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Formation of Cylindrical-Shaped Coordination Polymer by Self-Assembling of 2, 2, 4, 4, 6, 6-Hexakis(4-pyridylmethoxy)-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) with Silver Nitrate

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The self-assembling of 2, 2, 4, 4, 6, 6-hexakis(4-pyridylmethoxy)-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) (PyPN) and $AgNO_3$ in DMSO gives a white rod-shaped coordination polymer. FT-IR and X-ray absorption fine structure spectra, X-ray diffraction data, and elemental analysis showed that the coordination polymer takes a cylindrical structure and is laterally packed into a hexagonal arrangement.

Recently, polymers with spherical structure such as dendrimers and hyperbranched polymers have been prepared, and applications of these polymers have been explored in various fields such as drug delivery systems or liquid crystals.[1—8] Few studies have, however, been reported on the syntheses of rod-, tube-, or cylindrical-shaped polymers.[9]

Hydrogen and coordination bondings have emerged as a new motif in the construction of unique supramolecular species with well defined shapes and geometries.[10—18] We have recently described the design and construction of a new class of cylindrical structures, which are formed by the complementary hydrogen bondings between 2, 2, 4, 4, 6, 6-hexakis(4-carboxyphenoxy)-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) (CPN) and 2, 2, 4, 4, 6, 6-hexakis-(4-pyridylmethoxy)-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) (PyPN), between terephthalic acid (TPA) and PyPN.[19,20] This indicates that cyclotri(phosphazene) derivative is one useful building block to create polymeric and ordered supramolecules.

The use of metal cations to link PyPN is an alternative method for the design of new inorganic and organometallic supramolecules (coordination polymers). By a careful and appropriate choice of the metal, it is possible to closely control the structure of coordination polymers. In this paper, we report on the preparation and structural characterization of the coordination polymer by self-assembling of PyPN with $AgNO_3$.

Experimental

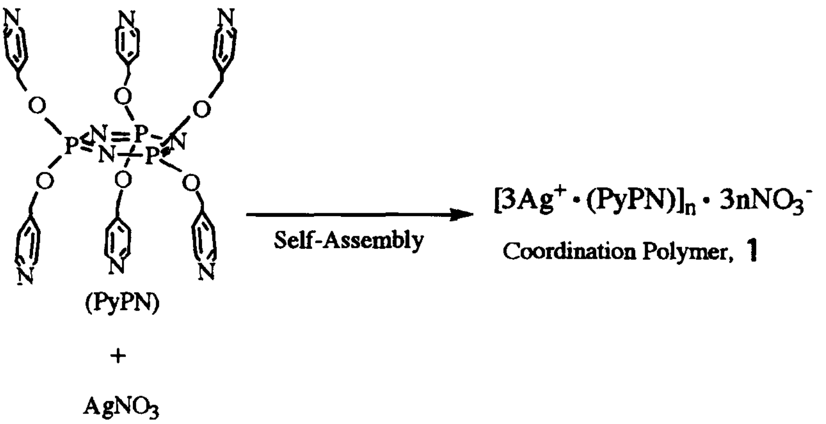
Materials. 2, 2, 4, 4, 6, 6-hexakis(4-pyridylmethoxy)-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) (PyPN) was synthesized from the reaction of 2, 2, 4, 4, 6, 6-hexachloro-2λ^5, 4λ^5, 6λ^5-cyclotri(phosphazene) with sodium 4-pyridylmethoxide, prepared from 4-pyridinemethanol and NaH in THF, as described in a previous paper.[19] Other reagents were of analytical grade and were used without further purification.

Preparation of Coordination Polymer. A typical preparation of the coordination polymer **1** of PyPN with $AgNO_3$ was as follows. A DMSO solution of PyPN (0.030 g, 3.9×10^{-5} mol) was added to a DMSO solution of $AgNO_3$ (0.021 g, 1.3×10^{-4} mol), and then the mixture was allowed to stand for one day at room temperature, giving **1** as white precipitate in 70% isolated yield. Found: C, 33.69; H, 3.04; N, 12.90 %. Anal. Calcd for $(C_{36}H_{36}N_{12}O_{15}P_3Ag_3)_n$: C, 33.43; H, 2.81; N, 13.00 %.

