

# Oligomeric Surfactant and Triblock Copolymer Syntheses of Aluminum Organophosphonates with Ordered Mesoporous Structures

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Mesostructural control of aluminum organophosphonates (AOPs) with methylene groups inside the inorganic–organic hybrid frameworks was performed by using oligomeric surfactants ( $C_{16}EO_{10}$  and  $C_{16}EO_{20}$ ) and triblock copolymers ( $EO_{80}PO_{30}EO_{80}$ ,  $EO_{106}PO_{70}EO_{106}$ , and  $EO_{20}PO_{70}EO_{20}$ ). The templating by oligomeric surfactants with hexadecyl chains that directed the formation of 2-D hexagonal mesostructured and mesoporous AOPs (BET surface areas;  $\sim 579 \text{ m}^2 \text{ g}^{-1}$ , pore volumes;  $\sim 0.53 \text{ cm}^3 \text{ g}^{-1}$ ), especially highly ordered materials, can be obtained by using  $C_{16}EO_{20}$ . Mesoporous materials with 2-D hexagonal phases ( $\sim 279 \text{ m}^2 \text{ g}^{-1}$ ,  $\sim 0.76 \text{ cm}^3 \text{ g}^{-1}$ ) were also prepared through triblock copolymer templating. The pore diameters (6.0–9.2 nm) were largely expanded by using triblock copolymers as compared with those of oligomeric surfactant templated materials (3.3–3.8 nm). Low-temperature calcination of the mesostructured AOPs was useful for removing surfactant molecules to afford periodic non-silica-based hybrid mesoporous materials. Once internal organic moieties are eliminated by calcination at high temperatures, the frameworks are composed of only inorganic units containing two adjacent phosphate groups ( $-P-OH + HO-P-$ ). Further condensation in the inorganic frameworks is therefore not preferable. Inorganic units are supposed to be restructured to form aluminophosphate-like frameworks ( $-Al-O-P-$ ) composed of alternating  $AlO_4$  and  $PO_4$  units and then the mesostructures collapse. Therefore, mesostructural stabilities of AOPs are related to stabilities of methylenediphosphonate groups ( $\equiv PCH_2P \equiv$ ) and the inner organic groups of the hybrid frameworks.

## Introduction

Ordered mesoporous silicas prepared by using surfactants have attracted much attention because of the interesting applications to catalysts, catalyst supports, and adsorbents for relatively large molecules.<sup>1</sup> The mesoporous silicas have also been developed as electronics and optics combined with the insertion techniques of functional molecules. The synthesis of ordered mesoporous silicas was initially conducted by using alkyltrimethylammonium ( $C_nTMA$ ) surfactants.<sup>2–5</sup> Since then, a wide variety of ammonium-type surfactants have been utilized for controlling mesostructures of silicas.<sup>6,7</sup> According to the synthetic conditions, two electrostatic interactions between silicate species and cationic surfactant molecules are proposed as  $S^+I^-$  under basic conditions and  $S^+X^-I^+$  under acidic conditions.<sup>8,9</sup> A neutral templating route ( $S^0I^0$ ) by using alkylamine surfactants has also been proposed

for synthesizing mesoporous silicas.<sup>10–13</sup> Alkylamine molecules are not interacted with silicate species strongly and therefore the surfactant molecules are easy to recover by extraction and the surfactants can be reused. However, it is difficult to obtain highly ordered mesoporous silicas because the weak interaction encourages condensation of silicate species during the syntheses. Another neutral templating pathway ( $N^0I^0$ ) has been suggested by using oligomeric surfactants such as polyoxyethylene glycol alkyl ethers ( $C_nH_{2n+1}(PEO)_m$ ) and triblock copolymers such as poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) ( $PEO_nPPO_mPEO_n$ ).<sup>14,15</sup> The formation of disordered mesoporous silicas was reported in the first paper on oligomeric surfactant and triblock copolymer syntheses of silicas.<sup>14</sup> After that, it was found that acidic syntheses using oligomeric surfactants are useful for obtaining silicas with highly ordered mesoporous structures such as 2-D hexagonal ( $P6mm$ ), cubic ( $Pm3m$ ), and 3-D hexagonal phases ( $P6_3/$

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*mmm*).<sup>16</sup> Triblock copolymers syntheses of silicas are also conducted through a neutral synthetic pathway similar to that of  $(\text{N}^0\text{H}^+)(\text{X}^-\text{I}^+)$  and highly ordered mesoporous silicas with 2-D hexagonal (*p6mm*) and cubic (*Im $\bar{3}m$* ) structures can be obtained under acidic conditions.<sup>16,17</sup> In addition, expansion of ordered mesopores up to 30 nm was achieved by using auxiliary additives in the presence of triblock copolymers.<sup>17</sup> Moreover, oligomeric surfactants and triblock copolymers are commercially available, low cost, nontoxic, biodegradable, and extractive. Mesostructural and morphological controls including pore size control of MSU-type mesoporous silicas prepared by using oligomeric surfactants have also been investigated in detail.<sup>18–23</sup> Accordingly, oligomeric surfactant and triblock copolymer syntheses of materials are useful for mesostructural and pore size controls, as well as  $\text{C}_n\text{TMA}$ -type surfactant templated syntheses.

Mesostructural control by nonionic PEO-based surfactants such as  $\text{C}_n\text{H}_{2n+1}(\text{PEO})_m$  and  $\text{PEO}_n\text{PPO}_m\text{PEO}_n$  is not limited to silica.<sup>14,24,25</sup> A mesoporous alumina which is expected as different catalytic supports and adsorbents from mesoporous silicas was prepared by using a triblock copolymer.<sup>14</sup> Likewise, the preparation of a larger number of ordered mesoporous metal oxides has been reported by using triblock copolymers.<sup>24,25</sup> From the viewpoint of potential applications according to chemical properties such as electric and optical devices, fuel cells, nonlinear optics, and so on,<sup>26</sup> non-silica-based metal oxides should be paid much more attention than silica-based materials which have usually been applied to catalysts, catalytic supports, and adsorbents.<sup>1</sup> Porous materials design of inorganic–organic hybrid materials is a promising strategy to deal with unique functions including combined properties due to inorganic species and organic groups.<sup>27</sup> Although there have been many reports on the preparation of hybrid mesoporous silicas composed of a wide variety of organic groups,<sup>28–33</sup> the functions of silica are limited to

physical properties concerned with catalytic supports and adsorbents.

