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Shape-controlled synthesis of hydroxyapatite from α-tricalcium bis(orthophosphate) in organic-aqueous binary systems

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Hydrolyses of α-tricalcium bis(orthophosphate) $Ca_3(PO_4)_2$ (α-TCP) were carried out in a heterogeneous solvent system (hydrophobic organic solvent-water). The hydroxyapatites (HAp) formed were deficient in calcium (Ca/P = 1.56–1.61, *a*-axis = 0.9440 nm, *c*-axis = 0.6880 nm) and contained acid phosphate (and sometimes carbonate depending on the organic solvent used). The HAp was in the form of needles with a length (1–4 μm) that depended on the polarity of the hydrophobic organic solvent. The aspect ratio was highest in 1-octanol with a polarity of $E_T = 48.3$. On the other hand, in a hydrophobic organic solvent system without OH groups such as *n*-octane ($E_T = 31.1$), HAp formed fine particles that are similar to HAp prepared in a system without an organic solvent. Thus, hydrophobicity and OH groups of organic solvents affect the crystal growth of HAp.
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1. Introduction

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) is a major component of bones and teeth and is also an important biomaterial [1]. It has been recognized that control of the morphology of HAp for use as a biomaterial is an important aspect of its manufacture. Whisker-like or plate-like HAp particles are especially useful for the improvement of mechanical properties such as fracture toughness/strength of HAp in the biomedical/dental field [2].

In biological systems, shape-controlled formation of HAp takes place on collagen. Collagen possesses a repeat pattern, gly-X-Y, where X and Y may be hydrophobic amino acids such as proline and alanine etc, or hydrophilic amino acids such as serine, hydroxylysine and hydroxyproline etc. HAp forms on the surface and interior of collagen fibrils that have hydrophobic and hydrophilic sites. Thus in biological HAp-formation, participation of a hydrophobic and heterogeneous environment, as well as OH groups, are considered to be factors in the shape-controlled formation of HAp.

Shape-controlled syntheses of inorganic materials have been developed in organic systems. We have

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recently reported that aluminium orthophosphate, $AlPO_4$, could be effectively prepared in organic media [3]. Therefore, we investigated the hydrolysis of α-tricalcium bis(orthophosphate) [$Ca_3(PO_4)_2$] (α-TCP) in a heterogeneous organic solvent involving the factors mentioned above.

2. Experimental procedure

α-TCP (2 mmol) was hydrolyzed, with stirring, for from 2 to 120 hours at 70°C in an organic solvent-water system comprising an aqueous solution (18 cm^3) and an organic solvent (25 cm^3). The α-TCP (Taihei Chemical Industrial Co. Ltd) [4] was ground to a fine powder and passed through a 200 mesh sieve. X-ray diffraction [5] and 31-P MAS-NMR [6] measurements as show in Figs 10 and 11 of the below section also confirmed the crystallinity of the α-TCP. The organic solvents used were: ethanol, 1-butanol, 1-hexanol, 1-octanol, *n*-octane, cyclooctanol, cyclooctane, benzyl alcohol or toluene. All were provided by Wako Pure Chemical Industries, except cyclooctanol, which was from the Aldrich Chem. Co. The initial pH was adjusted to 11.0–12.3 by addition of ammonia, 2-aminoethanol, diethanol amine, or triethanol amine (Wako Pure Chemical Industries). The reaction products were collected by filtration, washed with ethanol and distilled water, and air-dried at 40°C for 5 hours.

The products obtained in this procedure were studied by X-ray diffractometry (XRD; Rigaku Geigerflex RAD—I A) using a graphite monochromator (Cu $K\alpha_1$), differential thermal analysis-thermogravimetric analysis (DTA-TG; Shimadu TA-50 WS) and Fourier transform infrared spectrometry (FTIR; Bruker IFS-113V). The conversion ratio of α-TCP to HAp was estimated from the intensity ratio of X-ray diffraction lines due to α-TCP and HAp. The reaction rate constant was estimated, assuming first-order kinetics, from the slope of a plot of logarithmic concentration [s] ($\ln s$) vs reaction time [h]. The relative yields of α-TCP to HAp were used as a measure of [s]. Calcium and phosphate concentrations were determined by X-ray fluorescence analysis (Philips PW1480). The HAp morphology was studied by scanning electron microscopy (SEM; Hitachi S-800, 10 kV) and transmission electron microscopy (TEM; Hitachi H8000, 200 kV). The samples for SEM were gold coated. For TEM, the powder was put on a carbon coated collodion film on a copper grid. Length to width aspect ratios of the HAp particles were determined from SEM observation of ~50 particles. 31-P MAS NMR spectra with 1-H high-power decoupling were recorded on a Bruker DSX200 spectrometer at room temperature using a 7 mm MAS rotor (spinning rate 4 kHz). α-zirconium phosphate was used as an external standard.

3. Results and discussion

3.1. Hydrolysis of α-TCP in a series of aliphatic alcohols

We hydrolyzed α-TCP in aqueous ammonia solution without any organic solvent in order to examine the influence of pH in plain aqueous systems. Fig. 1 shows the change with reaction time of the pH and conversion ratio of α-TCP to HAp for two different starting pH values (pH 8.2, dashed line; pH 11.0, solid line). For reaction times up to ~4 hours, more HAp is formed for an initial pH of 8.2 compared with a pH of 11.0. After ~4 hours, there is little difference in HAp content between the solutions. The pH of the solutions decreased gradually to 9.3 and 4.9 respectively after a reaction time of 24 hours. This pH change resulted from H_3PO_4 produced from the hydrolysis of α-TCP. Such a fall in pH might induce the formation of other compounds such as calcium hydrogen phosphate dihydrate $CaHPO_4 \cdot 2H_2O$ (DCPD) and octacalcium dihydrogen hexakis(orthophosphate) pentahydrate $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (OCP) [7], but no evidence for this was seen from XRD.