Measurements. Scanning electron microscope (SEM) photographs were obtained by use of a JEOL JSM-5300 instrument. FT-IR spectra were recorded on a JASCO FT-IR 230 spectrophotometer applying the KBr pelleting technique. Extended X-ray absorption fine structure (EXAFS) measurements were performed by using the EXAC 820 system (TECHNOS). The silver K-edge absorption spectra were taken with the transmission mode at room temperature, using a beam line with Ge(840) crystal monochromator under a condition of 40 kV and 200 mA. In order to determine the structural parameters, we carried out the nonlinear least-squares fitting to the filtered data with a multiple-term semiempirical expression of the EXAFS formula.[21] Both the Ag–N pair and Ag–O pair were analyzed using FEFF ab initio tables, where FEFF is an automated program for ab initio multiple scattering calculation of X-ray absorption fine structure.[22] Wide-angle X-ray diffraction patterns were obtained using a Rigaku RINT 2000 system. Differential scanning calorimetry was done using a Shimadzu DSC-50 calorimeter in sealed aluminium pans at a heating rate of 10 °C min^{-1}. Thermogravimetry was performed on a Shimadzu TGA-50/50H thermogravimetry system at a heating rate of 10 °C min^{-1}.

Results and Discussion

The symmetry and preorganization of component molecules are important keys for the construction of supramolecules with highly ordered structure.[23] In a previous paper, PyPN has an approximate C_2 symmetry axis along a P–N direction in the hydrogen-bonded supramolecule composed of PyPN and terephthalic acid (TPA).[20] The single crystal X-ray analysis indicates that the pyridyl groups are located perpendicularly above and below a nearly planar cyclotri(phosphazene) ring, i.e., pyridyl units preorganize and take positions that enable directional and selective



Scheme 1. Self-assembly of PyPN and $AgNO_3$.

interactions with TPA, in spite of having a flexible OCH_2 group. The structural features of organophosphazenes were also been reported for 2, 2, 4, 4, 6, 6-hexakis(phenoxy)-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene).[24] If the geometrical arrangement holds for the coordination polymers composed of PyPN and metal ions, the polymers would be expected to take a cylindrical structure.

The preparation of the coordination polymer by self-assembling of PyPN with $AgNO_3$, or $AgBF_4$ was attempted in various solvents such as EtOH, DMF, DMSO, 1 : 1 EtOH/DMF, and 1 : 1 EtOH/DMSO solutions. The white crystalline solids **1** grew gradually in DMSO solution containing of PyPN and $AgNO_3$ in 1 : 3 molar ratio (Scheme 1). **1** is stable indefinitely in air, and is insoluble in water, polar and nonpolar organic solvents. The scanning electron micrograph shows that **1** is a rod-shaped crystalline material (Fig. 1).[25] The apparent morphological feature is not affected by changing either the molar ratio of PyPN and $AgNO_3$ in the feed or their total concentrations.

From elemental analysis the stoichiometry of **1** was shown to be PyPN : $AgNO_3$ = 1/3. The peak of pyridyl unit at 1605 cm^{-1} (free PyPN) disappeared in the FT-IR spectrum of **1** and shifted to 1612 cm^{-1}, indicating that all of the pyridyl units in PyPN participate in the formation of the coordination polymer (Fig. 2). These results indicate that PyPN molecules interact with $AgNO_3$ to give coordination polymers composed of $[3Ag^+ \cdot (PyPN)]_n \cdot 3nNO_3^-$. When PyPN and $AgNO_3$ were mixed in the solvents such as EtOH, DMF, 1 : 1 EtOH/DMF and 1 : 1 EtOH/DMSO, white solids precipitated instantly and did not have a definite stoichiometry, suggesting a random bridge structure. Combination of PyPN and $AgBF_4$ also did not give a coordination polymer with a well-controlled structure. Thus, the assembly process is significantly influenced by both the solvent and the counter ion.