The preparation of a mesoporous aluminum organophosphonate (AOP) containing internal methylene groups by using  $\text{C}_n\text{TMA}$  molecules was reported as a first example of surfactant templated and non-silica-based inorganic–organic hybrid mesoporous materials,<sup>34</sup> though a large number of hybrid porous materials showing interesting properties had been reported.<sup>35,36</sup> However, internal methylene moieties are partly decomposed during calcination at low temperatures which possibly decompose only  $\text{C}_n\text{TMA}$  molecules.<sup>34</sup> Haskouri et al. have reported the synthesis of a pure mesoporous AOP with ethylene groups.<sup>37,38</sup> Surfactant molecules were successfully removed by acid treatment. They also synthesized a pure mesoporous AOP composed of aluminophosphate (AIPO)-like frameworks with surface methyl groups by using methylphosphonic acid.<sup>37,38</sup> However, those materials including the original mesostructured AOPs are disordered and the  $\text{N}_2$  adsorption–desorption isotherms contained hysteresis loops. One-pot synthesis of organically modified materials whose frameworks are mainly composed of AIPOs have also been conducted by using organosilane compounds.<sup>39,40</sup> Recently, the preparation of a highly ordered mesoporous AOP with a 2-D hexagonal structure (designated as AOP-2) was succeeded under acidic conditions by using  $\text{C}_n\text{TMA}$  surfactants, which are eliminated by low-temperature calcination.<sup>41</sup>

In the present study, oligomeric surfactant and triblock copolymer syntheses of AOPs by using methylene diphosphonic acid were investigated to obtain highly ordered mesoporous materials as typical non-silica-based inorganic–organic hybrid mesoporous materials. Mesoporous AOPs with different pore sizes and wall thicknesses can be obtained and then mesostructural stabilities of AOPs were investigated in detail.

## Experimental Section

**Materials.** Oligomeric surfactants and triblock copolymers were obtained from Sigma-Aldrich. Polyoxyethylene glycol hexadecyl ethers ( $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ,  $\text{C}_{16}\text{EO}_n$ ) such as Brij 56 ( $\text{C}_{16}\text{EO}_{10}$ ) and Brij 58 ( $\text{C}_{16}\text{EO}_{20}$ ) were used as oligomeric surfactants. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) ( $\text{H}(\text{OCH}_2\text{H}_2)_n[\text{OCH}(\text{CH}_3)\text{CH}_2]_m(\text{OCH}_2\text{CH}_2)_n\text{OH}$ ,  $\text{EO}_n\text{PO}_m\text{EO}_n$ ) such as Pluronic F68 ( $\text{EO}_{80}\text{PO}_{30}\text{EO}_{80}$ ), Pluronic F127 ( $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ ), and Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) were used as triblock copolymers. Methylene diphosphonic acid ( $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$ ) was purchased from AZmax Co. Ltd. Aluminum chloride ( $\text{AlCl}_3$ ) and ethanol were obtained from Wako Chemical Co.

**Synthesis of Aluminum Methylene diphosphonates Using Oligomeric Surfactants.** On the basis of the acid–base pair routes to prepare a wide variety of metal phosphates,<sup>42–44</sup> mesostructured

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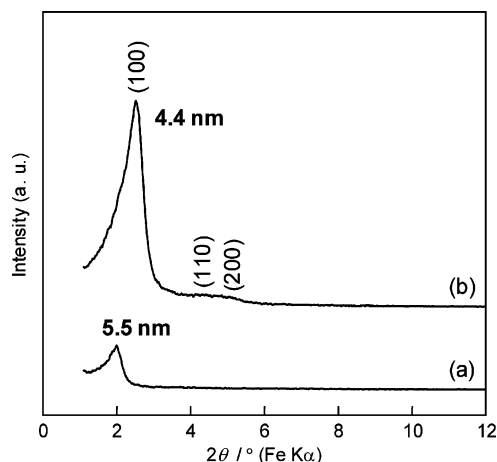
aluminum organophosphonates (AOPs) were synthesized by using  $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$  and  $\text{AlCl}_3$  in the presence of  $\text{C}_{16}\text{EO}_n$  surfactants. In a typical synthesis, 1.5 g of  $\text{C}_{16}\text{EO}_n$  was dissolved in a mixed solvent of ethanol (10 mL) and water (5 mL) and then 0.97 g of  $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$  was added to the surfactant solution. After the diphosphonic acid was dissolved completely, 0.98 g of  $\text{AlCl}_3$  was added to the solution very slowly under vigorous stirring ( $\text{Al}:\text{2P} = 1:0.75$ ). The stirring was maintained for 30 min and then a clear solution was obtained. The clear solution was transferred into a dish to evaporate the solvents at room temperature and the solid product was completely dried at 50 °C. The product was calcined at 400 °C, which is possibly useful for removing only surfactant molecules because methylene groups in 2-D hexagonal mesoporous aluminum methylenediphosphonate (AOP-2) are thermally stable up to 450 °C.<sup>34,39</sup> Therefore, the product was heated at 400 °C for 1 h in flowing  $\text{N}_2$ , followed by calcination at this temperature for 6 h in flowing  $\text{O}_2$ .