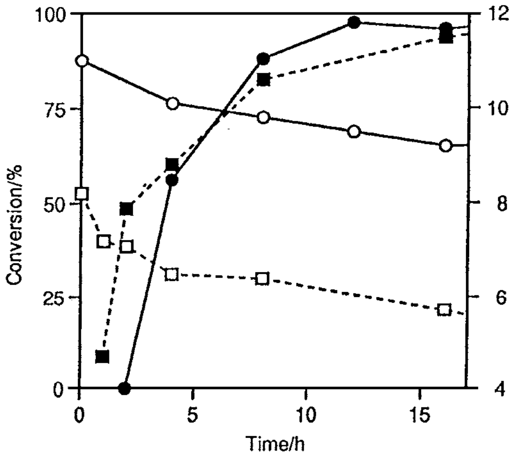

Figure 1 Relation between reaction time and conversion ratio of α-TCP to HAp (left), and pH (right) for initial pH 8.2 and 11.0 in aqueous solution. The contents of α-TCP and water are 2 mmol and 18 cm^3, respectively. ●: conversion ratio (initial pH 11.0), ■: conversion ratio (initial pH 8.2), ○: variation of pH (initial pH 11.0), □: variation of pH (initial pH 8.2).

In order to estimate the influence of hydrophobicity and hydrophilicity of organic solvents on HAp formation, we carried out hydrolyses of α-TCP in various aliphatic alcohol (ethanol, 1-butanol, 1-hexanol, or 1-octanol)-water systems. The initial pH was adjusted to about 11.0 with ammonia. The reaction proceeds homogeneously only for ethanol; it is biphasic for the other solvents which, unlike ethanol, are not fully miscible in water. Fig. 2 shows the relationship between reaction

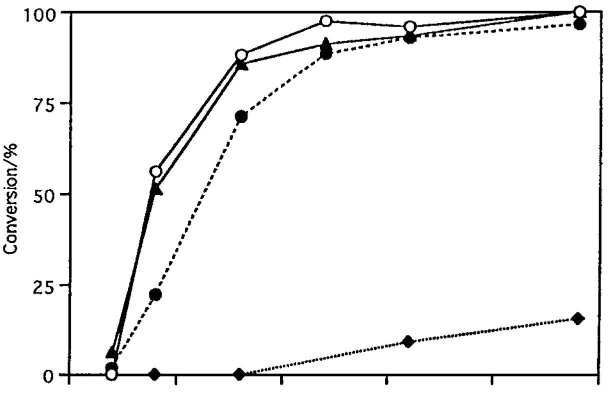

Figure 2 Relation between reaction time and conversion ratio of α-TCP to HAp in various aliphatic alcohol-water systems at 70°C. The contents of α-TCP, water and organic solvent are 2 mmol, 18 cm^3 and 25 cm^3, respectively. ○: water system without organic solvent, ◆: ethanol-water system, ●: 1-butanol-water system, ▲: 1-octanol-water system.

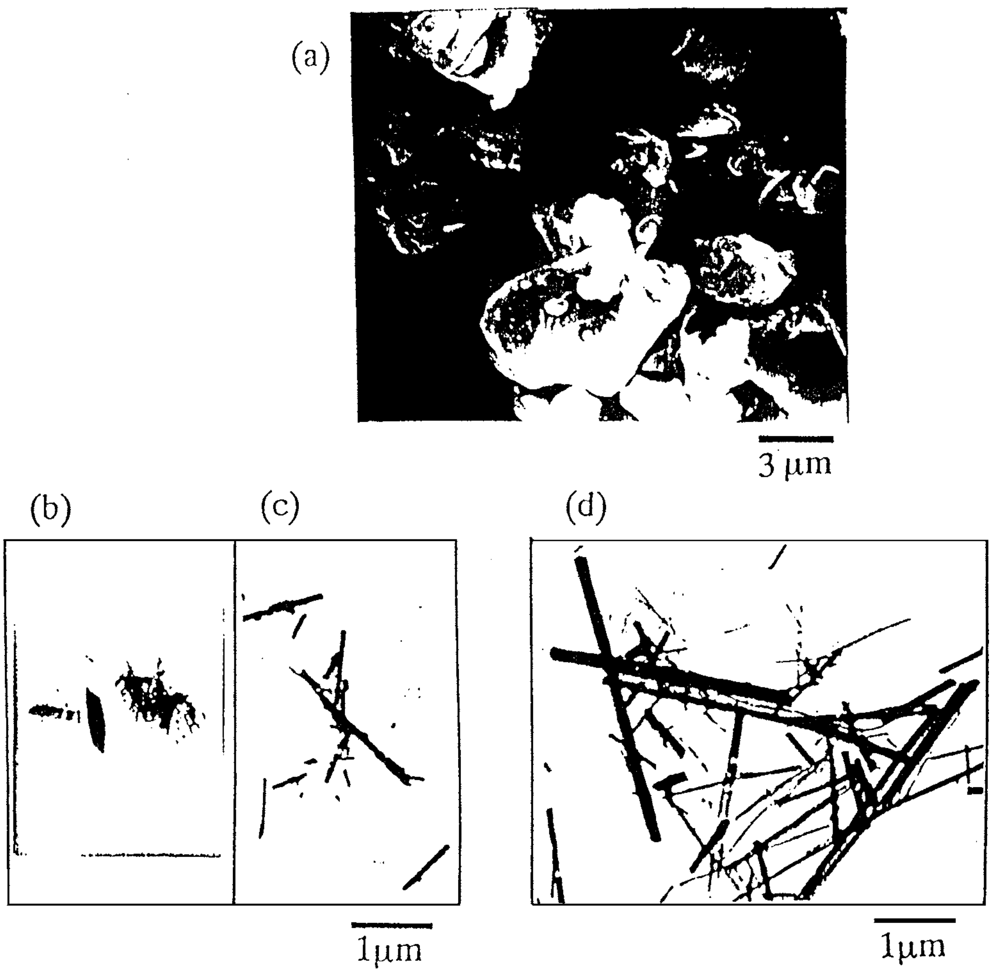

Figure 3 (a) SEM photograph of α-TCP, (b) and (c) TEM photographs of particles of HAp formed by hydrolyses of α-TCP in water without organic solvent and (d) in 1-octanol-water systems.

