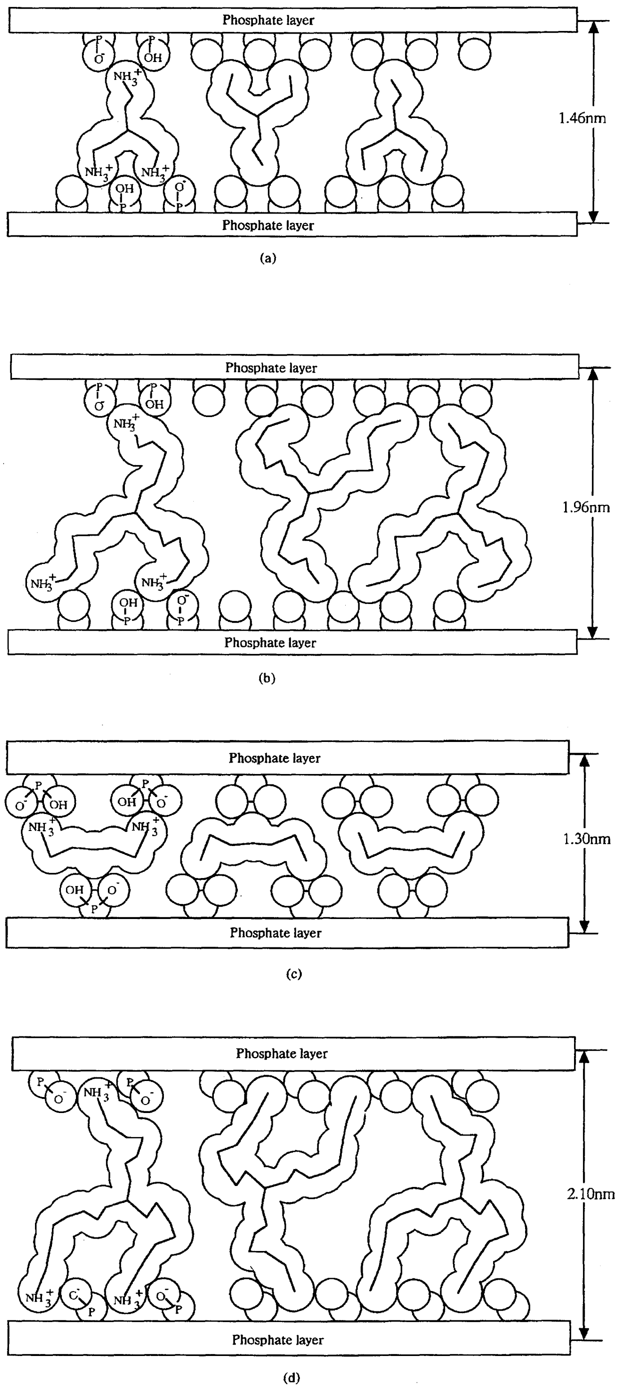


Fig. 6. Uptake of **1**, **2**, or **3** by α- and γ-zirconium phosphates as a function of polyamine added. Key as in Fig. 3.

was observed over the entire range of amine added for both the α- and γ-zirconium phosphate/**3** systems (Figs. 1(c) and 2(c). The intercalation parameters for the resulting intercalates with **3** are summarized in Table 1.

The arranging manner of intercalated polyamine molecules in the resulting solids can be estimated from the observed intercalation parameters on the basis of the crystal structure of their host phases as well as the dimensions of the amine molecules. α-Zirconium phosphate possesses a layer structure in which each layer consists of plane of zirconium atoms bridged through phosphate groups located alternately above and below this plane.[18] Three oxygen atoms of the tetrahedral phosphate group are bonded to three zirconium atoms in the plane, and the fourth oxygen atoms bears a hydrogen and points toward an adjacent layer in the structure. The POH groups pointing up or down in each layer surface are located in a monoclinic cell with distances of 0.92 and 0.53 nm along the a and b axes, respectively.