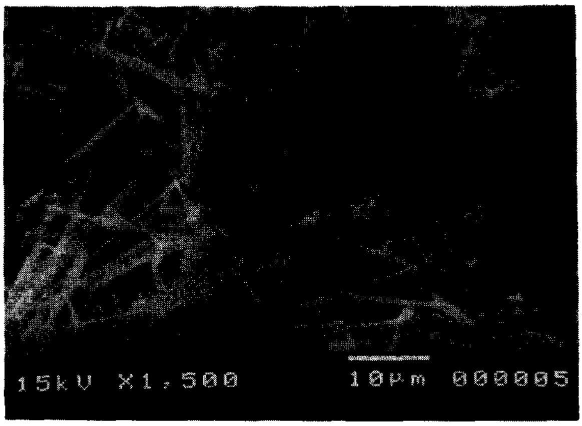


Fig. 1. SEM photograph of **1**.

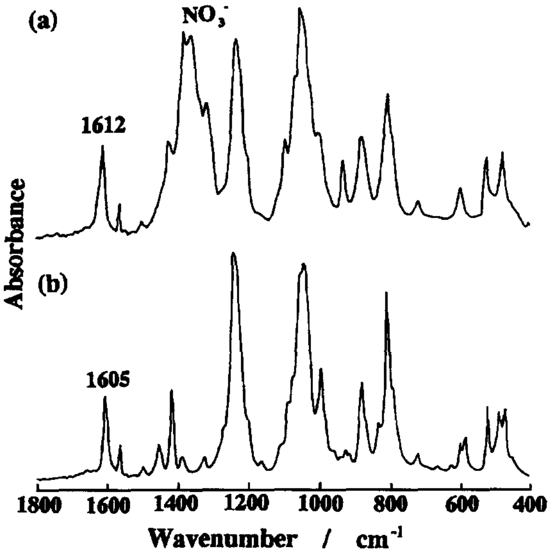


Fig. 2. FT-IR spectra of **1** (a) and PyPN (b).

X-ray absorption fine structure (XAFS) spectroscopy is quite suitable to get the information about the environment of the absorbing atoms such as the number and the arrangement of ligand atoms. The experimental X-ray absorption spectra for silver K-edge of **1**, $AgNO_3$, and bis(pyridine)silver nitrate ($[Ag(Py)_2]NO_3$) as a model compound for **1** are shown in Fig. 3. The spectrum of **1** is clearly different from that of $AgNO_3$, in which only oxygen atoms of NO_3^- bind to Ag^+. On the other hand, the spectrum of **1** was very similar to that of $[Ag(Py)_2]NO_3$, in which Ag^+ ion is coordinated by two nitrogen atoms (pyridine) and oxygen atoms (NO_3^-).[26] This result indicates that the coordination bonding through an alternating sequence of one PyPN and three Ag^+ ions gives a cylindrical-shaped polymer, as shown in Scheme 2, in a