**Synthesis of Aluminum Methylenediphosphonates Using Triblock Copolymers.** Triblock copolymer ( $\text{EO}_n\text{PO}_m\text{EO}_n$ ) syntheses of AOPs were also conducted by using  $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$  and  $\text{AlCl}_3$ . In a typical synthesis,  $\text{EO}_n\text{PO}_m\text{EO}_n$  (Pluronic F68; 1.2 g, Pluronic F127; 1.1 g, Pluronic P123; 1.0 g) was dissolved in ethanol/water (30 mL/5 mL).  $(\text{HO})_2\text{OPCH}_2\text{PO}(\text{OH})_2$  (0.88 g) was also dissolved in the solution of triblock copolymer.  $\text{AlCl}_3$  (0.67 g) was added to the solution very slowly under vigorous stirring and the stirring was maintained for 30 min ( $\text{Al}:\text{2P} = 1:1$ ). The solvents were removed at room temperature, followed by drying at 50 °C. Finally, triblock copolymers were removed from the mesostructured AOPs by calcination at 400 °C.

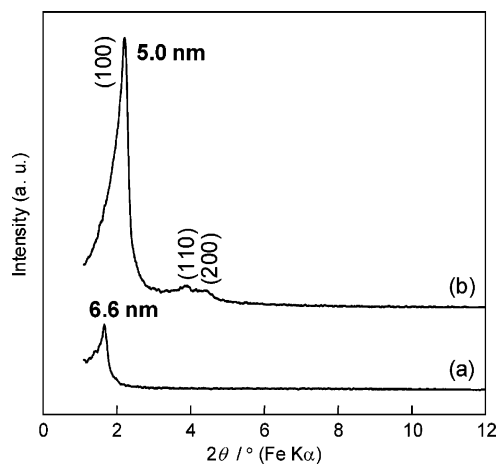
**Characterization.** Powder X-ray diffraction (XRD) patterns were obtained by using a Rigaku RINT 2100 diffractometer with monochromated  $\text{Fe K}\alpha$  radiation. Transmission electron microscopic (TEM) images were taken by a JEOL JEM 2010, operated at 200 kV. Solid-state  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS NMR measurements were performed on a JEOL JNM CMX-400 spectrometer at spinning rates of 10 kHz and 9 kHz and resonance frequencies of 104.17 and 161.84 MHz with 45° pulse lengths of 4.0 and 4.0  $\mu\text{s}$  and recycle times of 5 and 30 s, respectively. Solid-state  $^{13}\text{C}$  CP/MAS NMR measurements were performed at a spinning rate of 5 kHz and a resonance frequency of 100.54 MHz with a recycle time of 5 s. The organic contents of the products were measured by CHN (Thermo Finnigan Flash EA 1112). Nitrogen adsorption–desorption isotherms were measured by using a Quantachrome Autosorb-1 at 77 K. All of the samples were preheated at 110 °C for 6 h under vacuum. Specific surface areas were calculated by the BET method.<sup>45</sup> Pore size distributions of oligomeric surfactant templated materials were calculated by the H–K method<sup>46</sup> using adsorption data. Average pore diameters of triblock copolymer templated materials were estimated on the basis of TEM observations.

## Results and Discussion

**Oligomeric Surfactant Templated Mesoporous Aluminum Methylenediphosphonates.** Mesostructured aluminum methylenediphosphonates were prepared in the presence of



**Figure 1.** XRD patterns of (a) as-synthesized and (b) calcined (at 400 °C) aluminum methylenediphosphonates prepared in the presence of  $\text{C}_{16}\text{EO}_{10}$ .

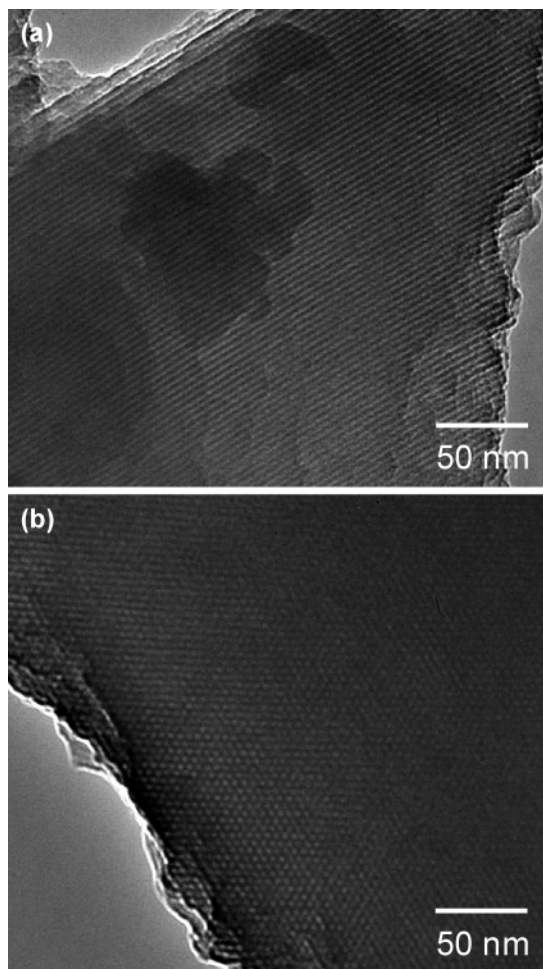


**Figure 2.** XRD patterns of (a) as-synthesized and (b) calcined (at 400 °C) aluminum methylenediphosphonates prepared in the presence of  $\text{C}_{16}\text{EO}_{20}$ .

oligomeric surfactants such as Brij 56 ( $\text{C}_{16}\text{EO}_{10}$ ) and Brij 58 ( $\text{C}_{16}\text{EO}_{20}$ ) and the conversion to periodic mesoporous materials was investigated. The XRD patterns of aluminum methylenediphosphonates prepared in the presence of  $\text{C}_{16}\text{EO}_{10}$  and  $\text{C}_{16}\text{EO}_{20}$  are shown in Figures 1 and 2, respectively. A main peak at the  $d$ -spacing of 5.5 nm was observed for the product prepared in the presence of  $\text{C}_{16}\text{EO}_{10}$ . The peak was maintained at  $2\theta = 2.53^\circ$  ( $d = 4.4$  nm) after calcination at 400 °C. According to the considerable increase of the peak intensity, broad peaks appeared in the range of 3.8–5.5°. The peaks are consistent with (110) and (200) reflections when the peak at  $2\theta = 2.53^\circ$  is assigned to a (100) reflection of a 2-D hexagonal phase ( $p6m$ , a unit cell parameter ( $a$ ) = 5.1 nm,  $d_{100} = 4.4$  nm). The result was also confirmed by the TEM observation and the  $\text{N}_2$  adsorption–desorption measurement of the calcined material. The presence of one-dimensional (1-D) mesopores was clearly observed by TEM (Figure 3a). The BET surface area, the pore volume, and the pore diameter were 579  $\text{m}^2 \text{g}^{-1}$ , 0.53  $\text{cm}^3 \text{g}^{-1}$ , and 3.3 nm, respectively.