According to the Corey–Pauling–Koltun (CPK) model, the tridentate polyamine **1** molecule with its flat conformation is a triangular prism in shape, with a van der Waals thickness of 0.42 nm and a side of 0.92 nm. The observed x value of 0.41 or ca. 2/5 for the maximum amine uptake in the α-zirconium phosphate/polyamine **1** system indicates that the tridentate molecules with their flat conformation are arranged as a monolayer to effectively occupy five POH sites per molecule by a mode in which they anchor through each three ammonium-ionic termini alternately to every two pointing-up or one pointing-down POH site along the b-axis in the lower and upper inorganic layers, as shown in Scheme 2(a). The observed value of 0.72 nm for the thickness of the amine monolayer also means that the monolayered amine molecules 0.80 nm high would be placed with their molecular planes tilted by ca. 64° relative to the inorganic layer. The horizontal component of the molecular height is 0.35 nm, being in close agreement with 0.307 nm for the shift of the pointing-up POH groups along the a-axis, relative to those pointing down in any adjacent layer. Although the polyamine **2** molecule is much longer in chain length than **1**, the amine uptake (x) of 0.38 for the former is close to 0.41 for the latter. This fact sug-



Scheme 2. Schematic representation of the probable arrangement of polyamine molecules in the interlayer space of (a,b) α- and (c,d) γ-zirconium phosphates. Polyamine: (a) **1**, (b) **2**, (c) **1**, and (d) **2**.

gests that the tridentate polyamine **2** molecules with their flat and compact conformation, roughly 1.38 nm long, 1.0 nm in width and 0.42 nm in thickness, would be arranged as an interdigitating monolayer along the *b*-axis with their molecular planes tilted by 62° relative to the inorganic layer, in nearly the same proportion of one molecule per every five POH sites as observed for the polyamine **1**, as shown in Scheme 2(b). Although the molecular structure of the polyamine **3** is much more complex, the ratio in molecular volume of **3** to **2** can be evaluated approximately as $(9v+v/8)/(3v+v/8)$ or 2.92, where v is the volume of the aminoethylamidoethyl group $-CH_2CH_2CONHCH_2CH_2NH_2$. It is noted that the amine uptake ratio of **3** to **2** for the α-system, 0.11/0.38 or 0.29, is close to a value of 0.34 for the reciprocal of their molecular volume ratio. It is therefore most likely that the hexadentate polyamidoamine molecules would also be arranged as a monolayer with their flat conformation to occupy 2/0.11 or 18 POH sites per molecule.

The γ-zirconium phosphate is formulated as $ZrPO_4H_2PO_4 \cdot 2H_2O$, in which two planes of zirconium atoms are linked through PO_4 groups, with tetrahedral $PO_2(OH)_2$ groups bonded to any two zirconium atoms in either plane.[23] The $PO_2(OH)_2$ groups in each layer surface are located in an orthorhombic cell with distances of 0.54 and 0.66 nm along the *a* and *b* axes, respectively. Any two polyamine molecules can be unlikely bonded to one $P(OH)_2$ group if the steric hindrance between them is taken into consideration. On the basis of the CPK models of the intercalated amine molecules as well as the observed uptakes of **1** and **2**, $x = 0.18$ and 0.26, respectively, it is likely that the polyamine molecules with their flat conformation would be arranged as a monolayer and grafted through their ammonium-ionic termini to the POH sites along the *a*-axis in the upper or lower phosphate layer at the $P(OH)_2$/amine ratio of roughly 6 for **1** or 4 for **2**, as shown in Scheme 2(c) and (d). The higher uptake for **2** than that for **1** might be because the longer chain molecules with conformationally higher flexibility are available for bonding through their cationic termini to the P(OH) site projected obliquely from the layer surface. It is also noted that the intercalated molecules of **2** in the γ-system are oriented is a similar manner as those in the α-system, whereas the monolayered molecules of **1** in the former are arranged with their planes approximately parallel to the inorganic layer, in contrast to the tilted form in the latter. The amine uptake ratio of **3** to **2** for the γ-system is 0.08/0.26 or 0.31 and this value is in close agreement with 0.34 for the reciprocal of their molecular volume ratio, as in the α-system. The hexadentate polyamidoamine molecules in the γ-zirconium phosphate/**3** system would also be arranged as a monolayer with their flat conformation to occupy 1/0.08 or 13 $P(OH)_2$ sites per molecule.

The extended chain length of the polyamine **3** molecule from the central to terminal nitrogen atoms is taken to be 1.65 nm. If the concentration of polyamine in aqueous solution is referred to as C, the intermolecular distance (ξ) is given by $\xi = 1/(N_A C)^{1/3}$, where N_A is Avogadro's number. The critical amine concentration of 0.04 mol dm^{-3} gives a ξ value of 3.43 nm, being less than twice the value of 1.85 nm for the van der Waals radius of the polyamine **3**, or 3.7 nm. Such close contact of long nonlinear chain molecules would result in molecular entanglement, which may be spatially and energetically disadvantageous for the penetration of the guest species into the interlayer space of the host phosphate. It would lead to selective intercalation of the small contaminant molecules of ethylenediamine in concentrated solutions of **3**. This fact also means that the layered zirconium phosphates are applicable as adsorbents in the purification of crude products of dendritic polyamines or other related polymers through such an intercalation reaction.