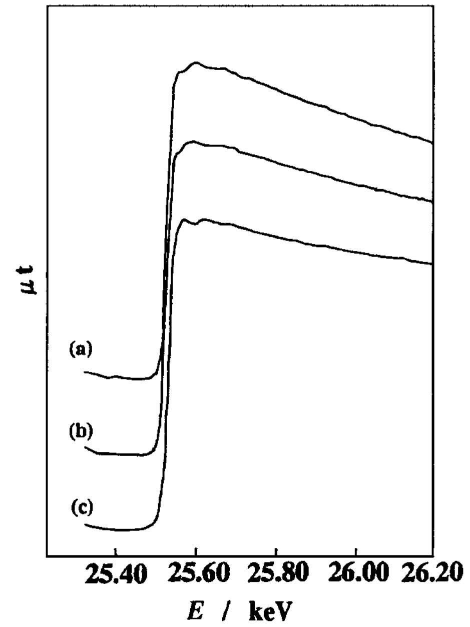
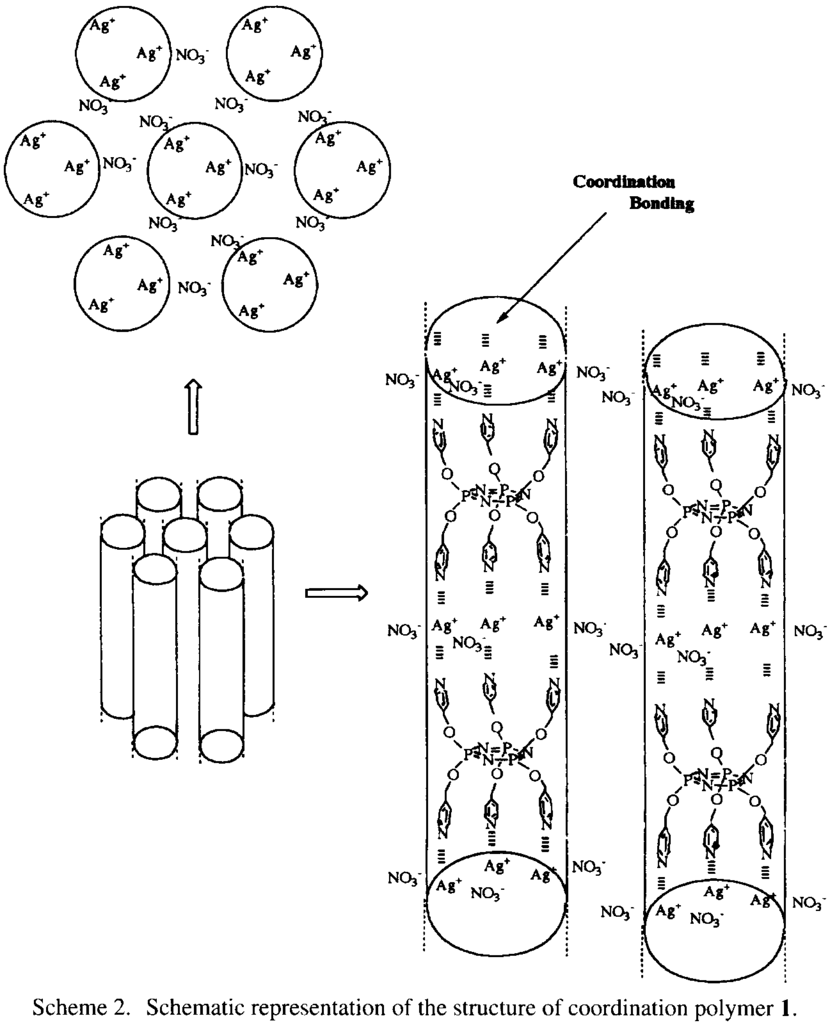


Fig. 3. X-ray absorption energy spectra for the silver K-edge of **1** (a), bis(pyridine)silver nitrate (b) and silver nitrate (c).

manner similar to the formation of supramolecules based on hydrogen bondings between PyPN and hexakis(4-carboxyphenoxy)cyclotri(phosphazene), between PyPN and terephthalic acid.[19,20]

The extended X-ray absorption fine structure (EXAFS) oscillations $\kappa^3\chi$ (k) vs. k (in Å^{-1}) of **1** are shown in Fig. 4(a). The Fourier transform of the oscillations show peaks corresponding to the atomic positions around Ag^+ ion, where the peak positions are shifted a few tenths of an angstrom from the actual interatomic distances because of the EXAFS phase shift (Fig. 4(b)).

The Fourier-Transformed curve (Fig. 4(b)) for the silver K-edge of **1** exhibits distinct radial structure peaks at about 1.8 and 2.9 Å, respectively. The structural parameters were determined by a curve-fitting analysis to the Fourier EXAFS data (Table 1). The best fit is derived from the model based on the nearest neighbor consisting of two nitrogens, the second-nearest neighbor consisting of one oxygen and the third-nearest neighbor consisting of three oxygens. The introduction of the splitting of the oxygens into two subshells with one nearest (2.68 Å) and three more distant (3.29 Å) oxygen atoms caused the R-factor to fall from $\geq 20\%$ down to 12.1%. These distances between Ag^+ and oxygen



Scheme 2. Schematic representation of the structure of coordination polymer **1**.