A highly ordered mesoporous aluminum methylenediphosphonate can be obtained by using  $\text{C}_{16}\text{EO}_{20}$ . A sharp peak ( $d = 6.6$  nm) was observed in low scattering angles in the XRD pattern of the as-synthesized aluminum methylenediphosphonate. The XRD pattern of the calcined aluminum meth-

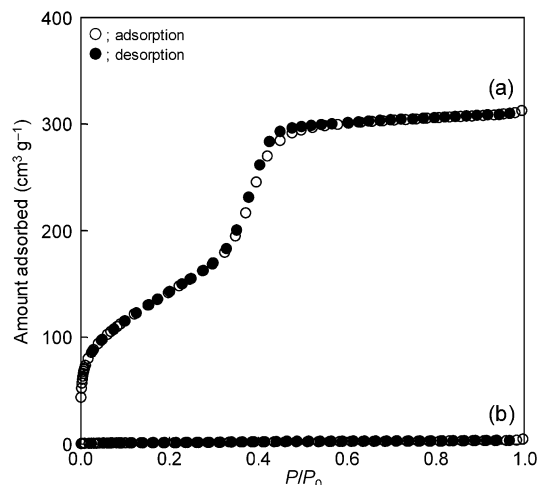
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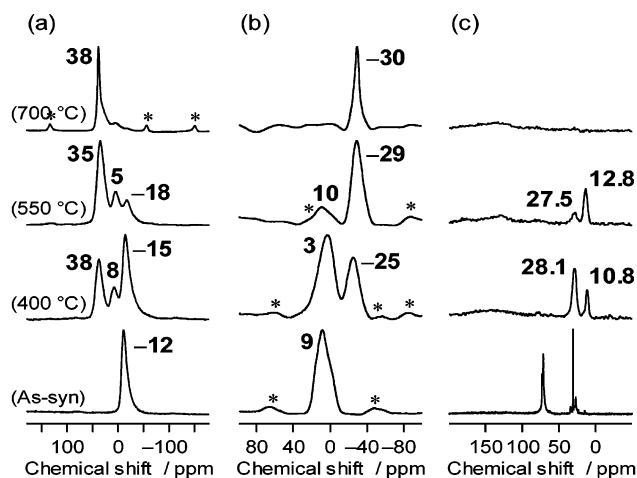
**Figure 3.** TEM images of calcined (at 400 °C) aluminum methylenediphosphonates prepared in the presence of (a)  $C_{16}EO_{10}$  and (b)  $C_{16}EO_{20}$ .

ylenediphosphonate showed the presence of well-resolved peaks assignable to (100), (110), and (200) reflections due to a 2-D hexagonal structure ( $p6m$ ,  $a = 5.7$  nm,  $d_{100} = 5.0$  nm). The TEM image of the calcined aluminum methylenediphosphonate is shown in Figure 3b. Well-ordered hexagonal arrays of 1-D mesopores were observed. The  $N_2$  adsorption–desorption isotherm of the calcined material is shown in Figure 4. The isotherm was type IV, typical for ordered mesoporous materials,<sup>4,5</sup> and a capillary condensation started at around  $P/P_0 = 0.3$ . The BET surface area, the pore volume, and the pore diameter were  $530$  m<sup>2</sup> g<sup>-1</sup>,  $0.48$  cm<sup>3</sup> g<sup>-1</sup>, and  $3.8$  nm, respectively.

The <sup>13</sup>C CP/MAS NMR spectra of the as-synthesized and calcined materials are shown in Figure 5. In the spectrum of the as-synthesized material, several peaks due to polyoxyethylene glycol hexadecyl ethers ( $C_{16}EO_{20}$ ) were mainly observed. Peaks at 73.0 and 71.4 ppm can be assigned to carbon atoms in polyoxyethylene moieties and carbon atoms in hexadecyl chains were observed in the range of 15–35 ppm (mainly at 30.9 ppm). A small peak centered at around 28 ppm is due to carbon atoms in methylenediphosphonate groups ( $\equiv PCH_2P\equiv$ ).<sup>35,41</sup> The <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectra of the as-synthesized and calcined materials are also shown in Figure 5. The <sup>27</sup>Al MAS NMR spectrum indicates that all of the aluminum species (–12 ppm) are six-coordinated in the as-synthesized material.<sup>47–50</sup> The <sup>31</sup>P MAS NMR spec-



**Figure 4.**  $N_2$  adsorption–desorption isotherms of aluminum methylenediphosphonates prepared in the presence of  $C_{16}EO_{20}$  calcined at (a) 400 and (b) 550 °C.



**Figure 5.** (a) <sup>27</sup>Al, (b) <sup>31</sup>P, and (c) <sup>13</sup>C(CP) MAS NMR spectra of as-synthesized and calcined (at 400, 550, and 700 °C) aluminum methylenediphosphonates prepared in the presence of  $C_{16}EO_{20}$ . Spinning sidebands are marked with asterisks.

trum of the as-synthesized material exhibits a broad peak centered at 9 ppm. The peak is assignable to diphosphonate groups ( $\equiv PCH_2P\equiv$ )<sup>35,37,38,41</sup> and no other peaks were observed for the as-synthesized material. The NMR results indicate that degradation of methylenediphosphonic groups has never proceeded during the synthesis.