References

1) T. J. Pinnavia, *Science*, **220**, 365 (1983).

2) Y. Ding, D. J. Jones, P. Maireles-Torres, and J. Roziere, *Chem. Mater.*, **7**, 562 (1995).

3) A. Weiss, *Angew. Chem.*, **2**, 134 (1963).

4) a) A. Clearfield and B. M. Tindwa, *J. Inorg Nucl. Chem.*, **41**, 871 (1979); b) L. Kornyei, L. Szirtes, and U. Costantino, *J. Radioanal. Nucl. Chem.*, **89**, 331 (1985); T. Kijima, S. Watanabe, and M. Machida, *Inorg. Chem.*, **33**, 2586 (1994).

5) H. Izawa, S. Kikkawa, and M. Koizumi, *Polyhedron*, **2**, 741 (1983); H. Miyata, Y. Sugawara, Y. Kuroda, and C. Kato, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2677 (1988).

6) A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Inorg. Chem.*, **24**, 3729 (1985); *Mater. Res. Bull.*, **22**, 45 (1987).

7) T. Kijima, S. Watanabe, K. Ohe, and M. Machida, *J. Chem. Soc., Chem. Commun.*, **1995**, 75.

8) "Intercalation Chemistry," ed by M. S. Whittingham and A. J. Jacobson, Academic Press, New York (1982).

9) T. Kijima, *Thermochim. Acta*, **59**, 95 (1982).

10) D. A. Odink, K. Song, and S. M. Kauziarich, *Chem. Mater.*, **4**, 906 (1992).

11) P. A. Joy and S. Vasudenvan, *J. Am. Chem. Soc.*, **114**, 7792 (1992).

12) T. Sasaki, F. Izumi, and M. Watanabe, *Chem. Mater.*, **8**, 777 (1996).

13) T. Kijima, S. Ueno, and M. Goto, *J. Chem. Soc., Dalton Trans.*, **1982**, 2499; T. Kijima and S. Ueno, *J. Chem. Soc., Dalton Trans.*, **1986**, 61.

14) T. Kijima and Y. Matsui, *Nature*, **322**, 533 (1986); b) T. Kijima, *J. Chem. Soc., Dalton Trans.*, **1990**, 425; **1992**, 2877.

15) T. Kijima, K. Sakoh, and M. Machida, *J. Chem. Soc., Dalton Trans.*, **1996**, 1245.

16) D. A. Tomalia and J. R. Dewald, PCT Int. Appl., WO8402705 (1984); *Chem. Abstr.*, **101**, 231194m (1985); U. S. Patent 4558120 (1985).

17) T. Kijima, S. Watanabe, and M. Machida, *Inorg. Chem.*, **33**, 2586 (1994).

18) A. Clearfield, G. H. Nancollas, and R. Blessing, "Ion Exchange and Solvent Extraction," ed by J. A. Marinsky and Y. Marcus, Marcel Dekker, New York (1973), Vol. 5, Chap. 1.

19) S. E. Horsley, D. V. Nowell, and D. T. Stewart, *J. Spectrochim. Acta*, **30A**, 535 (1974).

20) B. Bujoli, P. Palvadeau, and M. Queignec, *Eur. J. Solid State Inorg. Chem.*, **29**, 141 (1992).

21) A. Clearfield and R. M. Tindwa, *J. Inorg. Nucl. Chem.*, **41**, 871 (1979).

22) U. Costantino, *J. Inorg. Nucl. Chem.*, **43**, 1895 (1981).

23) N. C. Clayden, *J. Chem. Soc., Dalton Trans.*, **1987**, 1877; G. Alberti, M. G. Bernasconi, and M. Casciola, *React. Polym.*, **11**, 245 (1989); A. Christensen, E. K. Andersen, I. G. K. Andersen, G. Alberti, N. Nielsen, and M. S. Lehmann, *Acta Chem. Scand.*, **44**, 865 (1990); D. M. Poojary, B. Shpeizer, and A. Clearfield, *J. Chem. Soc., Dalton Trans.*, **1995**, 111.