time and the conversion ratio of α-TCP to HAp at 70°C. The HAp formation rate in ethanol-water was markedly low; on the other hand, the rate for 1-octanol was almost the same as that for water, i.e. in the absence of organic solvent. α-TCP was completely converted to HAp after 24, 24, 72, and 120 hours in the 1-octanol, 1-hexanol, 1-butanol, and ethanol systems, respectively. The pH had fallen to 9.8 at the point when all the α-TCP was hydrolyzed for the ethanol system, and 9.2–9.3 for the other systems. The reaction rate constants were estimated to be 0.35, 0.31, 0.21, and 0.0083 h^{-1} for the water, 1-octanol, 1-butanol, and ethanol systems, respectively. At any time, it is seen that the HAp formation ratio increases in the sequence ethanol < 1-butanol < 1-octanol i.e. with the hydrophobicity of the organic solvent. These results show that the hydrolysis rate is partially related to differences in solubility of the various alcohols in water. In the ethanol system especially, the reduction of ethanol/water proportion increased the HAp formation ratio. It is suggested that the very low hydrolysis rate can be attributed to the reduced activity of H_2O caused by the strong affinity between ethanol and H_2O.

Fig. 3 shows an SEM photograph of α-TCP and TEM photographs of the particles of HAp obtained. The particles of α-TCP had irregular forms with smooth surfaces (Fig. 3a). HAp particles prepared in aqueous solution without organic solvent were a mixture of platelets and fine needles (Fig. 3b and c). In HAp prepared in organic solvent-water systems, two kinds of needles were seen, short (about 1.0 μm) and long (~4.0 μm), depending on the type of solvent. Ethanol-water and 1-butanol-water systems gave short needles similar to Fig. 3c. On the other hand, long needles of HAp were formed in 1-octanol-water (Fig. 3d) and 1-hexanol-water systems (not shown). Fig. 4 gives the aspect ratio of the HAps prepared in each aliphatic alcohol-water system. It is seen that this ratio increased with the hydrophobicity of the aliphatic alcohol, as did the HAp formation rate (see above).

Since 1-octanol is insoluble in water and similar rates of hydrolysis were observed in 1-octanol-water and water alone, we did not expect that the presence or absence of 1-octanol would affect the hydrolytic process. However, the shape of the HAp particles obtained in 1-octanol-water was considerably different from that in water alone: long needles were formed in the 1-octanol-water system (Fig. 3d), whereas mixture of platelet-form and fine needles formed in the absence of organic solvent (Fig. 3b and c). These results show that the shape and size of HAp are influenced by the hydrophobic nature of the aliphatic alcohol.

3.2. Effect of OH group on the formation of HAp from α-TCP in heterogeneous hydrophobic solvent systems

In the previous section, it was reported that 1-octanol, with the highest hydrophobicity, had the greatest

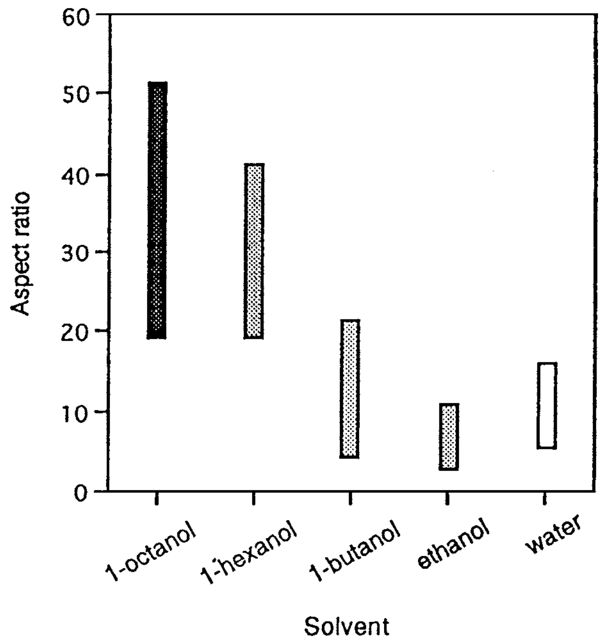

Figure 4 Aspect ratio of HAp prepared in each aliphatic alcohol-water system.

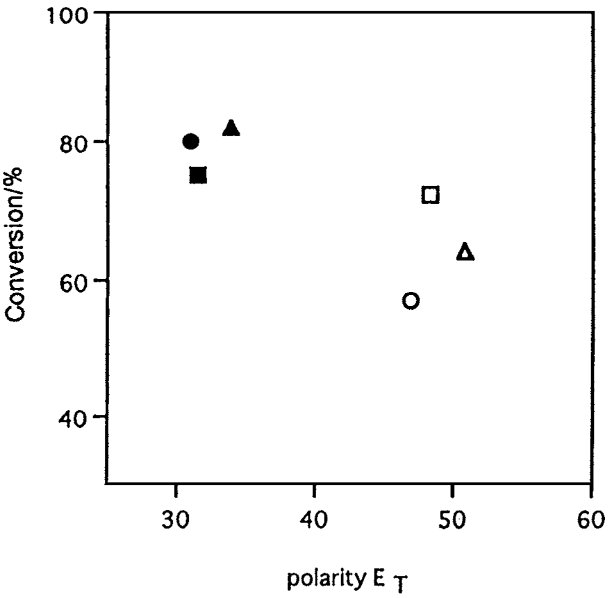

Figure 5 Relation between organic solvent polarity and conversion ratio of α-TCP to HAp in organic solvent-water systems at 70°C after 5 hours. □: 1-octanol-water system, ■: n-octane-water system, ○: cyclooctanol-water system, ●: cyclooctane-water system, △: benzyl alcohol-water system, ▲: toluene-water system.

influence on the formation of HAp. Therefore, studies with other heterogeneous hydrophobic systems of cyclooctanol and benzyl alcohol were undertaken. Furthermore, the corresponding hydrocarbons without an OH group (n-octane, cyclooctane and toluene) were compared in the light of the demonstrated effect of the OH group. The reaction conditions were as before, namely an initial pH of $\sim$11.0, derived from addition of ammonia solution, and a reaction temperature of 70°C.