After calcination at 400 °C, all of the peaks due to the surfactant molecules disappeared in the <sup>13</sup>C CP/MAS NMR spectrum. Additionally, methylenediphosphonate groups were decomposed to some extent and then new peaks appeared in the <sup>13</sup>C CP/MAS and <sup>31</sup>P MAS NMR spectra. A peak at 10.8 ppm in the <sup>13</sup>C CP/MAS NMR spectrum can be indexed to carbon atoms in methyl groups attached to phosphorus atoms ( $\equiv PCH_3$ ),<sup>38,51</sup> though the peak due to  $\equiv PCH_2P\equiv$  groups was observed distinctly. In addition to the peak due

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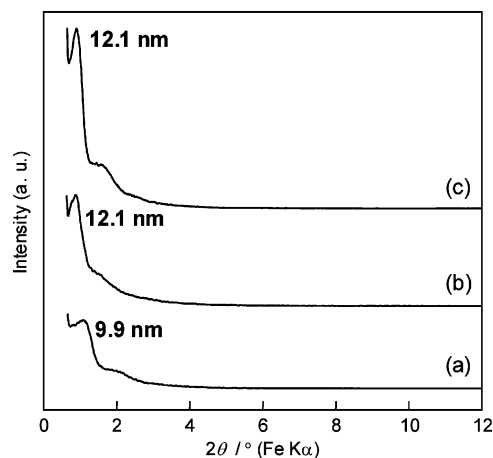
**Table 1. Organic Contents of As-Synthesized and Calcined (at 400 °C) Aluminum Methylene-diphosphonates Prepared in the Presence of C<sub>16</sub>EO<sub>n</sub> and EO<sub>n</sub>PO<sub>m</sub>EO<sub>n</sub>**

surfactant		C/mass %	H/mass %
Al <sub>3</sub> (O <sub>3</sub> PCH <sub>2</sub> PO <sub>3</sub> ) <sub>4</sub>	calculated	6.25	1.05
C <sub>16</sub> EO <sub>10</sub>	as-synthesized	30.4	6.9
	calcined	3.2	2.5
C <sub>16</sub> EO <sub>20</sub>	as-synthesized	28.2	6.4
	calcined	2.9	2.4
Al(O <sub>3</sub> PCH <sub>2</sub> PO <sub>3</sub> )	calculated	6.04	1.01
EO <sub>80</sub> PO <sub>30</sub> EO <sub>80</sub>	as-synthesized	26.2	5.9
	calcined	4.1	2.0
EO <sub>106</sub> PO <sub>70</sub> EO <sub>106</sub>	as-synthesized	24.9	5.7
	calcined	4.6	2.1
EO <sub>20</sub> PO <sub>70</sub> EO <sub>20</sub>	as-synthesized	26.3	6.1
	calcined	5.8	2.1

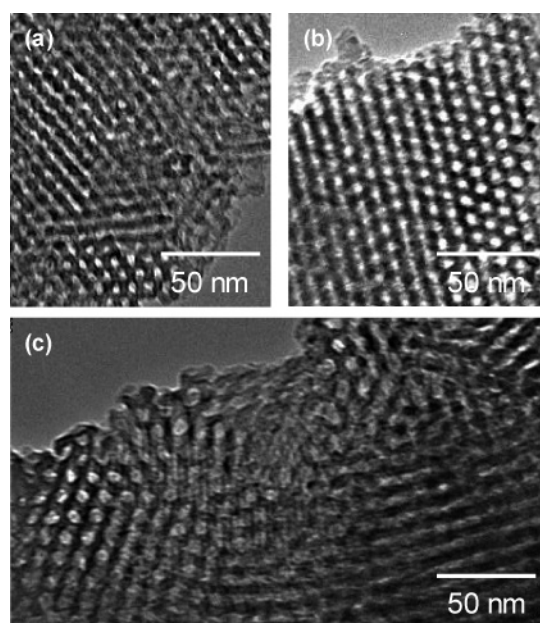
to ≡PCH<sub>2</sub>P≡ groups (at around 3 ppm), a peak at around -25 ppm assignable to phosphate groups (PO<sub>4</sub>) was observed in the <sup>31</sup>P MAS NMR spectrum.<sup>47–50</sup> The results mean that the mesoporous material is not composed of aluminum methylenediphosphonate completely and contains methylphosphonate and phosphate groups. The <sup>27</sup>Al MAS NMR spectra showed that the AlO<sub>6</sub> species were partly changed into four-coordinated species (38 ppm) such as Al(OP)<sub>4</sub> and/or Al(OP)<sub>4-x</sub>(OH)<sub>x</sub> by calcination through dehydration.<sup>47–50</sup> However, a peak at -15 ppm due to the AlO<sub>6</sub> species was largely retained even after calcination at 400 °C. The result reveals that a large amount of hydrated H<sub>2</sub>O molecules cannot be eliminated by low-temperature calcination. Condensation between phosphonate groups and Al species does not make progress adequately in the hybrid frameworks. The organic contents of the as-synthesized and calcined materials prepared in the presence of C<sub>16</sub>EO<sub>n</sub> are shown in Table 1. The amounts of carbon atoms in methylene groups (≡PCH<sub>2</sub>P≡) including methyl ones (≡PCH<sub>3</sub>) were approximately 3 mass %. This value is smaller than that calculated on the basis of the empirical formula (Al<sub>3</sub>(O<sub>3</sub>-PCH<sub>2</sub>PO<sub>3</sub>)<sub>4</sub>, 6.25 mass %), indicating that some methylene groups are eliminated. However, the calculated value of the carbon content should be estimated to be smaller because this calculation ignores the presence of a large amount of hydrated H<sub>2</sub>O molecules as well as OH groups which are not condensed yet.

