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Synthesis of cylindrical polyamides from hexakis (4-carboxyphenoxy)cyclotriphosphazene and *p*-xylyenediamine

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Summary

The synthesis of cylindrical polyamides by condensation of salts prepared from hexakis(4-carboxyphenoxy)cyclotriphosphazene (**2**) and diamines was investigated. Among the diamines used, *p*-xylylenediamine (**4**) gave the salt (**5**) composed of 1 : 3 **2** - **4**. The condensation of **5** at 240 °C for 60 h gave a polyamide (**6a**) but some carboxyl groups remained without reaction. By adding excess **4** to **5** in a sealed tube, however, polyamide (**6b**), which showed no significant peak assignable to the carboxyl group in FT-IR and ^{13}C-CPMAS spectra, was obtained. X-ray diffraction studies showed that **6a** was amorphous but **6b** has a high level of crystalline character. From these results and the structural feature of **2**, it appears that **6b** takes a three-dimensional cylindrical structure. The thermogravimetric analysis of **6b** exhibited that the onset temperature of decomposition was 300 °C under both nitrogen and air atmospheres.

Introduction

Various flat and/or bulky rigid compounds as motif have been used for the construction of two- or three-dimensional supramolecules, which have attracted enormous attention from both their academic importance and potential applications in technology [1-3]. The most studies directed to self-assemblies have been based on hydrogen bondings and metal-ligand coordination bondings. As part of studies of self assembly in hydrogen bonding systems, we recently reported that complementary interactions between hexakis(4-carboxyphenoxy)cyclotriphosphazene (**2**) and hexakis(4-pyridylcarbinoxy)cyclotriphosphazene (**3**) provide a novel class of cylindrical self-assembly, suggesting that the molecules could be components for the sort of tailoring of three-dimensional intermolecular architectures [4-6|. Such a cylindrical assembly was based on a unique geometry of hexaphenoxycyclotriphosphazene derivatives, in which the phenoxy groups are aligned approximately perpendicular to the nearly planar phosphazene ring [7, 8].

So far, studies on synthesis and properties of various polyamides with dendritic or hyperbranched structures have been reported [9-12]. Our interests lay in extending to the preparation of covalently bonded polymers from self-assembled supramacromolecules with three-dimensional structure. This might be considered as another example of the template polymerization, where directional and specific interactions allow the preparation of polymers with a regular structure without undesired side reactions.

The salts composed of **2** and diamines would be expected to take a similar cylindrical structure and give three-dimensional polyamides when the salts are heated at moderate temperatures. In this paper, we wish to report the results of our initial studies on the preparation of a cylindrical polyamide by the polycondensation of salt composed of cyclotriphosphazene bearing carboxyl group (**2**) and *p*-xylylenediamine (**4**).

Experimental

Materials

Hexachlorocyclotriphosphazene (**1**, Ootsuka Chemical Co.) was recrystallized from n-hexane. 4-Hydroxybenzoic acid methyl ester was purchased and used without further purification. Hexakis(4-carboxyphenoxy)cyclotriphosphazene (**2**) was prepared as reported previously [4]. Diamines were purified by distillation or recrystallization.

Measurements

^{1}HNMR spectra were recorded with a JEOL JNM-GSX270 spectrometer. Infrared spectra were recorded with a Jasco FT-IR 230 spectrometer. ^{13}C-CP/MAS NMR spectra were recorded with a JEOL JNM-CMX300. The rotor was spun at about 4.0 KHz. Contact time was 2 ms, repetition time 5 s. The spectral width was 27 KHz and 8 K data points were taken. Wide-angle X-ray diffractograms were obtained on a Rigaku RINT 2000, using Cu Kα radiation(40 kv, 20 mA). Thermogravimetric analyses were carried out using a Shimadzu TGA-50. Measurements were made in an atmosphere of nitrogen and oxygen (20 mL/min) at a heating rate of 10 °C/min.