Our studies showed that the HAp formation rates in the presence of hydrocarbons without an OH group (n-octane, cyclooctane and toluene) were faster than for hydrophobic organic solvents with an OH group (1-octanol, cyclooctanol and benzyl alcohol). This is seen in Fig. 5 which shows the relationship between organic solvent polarity [8] and conversion ratio of α-TCP to HAp in these organic solvent-water systems at 70°C after 5 hours. After 24 hours, the formation of HAp was completed (the final pH was 9.2–9.3).

TEM photographs of the HAps prepared in each solvent system (Fig. 6) show needles whose lengths (0.5–4 μm) depend on the organic solvent used. The shortest needles (less than 1.0 μm) were obtained in the n-octane-water system. The relationship between polarity of the hydrophobic organic solvent [8] and aspect ratio of the product is given in Fig. 7. This also includes results for the aliphatic alcohols shown in Fig. 4. A tendency is seen within the group of solvents with OH groups for the aspect ratio to be highest for solvents having a polarity $E_T \sim 48.3$, and to fall with an increase in polarity. It also seems that the aspect ratio is smaller for the solvents without OH groups when compared with the corresponding solvent with OH groups. These results suggest that the hydrophobicity and the presence of OH groups in organic compounds affect the growth of HAp crystals.

In further studies of the hydrolysis of α-TCP, amino alcohol solutions (18 cm^3) were used instead of an aqueous ammoniacal solution (18 cm^3) to investigate the effect of the OH group. The systems used were: an aqueous solution without organic solvent; 1-octanol; and n-octane. To each of these was added either 0.1 M 2-aminoethanol $[NH_2(C_2H_4\text{-}OH)]$ solution (pH 12.3), 0.1 M diethanolamine $[NH(C_2H_4\text{-}OH)_2]$ solution (pH 11.3), or 0.1 M triethanolamine $[N(C_2H_4\text{-}OH)_3]$ solution (pH 11.2).

TEM photographs of HAp from six of the systems (Fig. 8) show that needles are formed. These were longest ($\sim$3 μm) for the 2-aminoethanol-1-octanol system , and shorter ($<$1 μm) for the 2-aminoethanol-n-octane or -water system. These results indicated that the HAp particles produced were, respectively, long and short needles for the 1-octanol and n-octane systems. This is consistent with the results given above for systems without amino alcohol solvents. On the other hand, HAp particles from the triethanolamine-n-octane or -water systems were longer than from the 2-aminoethanol-n-octane or -water systems. It seems that the growth of HAp crystals might be affected by OH groups of triethanolamine. However, HAp particles from the triethanolamine-1-octanol system were shorter than from the 2-aminoethanol-1-octanol systems. This result might be derived from the change of polarity of 1-octanol. Studies with amino alcohols also shows that the presence of OH groups in organic compounds affects the growth of HAp crystals.

The formation rate of HAp in the amino alcohol systems differed from the system without an amino alcohol. Fig. 9 shows the conversion ratios of α-TCP to HAp after 4 hours. Although the HAp-formation rate is almost the same for the three solvent (water, 1-octanol-water, n-octane-water) plus NH_3 systems, systems with an amino alcohol instead of NH_3 either increased or decreased the rate depending on the solvent. The HAp-formation rate for 2-aminoethanol-water