The hybrid frameworks contain couples of aluminum methylphosphonates (≡PCH<sub>3</sub>) and aluminum phosphates (PO<sub>4</sub>) as well as aluminum methylenediphosphonates (≡PCH<sub>2</sub>P≡). However, further removal of the organic moieties (methylene and methyl groups) directed to the formation of aluminophosphate (AlPO) framework composed of alternating AlO<sub>4</sub> and PO<sub>4</sub> units and then mesoporous structures collapsed, as described later. Extraction of C<sub>16</sub>-EO<sub>n</sub> molecules by acid treatment is not possible at present as in the case of previously reported aluminum organophosphonates (AOPs) prepared in the presence of alkyltrimethylammonium (C<sub>n</sub>TMA) surfactants.<sup>34,41</sup> Therefore, a calcination process at low temperatures which allows elimination of only surfactant molecules is quite important for obtaining mesoporous AOP-based materials in the present study.

**Triblock Copolymer Templated Mesoporous Aluminum Methylene-diphosphonates.** Triblock copolymer syntheses of AOPs were conducted by using (HO)<sub>2</sub>OPCH<sub>2</sub>PO-

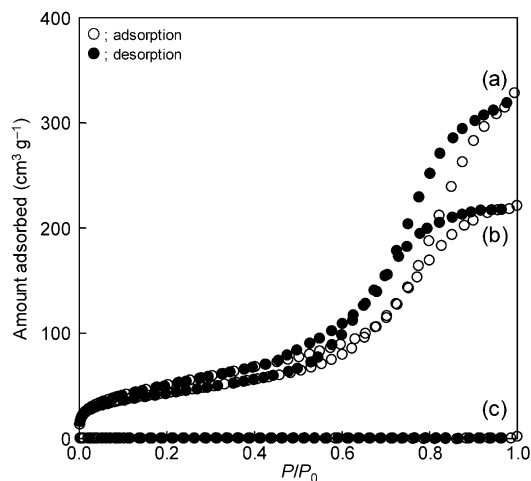


**Figure 6.** XRD patterns of calcined (at 400 °C) aluminum methylenediphosphonates prepared in the presence of (a) EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, (b) EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and (c) EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>.



**Figure 7.** TEM images of calcined (at 400 °C) aluminum methylenediphosphonates prepared in the presence of (a) EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, (b) EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and (c) EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>.

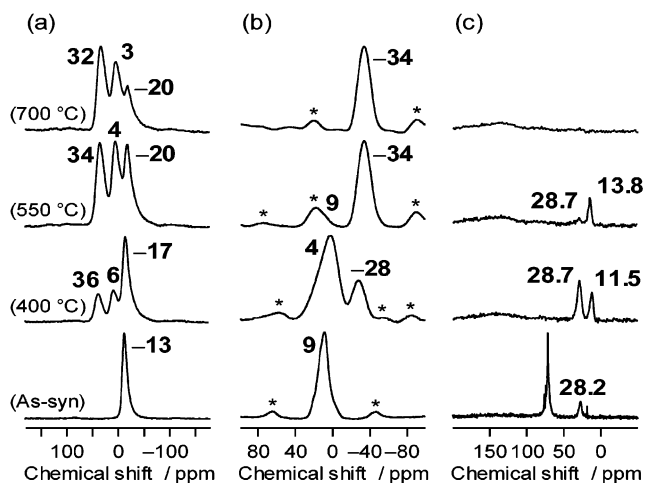
(OH)<sub>2</sub> and AlCl<sub>3</sub> in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>. The XRD patterns of calcined aluminum methylenediphosphonates prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> are shown in Figure 6. Main peaks with larger *d*-spacings more than ca. 10 nm were observed in all of the XRD patterns. In addition, broad peaks were observed as higher order reflections possibly related to 2-D hexagonal phases. The TEM images of the calcined materials are shown in Figure 7. The presence of 1-D large mesopores and the hexagonal arrangements were observed. For example, the N<sub>2</sub> adsorption-desorption isotherm of the calcined material prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub> is shown in Figure 8. The isotherm showed a type IV behavior, which is typically observed for 2-D hexagonal SBA-15 prepared in the presence of triblock copolymers such as Pluronic P123.<sup>16,17</sup> The BET surface areas, the pore volumes, and the pore diameters of the calcined materials prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> are listed in Table



**Figure 8.** N<sub>2</sub> adsorption–desorption isotherms of aluminum methylenediphosphonates prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub> calcined at (a) 400, (b) 550, and (c) 700 °C.

2. The unit cell parameters (calculated by XRD) and the wall thicknesses are also estimated. Because of the thicker walls, the BET surface areas of the triblock copolymer templated materials seem to be smaller than those of the oligomeric surfactant templated materials. The pore volumes are much more than those of oligomeric surfactant templated materials because the pore diameters are twice or three times larger than those of oligomeric surfactant templated materials.

The <sup>27</sup>Al MAS, <sup>31</sup>P MAS, and <sup>13</sup>C CP/MAS NMR spectra of the as-synthesized and calcined materials prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub> are shown in Figure 9. The NMR results are similar to those observed for the oligomeric surfactant templated materials (Figure 5). In the as-synthesized material, several peaks due to triblock copolymer (EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>) were observed at 76.2, 74.2, 71.5, and 18.6 ppm and a peak at 28.2 ppm is assignable to carbon atoms in methylenediphosphonate groups (≡PCH<sub>2</sub>P≡).<sup>34,41</sup> In addition to the peak (28.7 ppm), a new peak appeared at 11.5 ppm after calcination at 400 °C as carbon atoms in methyl groups attached to phosphorus atoms (≡PCH<sub>3</sub>).<sup>38,51</sup> Although only one broad peak was observed at around 9 ppm in the <sup>31</sup>P MAS NMR spectrum of the as-synthesized material, peaks at 4 ppm (≡PCH<sub>2</sub>P≡ and ≡PCH<sub>3</sub>) and –28 ppm (PO<sub>4</sub>) were observed after calcination at 400 °C. The results indicate that diphosphonate groups are partly converted to methylphosphonate and phosphate groups during calcination. The <sup>27</sup>Al MAS NMR spectrum of the as-synthesized material showed a broad peak at around –13 ppm. The asymmetric profile reveals that six-coordinated Al atoms are surrounded by PO<sub>3</sub> groups, OH groups, and H<sub>2</sub>O ligands.<sup>41,47–50</sup> How-