Preparation of salt and polyamide

A solution of hexakis(4-carboxyphenoxy)cyclotriphosphazene (**2**, 1.0 g, 1.04 mmol) in DMF was added to a stirred solution of *p*-xylylenediamine (**4**, 0.44 g, 3.23 mmol) in DMF. The precipitate (**5**) was separated by filtration and recrystallized from water. The mixture of the salt **5** and **4** was placed in a reaction tube. The tube was slightly degassed, sealed, and then heated in an oven maintained at 240 °C. After a definite time, the tube was opened, and the polymer (**6b**) was crushed and then washed with water.

5, FT-IR(KBr): 3000, 1635, 1598, 1544, 1500, 1400, 1292, 1265, 1193, 1155, 1091, 1014, 952 cm^{-1}.

^{13}C-CPMAS NMR (hexamethylbenzene): 172.2, 153.8, 134.9, 131.9, 121.9, 43.3 ppm.

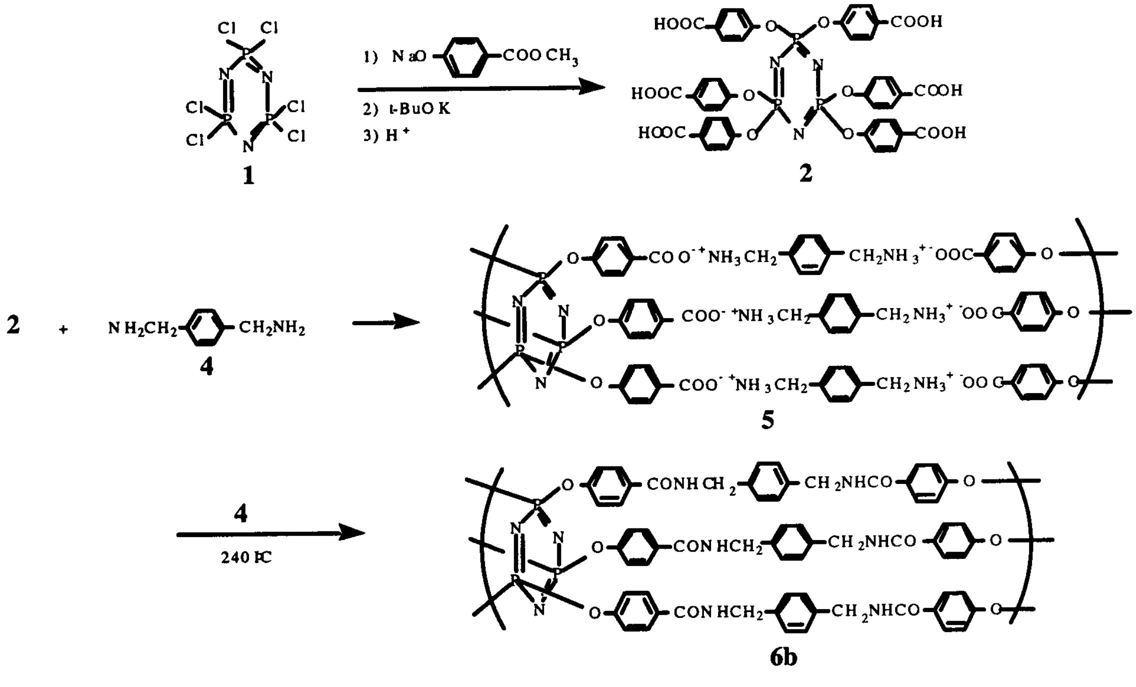
Elemental analysis Calcd. for $C_{66}H_{66}O_{18}N_9P_3$ = 1365.49 : C, 58.00 %; H, 4.87 % ; N, 9.23 %. Found C, 57.49 %; H, 4.86 % ; N, 9.16%.

6b, FT-IR(KBr) : 3276, 1645, 1604, 1540, 1490, 1421, 1360, 1276, 1208, 1184, 1157, 940 cm^{-1}.

^{13}C-CPMAS NMR(hexamethylbenzene) : 168.5, 153.2, 137.8, 129.7, 121.9, 42.3 ppm.