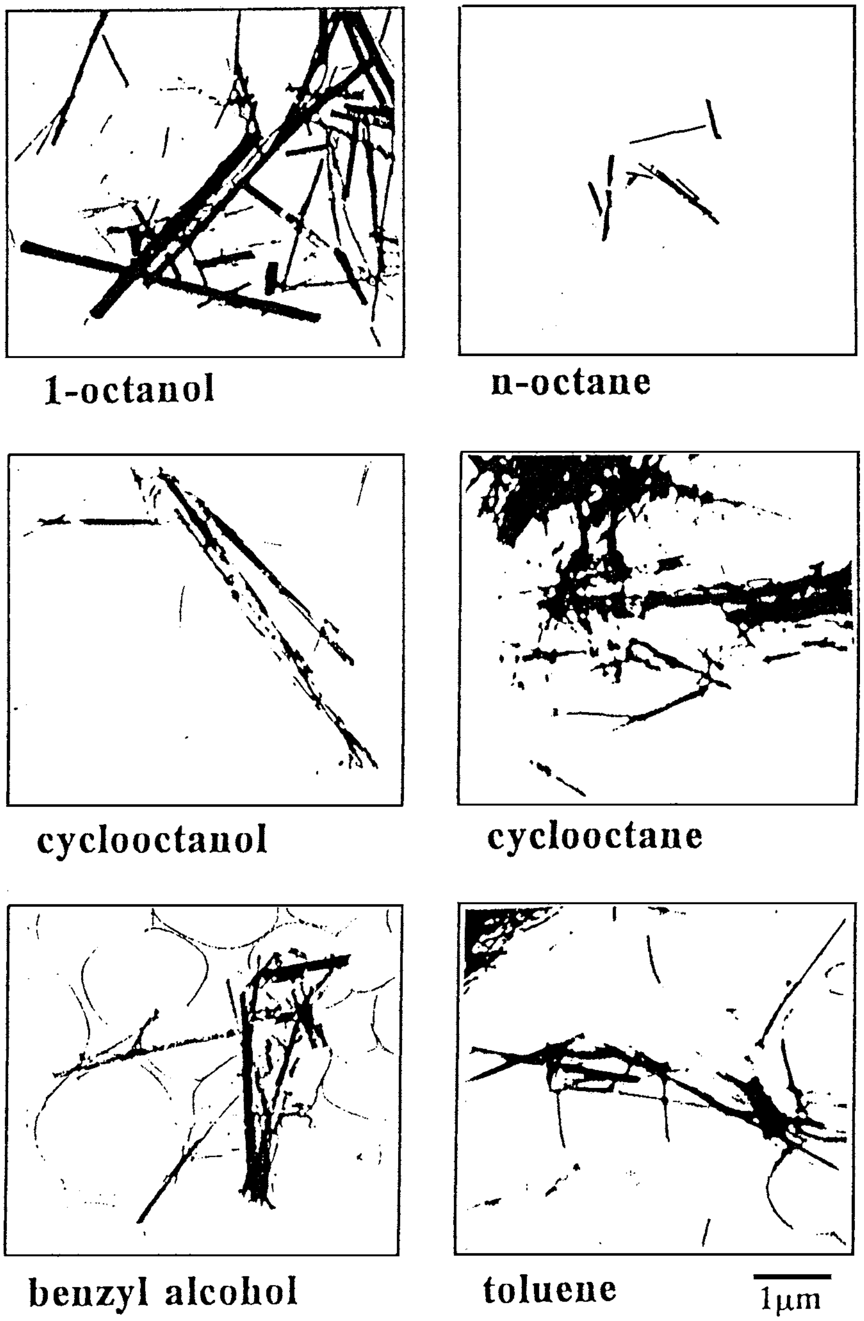

Figure 6 TEM photographs of HAp prepared by hydrolyses of α-TCP in various hydrophobic organic solvent-water systems at 70°C.

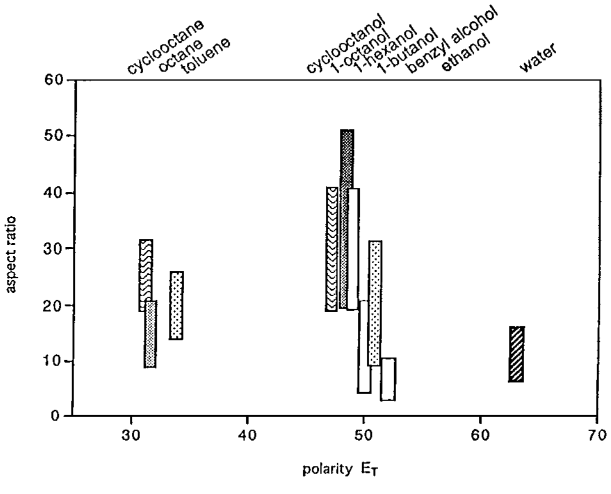

Figure 7 Influence of organic solvent polarity on aspect ratio of HAp crystals.

system was particularly reduced, as was seen earlier for hydrophilic ethanol. For the diethanolamine and triethanolamine-water systems, the formation rate became higher than for the 2-aminoethanol-water system. The hydrophilicity of amino alcohols decreases in the sequence 2-aminoethanol > diethanolamine > triethanolamine. Therefore, this phenomenon might be derived from the fact that the activity of H_2O in the diethanolamine and triethanolamine-water systems was increased over that in the 2-aminoethanol-water system. On the other hand, the hydrophobic organic solvents gave higher formation rates, especially triethanolamine in the octane-water system which had the highest rate of all. These results suggest that the HAp formation rate is affected by a co-existing organic compound and is also strongly dependent on its hydrophobicity and the presence of OH groups.