**Figure 9.** (a) <sup>27</sup>Al, (b) <sup>31</sup>P, and (c) <sup>13</sup>C(CP) MAS NMR spectra of as-synthesized and calcined (at 400, 550, and 700 °C) aluminum methylenediphosphonates prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>. Spinning sidebands are marked with asterisks.

ever, the presence of OH groups in the as-synthesized material have not been shown because of the presence of a large number of hydrated H<sub>2</sub>O molecules. The AlO<sub>6</sub> species were partly converted to four-coordinated species (36 ppm) by calcination at 400 °C; however, a large number of the six-coordinated Al species (–17 ppm) were maintained even after calcination.

The organic contents of the as-synthesized and calcined materials prepared in the presence of EO<sub>n</sub>PO<sub>m</sub>EO<sub>n</sub> are also shown in Table 1. The amounts of carbon atoms in the calcined materials prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>, EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, and EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> were 4.1, 4.6, and 5.8 mass %, respectively. Compared with a calculated carbon content (Al(O<sub>3</sub>PCH<sub>2</sub>PO<sub>3</sub>), 6.04 mass %), considerable amounts of carbon atoms were retained in the calcined materials. Considering the presence of hydrated H<sub>2</sub>O molecules and OH groups in the hybrid mesoporous materials, methylene groups are not discharged from the hybrid frameworks of triblock copolymer templated materials during calcination so much, though methylenediphosphonate groups are slightly decomposed into couples of methylphosphonate and phosphate groups.

**Mesostructural Stabilities of Aluminum Methylenediphosphonates.** Mesostructures of aluminum methylenediphosphonates were almost maintained after calcination at 400 °C and then various mesoporous aluminum methylenediphosphonates can be obtained by using oligomeric surfactants and triblock copolymers as well as C<sub>n</sub>TMA surfactants.<sup>34,41</sup> However, mesostructural orderings were gradually

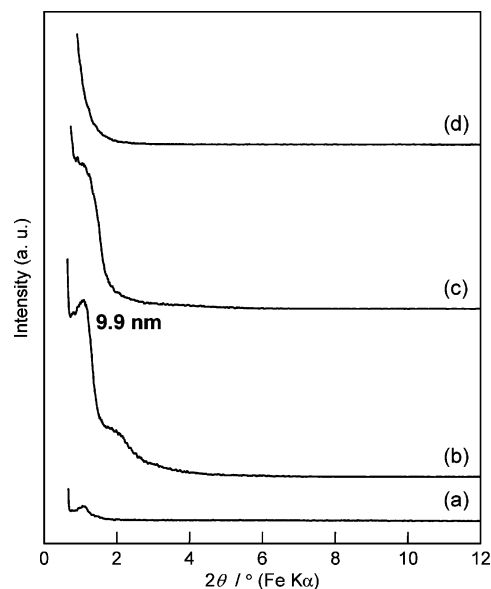
**Table 2. Porous Structures of Calcined Aluminum Methylenediphosphonates Prepared in the Presence of C<sub>16</sub>EO<sub>n</sub> and EO<sub>n</sub>PO<sub>m</sub>EO<sub>n</sub>**

surfactant	<i>d</i> -spacing (nm)	unit cell parameter (nm)	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	pore volume (cm <sup>3</sup> g <sup>-1</sup> )	pore diameter (nm)	wall thickness (nm)
C <sub>16</sub> EO <sub>10</sub> (400 °C)	4.4	5.1	579	0.53	3.3	1.8
C <sub>16</sub> EO <sub>20</sub> (400 °C)	5.0	5.8	530	0.48	3.8	2.0
EO <sub>80</sub> PO <sub>30</sub> EO <sub>80</sub> (400 °C)	9.9	11.4	279	0.76	6.0	5.4
(550 °C)			239	0.51		
EO <sub>106</sub> PO <sub>70</sub> EO <sub>106</sub> (400 °C)	12.1	14.0	249	0.59	8.2	5.8
(550 °C)			150	0.34		
EO <sub>20</sub> PO <sub>70</sub> EO <sub>20</sub> (400 °C)	12.1	14.0	185	0.47	9.2	4.8
(550 °C)			169	0.36		

lost by increasing the calcination temperature. The importance of thermal stabilities of inner organic groups was already reported in a previous paper.<sup>41</sup> When thermally unstable organic groups such as propylene ones are present in the hybrid frameworks, mesostructures of AOPs collapse even by calcination at 400 °C. Here, framework structures after the complete removal of inner organic groups are discussed to investigate the mesostructural stabilities of AOPs in more detail.