Results and discussion

The needle crystals of salt (**5**) were obtained by mixing a solution of **2** and *p*-xylylenediamine (**4**) in DMF (yield 80 %). In FT-IR spectra of **5** the characteristic bands attributed to self-association of carboxylic acids of **2** at 1700 cm^{-1} disappeared and two broad bands were observed at 1544 and 1400 cm^{-1} assignable to $-COO^{-}NH_3^{+}$ group. ^{1}H NMR spectra and elemental analysis of **5** showed the formation of the salt composed of 1: 3 **2** - **4**, suggesting that all of carboxyl group in **2** participate in the salt formation. When *p*-diaminodiphenylmethane, *p*-diaminodiphenylsulfone,



Scheme 1 Preparation of polyamide **6b**

Table 1 Polycondensation of salt (**5**)[a)]

Temperature (°C)	time (hr)	conversion (%)	-COOH in polyamides
220	30	48	+++
220	60	72	++
240	30	91	++
240	60	93	+
240[b)]	60	95	-
240[c)]	60	99	-

a) A 0.5 g of salt was used. b) A 5 mg of **4** was added.
c) A 10 mg of **4** was added.

p-phenylenediamie, and *p*-diaminodiphenyl ether were used, the salts with a defined stoichiometry were not obtained.

In the previous papers, we showed that the self-assembling heteropolymer was constructed by the complementary hydrogen bondings between **2** and hexakis(4-pyridylcarbinoxy)cyclotriphosphazene (**3**) or between naphthalene-1,4-dicarboxylic acid and **3**, both of which form cylindrical structures [4-6]. This result suggests that the organic groups attached to the phosphazene ring are located perpendicularly above and below a nearly planar phosphazene ring, in agreement with the observation of X-ray analysis of single crystal of hexaphenoxycyclotriphoshazene [7, 8]. This also suggests that the carboxyl groups on the phosphazene ring do not expand radially. Such carboxyl groups might be captured by **4** to form easily the salt **5** with three-dimensional cylindrical structure. The fact that pure salts were not obtained from diamines except for **4** indicates that the rigid and symmetrical structures of diamines are required for the formation of well-defined salts. In addition, an unsuccessful formation of the salt for the **2** - *p*-phenylenediamine system suggests that a short spacer, methylene units, is necessary to form the salt, which might contribute to reduce steric crowdedness around $-COO^{-}-NH_3^{+}-$ units.

The results of polycondensation were summarized in Table 1. IR spectra of polyamide (**6a**) obtained from the polycondensation of salt **5** at 240 °C in a sealed tube showed that the peak corresponding to the $-COO^{-}NH_3^{+}$ at 1544 cm^{-1} decreased as well as the peak at 1400 cm^{-1} and that the intensity of amide peak at 1645 cm^{-1} increased with increasing reaction time. Even the polymer obtained at 240 °C for 60 h, however, the shoulder peak at 1700 cm^{-1} was still observed, indicating the presence of unreacted carboxyl group in **6a**. If only dehydration process is operative, the weight loss by polycondensation should be 7.9 wt % under conditions. However, the isothermal thermogravimetric analysis at 240 °C showed that ca. 13 wt % loss was observed within a relatively short period (< 5 h), suggesting that the polycondensation competes with a decomposition of the salt. The cyclotriphosphazene ring was stable at the temperature but the analysis of gas formed during polycondensation showed the occurrence of the elimination of **4.** This unfavorable decomposition, however, could be avoided by the addition of small amount of **4** in a sealed tube. The IR spectra of polyamide (**6b**) obtained showed no significant peak of carboxyl group, as shown in Fig. 1 (c), suggesting the formation of a cylindrical polyamide with regular structure.