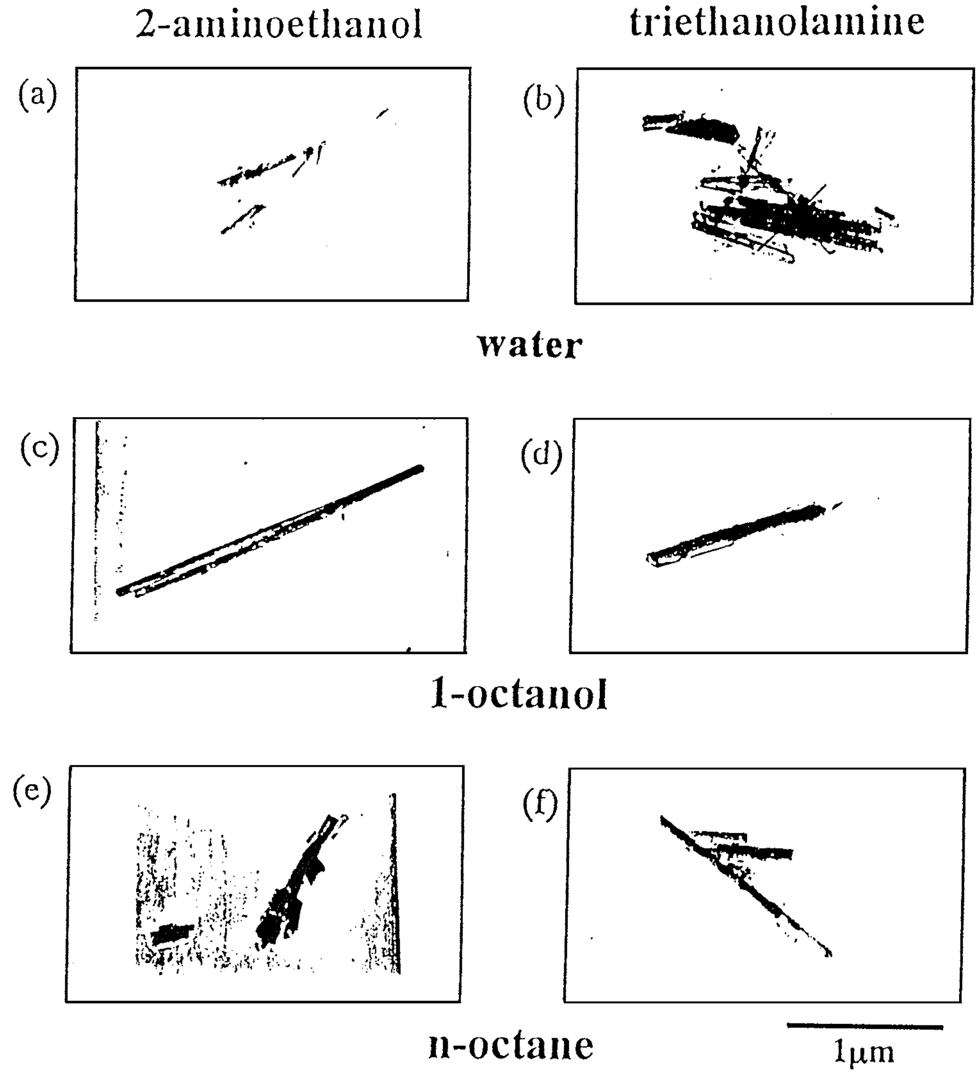

Figure 8 TEM photographs of HAp prepared in (a) 2-aminoethanol-water (b) triethanolamine-water (c) 2-aminoethanol-1-octanol (d) triethanolamine-1-octanol (e) 2-aminoethanol-*n*-octane and (f) triethanolamine-*n*-octane systems.

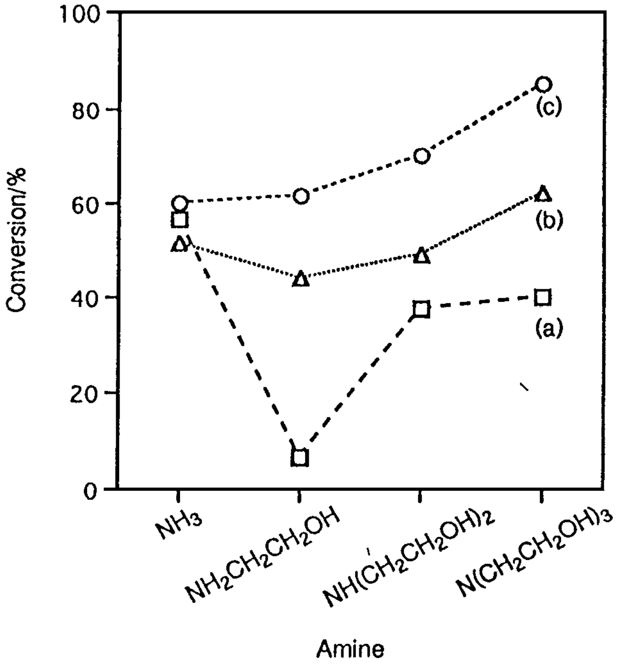

Figure 9 Conversion ratio of α-TCP to HAp in (a) amino alcohol-water (b) amino alchohol-1-octanol and (c) amino alcohol–*n*-octane systems after 4 hours at 70°C.

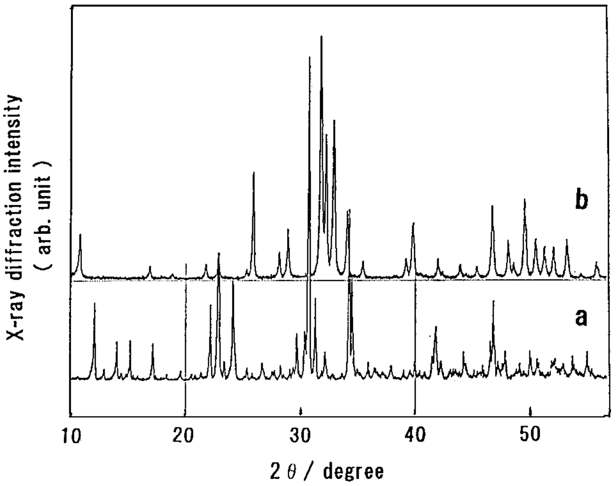

Figure 10 X-ray diffraction patterns of (a) α-TCP and (b) HAp prepared in 1-octanol-water system.

3.3. Characterization of the HAp products

HAp products were confirmed from the X-ray diffraction pattern and 31-P MAS-NMR spectrum as show Figs 10 and 11. Preparation conditions are summarized in Table I (organic solvent, agent for pH adjustment, and initial and final pH). All products were

TABLE I Characterization of HAps prepared by hydrolyses of α-TCP

		pH			IR absorption	
Organic solvent	pH adjustment	Initial	Final	Ca/P ratio	$(HPO_4)^{2-}$	$(CO_3)^{2-}$
–	NH_3	8.2	4.9	1.52	++	–
–	NH_3	11.0	9.2	1.58	++	–
ethanol	NH_3	11.0	9.8	1.58	++	+
l-butanol	NH_3	11.0	9.3	1.57	++	–
l-hexanol	NH_3	11.0	9.2	1.58	++	–
l-octanol	NH_3	11.0	9.3	1.58	++	–
n-octane	NH_3	11.0	9.3	1.58	++	–
cyclooctanol	NH_3	11.0	9.2	1.59	++	+
cyclooctane	NH_3	11.0	9.3	1.59	++	+
benzyl alcohol	NH_3	11.0	9.2	1.57	++	+
toluene	NH_3	11.0	9.2	1.57	++	+
–	$NH_2(C_2H_4OH)$	12.3	10.5	1.60	++	+
l-octanol	$NH_2(C_2H_4OH)$	12.3	10.6	1.60	++	+
n-octane	$NH_2(C_2H_4OH)$	12.3	10.5	1.61	++	+
–	$NH(C_2H_4OH)_2$	11.3	9.3	1.61	++	+
l-octanol	$NH(C_2H_4OH)_2$	11.3	9.9	1.59	++	–
n-octane	$NH(C_2H_4OH)_2$	11.3	10.0	1.57	++	–
–	$N(C_2H_4OH)_3$	11.2	8.8	1.57	++	+
l-octanol	$N(C_2H_4OH)_3$	11.2	8.9	1.56	++	–
n-octane	$N(C_2H_4OH)_3$	11.2	8.9	1.57	++	–

++ : strong, + : weak.