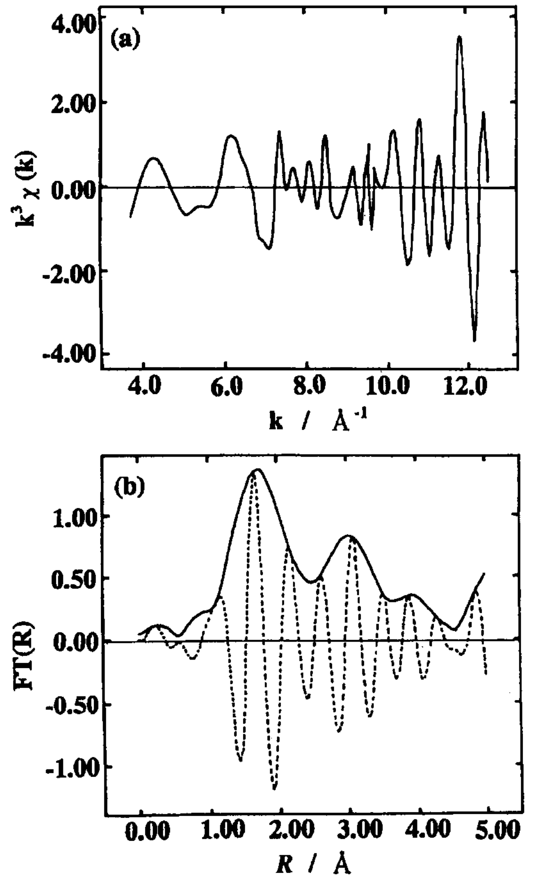


Fig. 4. $\kappa^3\chi$ (k) vs. k plot (a) and Fourier transform (b) for **1**.

Table 1. Best Fit Least-Squares Coordination Number, Interatomic Distance, and Debye–Waller Factor

Shell	Nearest neighbor	Coordination number	Distance Å	Debye–Waller factor Å
1	N	2	2.34	0.092
2	O	1	2.68	0.118
3	O	3	3.29	0.102

atoms are in agreement with those in metal nitrates.[27] These results suggest that Ag^+ ion in the polymer is coordinated by two pyridyl group of PyPN and oxygen atoms of NO_3^-, and that two types of binding are present in the coordination of the oxygen atom to Ag^+.

Figure 5(a) shows the wide-angle powder X-ray diffractogram of **1**. The patterns of sharp peaks were very similar to those of the supramolecule of hexakis(4-carboxyphenoxy)-cyclotri(phosphazene) (CPN) and PyPN determined by single-crystal X-ray analysis, in which all pyridyl and carboxy groups located at perpendicular positions on the phosphazene ring form hydrogen bonds to create a cylindrical structure.[19] In addition, we observed remarkable features in the diffractogram, i.e. the diffraction yielded *d* spacings with the 1, $1/\sqrt{3}$, 1/2, ··· ratio; the lower angle peak at $d = 7.68$ Å, and the small peaks at $d = 4.43$ Å and 3.83 Å, respectively. On the basis of these results, it seems that the cylindrical-shaped polymers are laterally packed into a hexagonal packing arrangement (Fig. 5(b)).

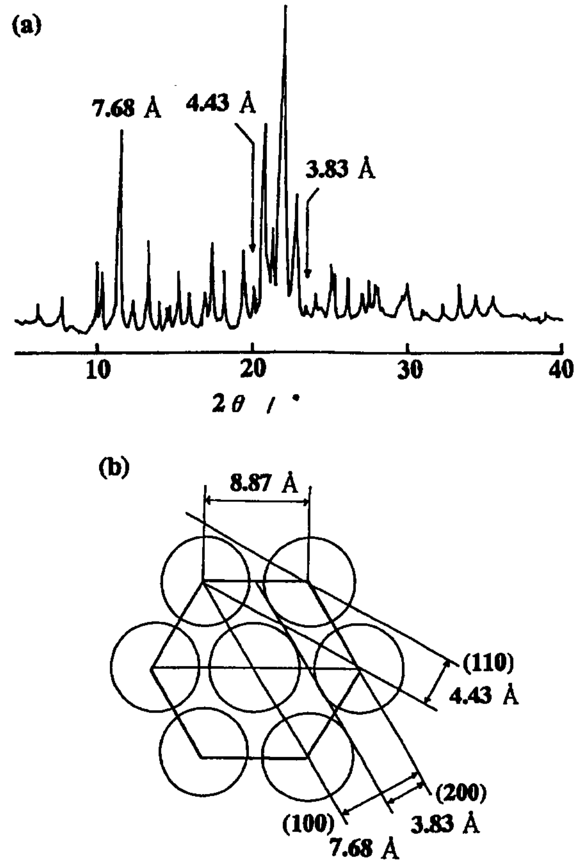


Fig. 5. Powder X-ray diffraction patterns of **1** (a). (b) represents the hexagonal packing structure for **1** together with Miller's indices.