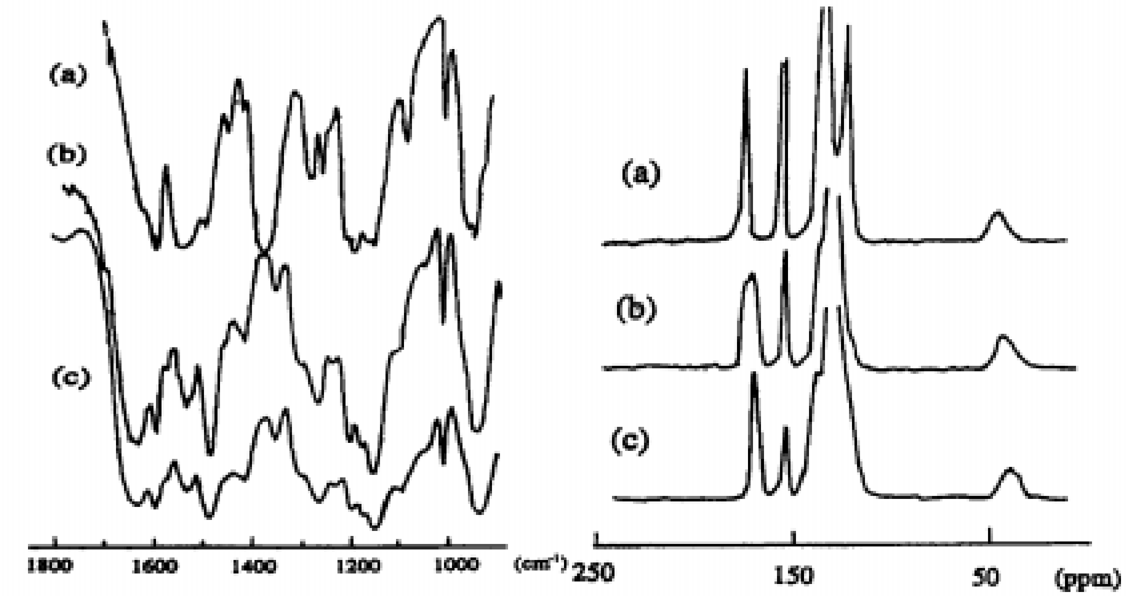


Fig. 1 FT-IR and ^{13}CP-MASNMR spectra of salt **5**(a), polyamides **6a**(b) and **6b**(c)

This was supported by ^{13}C-CPMAS NMR spectra of **6b**; the peak assignable to COO$^-$-NH$_3^+$ carbon at 172.2 ppm disappeared for the polyamide obtained in the presence of **4** and a characteristic peak at 168.5 ppm ascribable to the -NHC(O)- carbon. For the elemental analysis of the polyamide, the values of C, H, and N were inconsistent with the calculated values for the proposed structures, due to the formation of residue even at elevated temperatures. The structural characterization of polymers was evaluated by X-ray diffraction analysis with 2θ ranging from 5 to 40°. As shown in Fig. 2, **6b** showed a high level of crystalline character, whereas **6a** presented amorphous diffraction patterns [13]. The polyamides **6a** and **6b** obtained were insoluble in organic solvents such as phenol, formic acid, *m*-cresol, and H_2SO_4.

Thus, it appears that the polycondensation of the salts at both sides on the phosphazene ring gives a three dimensional cylindrical structure. The results might be considered as another example of the template polymerization, where directional and