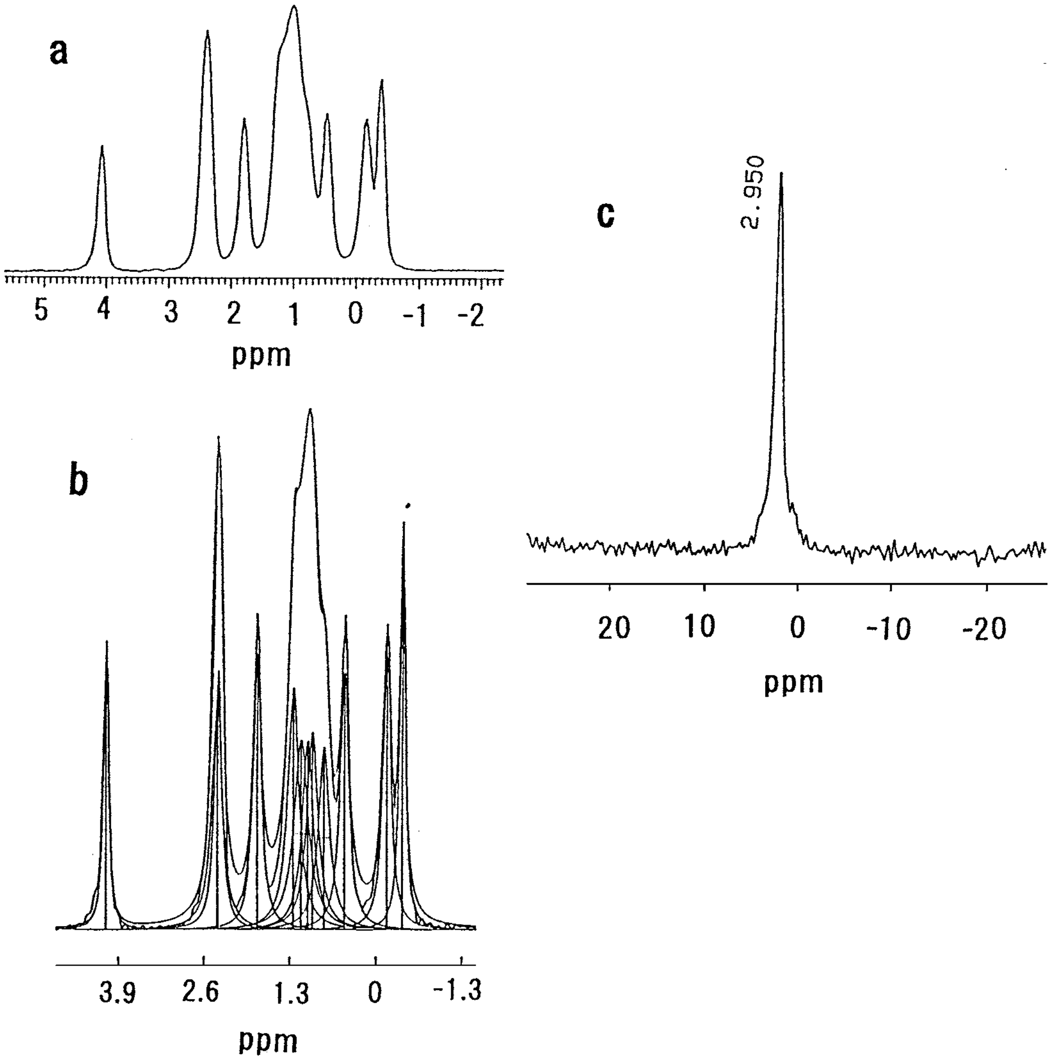

Figure 11 1-H high-power decoupling 31-P MAS-NMR spectra of (a) α-TCP (b) Gaussian deconvolution of (a) and (c) HAp prepared in 1-octanol-water system. Chemical shift for each line of α-TCP : 4.07 ppm, 2.38 ppm, 2.39 ppm, 1.78 ppm, 1.24 ppm, 1.12 ppm, 1.02 ppm, 0.95 ppm, 0.78 ppm, 0.47 ppm, −0.17 ppm, −0.40 ppm.