The diameter *L* of the cylindrical polymers packed into hexagonal arrangement is approximately $L = 2d_{100}/\sqrt{3} = 8.9$ Å, which is the value estimated from the molecular size of PyPN. NO_3^- ions exist as counter anions in the space of cylindrical polymers (Scheme 2). In addition, judging from the fact that a supramolecular polymer does not form from the combination of PyPN and $AgBF_4$, we conclude that NO_3 ions play an important role in the closely packing through the bridging among Ag^+ ions in the neighboring polymers with cylindrical structure. The above-mentioned EXAFS analysis data that two types of binding are present in the coordination of oxygen atom (NO_3^-) to Ag^+ suggest that one oxygen atom of NO_3^- coordinates to Ag^+ and two other oxygen atoms interact with Ag^+ ions in the neighboring polymers. As for the bridging, we can refer to the crystal structure of the pyrazine–$AgNO_3$ complex,[28] where the structure consists of almost planar-linked chains of the type $(\cdots Ag\cdots NC_4H_4N\cdots)_n$ with Ag···N distance of 2.213 Å, and the next nearest neighbors of Ag^+ are two oxygens of a nitrate group at 2.720 Å and two other nitrate oxygens at 2.943 Å.

Finally, the thermal behavior of **1** was examined by using differential scanning calorimetry (DSC) and thermal gravimetrical analysis (TGA) (Fig. 6). The DSC and TGA curves show an exothermic peak and an abrupt but clear weight loss

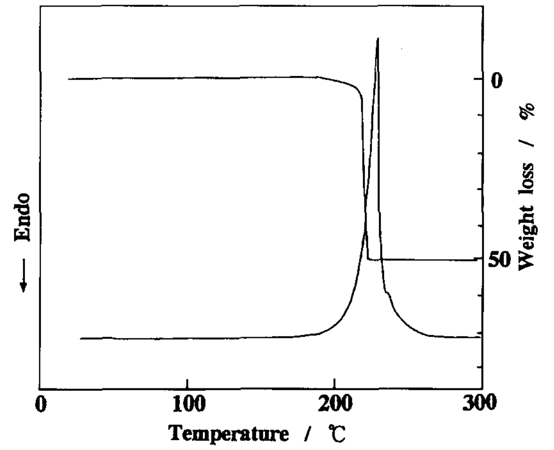


Fig. 6. DSC heating trace and TG analysis of **1**.

of 50.6% corresponding to six 4-pyridylmethoxy groups per formula unit (theoretical 50.2%) in the temperature range 190—220 °C, respectively. The temperature of decomposition was higher than that of PyPN (100 °C), indicating that PyPN become thermally stable in the polymers with cylindrical structure. In the DSC curve, an endothermic peak due to the coordination bond scission was not observed. Thus, **1** decomposes due to the pyrolysis of 4-pyridylmethoxy units in the polymers rather than the scission of the coordination bond. The ordered molecular packing of the polymers seems to contribute to the thermal stability.

In conclusion, we have found that an organometallic supramolecular polymer (coordination polymer) is formed by self-assembling of PyPN with $AgNO_3$ through the coordination bonding between pyridyl units of PyPN and Ag^+ ions. This coordination bonding gives a cylindrical-shaped polymer, which originates from the unique molecular structure of PyPN and the tendency of Ag^+ for linear coordination. The cylindrical polymers are laterally packed into a regular hexagonal arrangement and NO_3 ions seem to play an important role in the packing as counter anions to the polymer. Moreover, the ordered packing may contribute to the enhancement of thermal stability. Now we continue to explore novel supramolecular species based on cyclotriphosphazene.

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