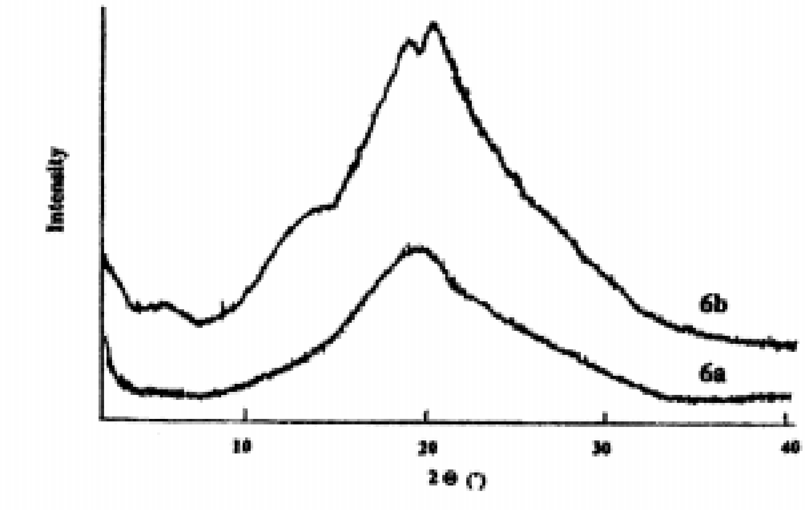


Fig. 2 Wide-angle X-ray diffractograms of **6a** and **6b**

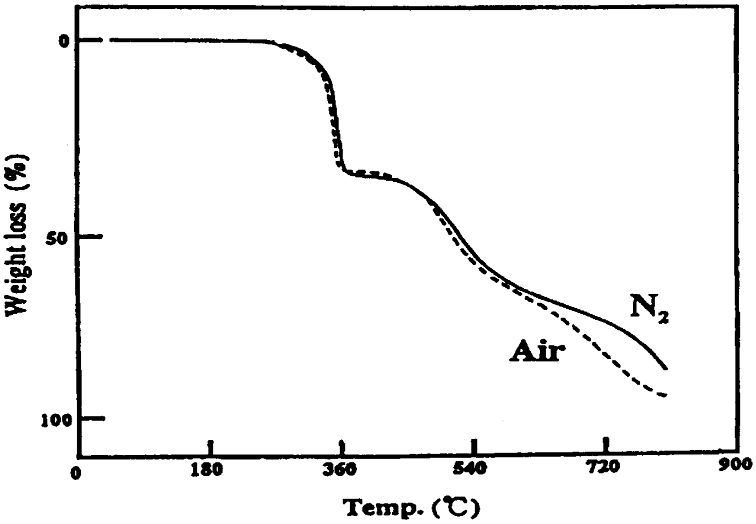


Fig. 3 Thermogravimetric analyses of polyamide **6b**

specific interaction between carboxylic acids on the phenoxycyclotriphosphazene and diamine allows the construction of three-dimensional structure without undesired side reactions.

Finally, we examined the thermal property of polyamides. The polymers decomposed at 300 °C under nitrogen and air atmospheres (Fig. 3). The onset temperature of decomposition (T_d) was somewhat low compared to that of the linear polyamide (T_d = 330 °C) prepared from terephthaloyl chloride with *p*-xylylenediamine, probably due to the ring stress. However, the char yields of **6b** at 800 °C were 3 times higher than that of linear polyamides, reflecting the involvement of flame-retardant properties of cyclophosphazene group.

So far, a variety of dendritic polyamides by the polycondensation of well-designed molecules have been reported. This paper, to our knowledge, is the first example for the preparation of cylindrical polyamide utilizing cyclotriphosphazene, which is a key component for the formation of three-dimensional structure. An approach to prepare covalently bonded polymers from supramolecules with a defined structure based on noncovalent bonding interactions should be broadly applicable to preserve the structural regularity. We are currently testing the template effects based on non-covalent interactions for the synthesis regular macromolecules.

References

1. MacDonald JC, Whitesides GM (1994) Chem Rev 94: 2383
2. Conn MM, Rebek J Jr (1997) Chem Rev 97: 1647.
3. Baxter P, Lehn J-M, DeCian A, Fischer J (1993) Angew Chem Int Ed Engl 324: 69
4. Inoue K, Itaya T, Azuma N (1998) Supramol Sci 5: 163
5. Itaya T, Azuma N, Inoue K (1998) Supramol Chem 9: 121
6. Itaya T, Inoue K (2000) Bull Chem Soc Jpn 73: 2829
7. Marsh W, Trotter J (1971) J Chem Soc (A): 169

8. Bandoli G, Casellato U, Gleria M, Grassi A, Montoneri E, Pappalardo GC (1989) J Chem Soc Dalton Trans 757

9. Backson SCE, Bayliff PM, Feast WJ, Kenwright AM, Parker D, Richards RW (1994) Macromol Symp 77: 1
10. Steve R, Davis N, McFarland H (2000) Polymer International 49: 1002
11. Ishida Y, Jijkei M, Kakimoto M (2000) Macromolecules 33: 3202
12. Kiyotsukuri T, Tsutsumi N, Sugimoto M, Saito N (1990) Polym Commun 31:56
13. Hsiao S–H, Yang C–P, Chu K-Y (1996) Macromolecules 30:165