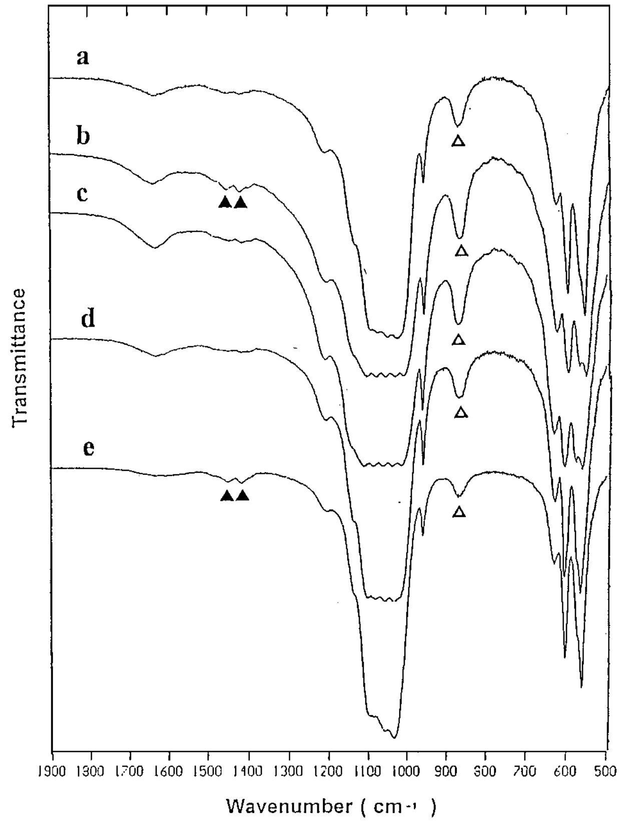

Figure 12 FTIR spectra of HAps (a) water system without organic solvent (b) ethanol-water system (c) 1-octanal-water system (d) *n*-octane-water system and (e) cyclooctane-water system. △: absorption due to $(HPO_4)^{2-}$, ▲: absorption due to $(CO_3)^{2-}$.

examined by FTIR; examples of spectra are shown in Fig. 12 for HAp formed in each system (water without organic solvent, ethanol-water, 1-octanol-water, *n*-octane-water, and cyclooctane-water). All these, and all other products, have absorption band due to acid phosphate, HPO_4^{2-}, near 860 cm^{-1}. Products prepared in ethanol-water and cyclooctane-water systems show absorption bands at 1410 and 1460 cm^{-1} (marked + in Table I) due to the carbonate anion. Table I also gives the mole Ca/P ratio of the HAp from X-ray fluorescence analysis. The range is 1.56–1.61 which is smaller than 1.67 for stoichiometric HAp. Taking this result together with the absorption due to HPO_4^{2-}, shows that the HAps are calcium-deficient apatites, with (for example) a general formula [9]

$$Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}(H_2O)_y$$
$$(z = 0.34\text{–}0.64).$$

The lattice parameters from X-ray diffraction were estimated to be $a = 0.9440$ and $c = 0.6880$ nm, which are typical of those found for HAps prepared in aqueous systems. The *a*-axis is larger than 0.94176 nm reported in the literature [10] for HAps prepared at high temperatures, probably because water expands the *a*-axis dimension.

DTA measurements of the HAps showed endothermic peaks around 560 and 830°C due to dehydration. The weight reduced gradually from room temperature to 820°C, and then suddenly decreased at around 830°C by about 0.4%. The total weight loss was 4.8% at 1000°C. At temperatures higher than ~830°C, stoichiometric HAp and ß-TCP were formed. This was confirmed by XRD and FTIR measurements. FTIR spectra of samples heated at 900°C for 3 hours showed the disappearance of HPO_4^{2-} and appearance of ß-TCP absorption bands. The formation of ß-TCP was also confirmed by XRD. These results show, assuming the above formula, that the Ca-deficient HAp decomposed according to the reaction:

$$\begin{aligned}&Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}(H_2O)_y\\&\quad\rightarrow (1-z)Ca_{10}(PO_4)_6(OH)_2 + 3zCa_3(PO_4)_2\\&\quad+ (z+y)H_2O\end{aligned}$$

4. Conclusion

The formation of HAp by hydrolysis of α-TCP in a binary system (hydrophobic organic solvent-water) has been studied. The HAps formed were Ca-deficient with a formula $Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}(H_2O)_y$ where $z = 0.34$–0.64. The Ca/P mole ratio = 1.56–1.61, *a*-axis = 0.9440 nm, and *c*-axis = 0.6880 nm. IR spectra showed absorption due to acid phosphate with or without carbonate depending on the type of organic solvent. The HAps changed to mixtures of ß-TCP and stoichiometric HAp on heating at 900°C for 3 hours.

The HAp was in the form of needles (length 1–4 μm, width 0.1 μm) with a size dependant on the polarity of the organic solvent. The aspect ratio was highest for the solvent with an OH group having a polarity E_T around 48.3, such as 1-octanol. On the other hand, for *n*-octane without an OH group, HAp was formed as fine particles (less than 1.0 μm) that are similar to HAp prepared in the absence of an organic solvent-system. These results suggest that the crystal growth of HAp is strongly affected by the hydrophobicity and OH groups of organic compounds because the hydrolytic process occurred in a water phase. Furthermore, the HAp formation rate was affected by a co-existing organic compound and was also strongly dependent on its hydrophobicity and the presence of OH groups.

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References

1. L. HENCH, *J. Amer. Ceram. Soc.* **74** (1991) 1487.
2. H. YOSHIMURA, K. SUDA, K. OKAMOTO and K. IOKU, *J. Mater. Sci.* **29** (1994) 3399.
3. K. SAKAMOTO, M. TSUHAKO, M. MURAKAMI and K. TANAKA, *Nippon Kagaku Kaishi* **1995** (1995) 681.

4. M. MATSUDA and H. KAJI, *Phosphorus Res. Bull.* **6** (1996) 185.
5. Card No 29-359, Powder Diffraction File, International Centre for Diffraction Data, Newton Square, PA.
6. M. BOHNER, J. LEMAITRE, A. P. LEGRAND, J. B. D'ESPINOSE DE LA CAILLERIE and P. BELGRAND, *J. Mater. Sci. : Mater. in Medicine* **7** (1996) 457.
7. H. MONMA, M. GOTO and T. KHOMURA, *Gypsum & Lime* **188** (1984) 11.
8. K. DIMROTH, C. REICHHARDT, T. SIEPMANN and F. BOHLMANM, *Liebigs Ann. Chem.* **661** (1963) 1.
9. H. MONMA and T. KANAZAWA, *Yogyo-Kyokai-Shi* **84** (1976) 209.
10. J. C. ELLIOTT, "Structure and Chemistry of the Apatites and Other Calcium Orthophosphates" (Elsevier, Amsterdam, 1994) p121.

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