The <sup>27</sup>Al MAS, <sup>31</sup>P MAS, and <sup>13</sup>C CP/MAS NMR spectra of calcined (at 550 and 700 °C) materials prepared in the presence of C<sub>16</sub>EO<sub>20</sub> are shown in Figure 5. The change of the <sup>27</sup>Al MAS NMR spectra according to the calcination temperatures indicates that four-coordinated Al species were formed through dehydration and condensation. The <sup>27</sup>Al and <sup>31</sup>P MAS NMR spectra reveal the frameworks were composed of alternative AlO<sub>4</sub> and PO<sub>4</sub> units with the complete removal of organic moieties inside the hybrid frameworks. Methylenediphosphonate groups ( $\equiv\text{PCH}_2\text{P}\equiv$ ) are partly decomposed into couples of methylphosphonate ( $\equiv\text{PCH}_3$ ) and phosphate groups (PO<sub>4</sub>) at 400 °C. Once organic groups within the hybrid frameworks are eliminated completely, two phosphate groups are adjacent to each other ( $-\text{P}-\text{OH} + \text{HO}-\text{P}-$ ). In silica-based hybrid materials, ordered mesoporous silicas can be obtained after the complete removal of organic moieties within the hybrid frameworks.<sup>31</sup> Further condensation is possible for constructing new silica networks (Si-O-Si). However, in the present study, it is said that further condensation leads to the formation of P-O-P bonds. This is not preferable because the framework ( $-\text{Al}-\text{O}-\text{P}-\text{O}-\text{P}-\text{O}-\text{Al}-\text{O}-$ ) is not homogeneous and has never been found among mesoporous AlPO<sub>4</sub>-based materials,<sup>52,53</sup> so rearrangements within the frameworks must have occurred to afford uniform AlPO<sub>4</sub> frameworks ( $-\text{Al}-\text{O}-\text{P}-\text{O}-\text{Al}-\text{O}-\text{P}-\text{O}-$ ). Therefore, mesostructures of aluminum methylenediphosphonates were lost by the complete removal of methylene groups.

The <sup>27</sup>Al MAS, <sup>31</sup>P MAS, and <sup>13</sup>C CP/MAS NMR spectra of calcined (at 550 and 700 °C) materials prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub> are shown in Figure 9. Those changes in the NMR spectra were quite similar to that observed for calcined materials prepared in the presence of C<sub>16</sub>EO<sub>20</sub>. However, the changes in the XRD patterns according to the calcination temperatures were different. In the C<sub>16</sub>EO<sub>20</sub>-AOP system, the XRD peaks almost disappeared after calcination at 550 °C and completely disappeared at 700 °C. The N<sub>2</sub> adsorption-desorption isotherm showed that the material calcined at 550 °C is not porous (Figure 4b). In contrast, in the EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub>-AOP system, the XRD peak was maintained even after calcination at 550 °C and disappeared at 700 °C (Figure 10). The N<sub>2</sub> adsorption-desorption isotherms of the materials calcined at 550 and 700 °C are shown in Figure 8. The isotherm of the material calcined at 550 °C was still type IV. A slight decrease of the surface area (239 m<sup>2</sup> g<sup>-1</sup>) and the pore volume (0.51 cm<sup>3</sup> g<sup>-1</sup>) was confirmed compared with those observed for the material calcined at 400 °C (279 m<sup>2</sup> g<sup>-1</sup> and 0.76 cm<sup>3</sup>



**Figure 10.** XRD patterns of (a) as-synthesized aluminum methylenediphosphonate prepared in the presence of EO<sub>80</sub>PO<sub>30</sub>EO<sub>80</sub> and the materials calcined at (b) 400, (c) 550, and (d) 700 °C.

g<sup>-1</sup>). The difference in the mesostructural stabilities between the oligomeric surfactant and triblock copolymer templated materials is related to wall thicknesses. It is difficult to assume that rearrangement of the frameworks to form uniform AlPO<sub>4</sub> frameworks occurs in thin inorganic walls. Therefore, triblock copolymer templated materials are more stable than oligomeric surfactant templated materials.

Mesostructures of the oligomeric surfactant templated materials were lost by calcination above 550 °C, while those of the block copolymer templated materials were maintained even after calcination at 550 °C. With the increase in the calcination temperatures, methylenediphosphonate groups are decomposed and organic moieties are eliminated, so the frameworks must be changed into homogeneous inorganic frameworks such as AlPO<sub>4</sub>-based ones. Therefore, it is considered that wall thicknesses effect on the mesostructural stability of aluminum methylenediphosphonates despite the complete removal of methylene groups destroys the mesostructural orderings eventually. Because of the thick walls, triblock copolymer templated mesoporous silicas such as SBA-15 show higher stabilities than MCM-41.<sup>17</sup> Even when silicate frameworks of SBA-15 are attacked by water molecules, only surface silicate frameworks are hydrolyzed and the mesostructures are maintained. All of the silicate frameworks of SBA-15 are not hydrolyzed. Similarly, the presence of P-OH groups would be allowed in thicker walls of mesoporous AOPs.

## Conclusions

Oligomeric surfactant (C<sub>16</sub>EO<sub>n</sub>) and triblock copolymer (EO<sub>n</sub>PO<sub>m</sub>EO<sub>n</sub>) syntheses of aluminum organophosphonates (AOPs) with ordered mesoporous structures have been achieved and the mesostructural stabilities of AOPs were investigated. Because of the stabilities of methylenediphosphonate groups and the inner organic groups of the hybrid frameworks, mesoporous materials composed of non-silica-based inorganic-organic hybrid frameworks can be obtained

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through low-temperature calcination. Thicknesses of the hybrid frameworks are also important for mesostructural stabilities of AOPs. In comparison with the pore diameters (ca. 2 nm) of previously reported 2-D hexagonal AOPs with methylene groups prepared by using a C<sub>16</sub>TMA surfactant,<sup>41</sup> the successful synthesis of ordered mesoporous AOPs with uniform large mesopores (3.3–3.8 nm for C<sub>16</sub>EO<sub>*n*</sub>, 6.0–9.2 nm for EO<sub>*n*</sub>PO<sub>*m*</sub>EO<sub>*n*</sub>) in the present study are important for extended applications such as catalysts, catalyst supports, and adsorbents of a wide variety of large organic molecules with various functions. The insights in the present study are useful for handling a wide variety of non-silica-based inorganic–organic hybrid materials which will be prepared by using organically bridged diphosphonic acids. Because a synthetic strategy of a wide variety of mesoporous metal phosphates

have already been proposed,<sup>42,44</sup> the successful synthesis of ordered mesoporous AOPs by using organically bridged diphosphonic acids in the presence of several types of surfactants will open a new route to obtain compositionally controlled non-silica-based hybrid mesoporous materials.

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