JOURNAL OF
Materials
CHEMISTRY

Prototype carbon nitrides similar to the symmetric triangular form of melon

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Received 5th September 2000, Accepted 4th December 2000
First published as an Advance Article on the web 26th January 2001

Solid polymerization of 2,5,8-tricarbodiimide-tris-*s*-triazine potassium salt (potassium melonate) and 2,5,8-trichloro-tris-*s*-triazine (cyameluryl trichloride) gave a symmetric triangular form of a prototype carbon nitride which is deammonation-polycondensed with fifteen 2,5,8-triamino-tris-*s*-triazine molecules.

Graphite-like C_3N_4 materials have recently attracted much attention for their potential as organic semiconductors and the precursors of hypothetical superhard β-C_3N_4. In 1922, Franklin introduced for the first time the concept of C_3N_4, the final deammonation of "melon" [an ill-defined polymer, first observed by Berzelius and named by Liebig, that is left after the ignition of mercuric thiocyanate], and obtained impure specimens by extremely cautious heating of mercuric thiocyanate.[1] Later, Redemann and Lucas assigned two structures to melon, a linear polymer and symmetric triangular form of polymer condensed with 2,5,8-triamino-tris-*s*-triazine, and deduced Franklin's material to be the latter form of melon condensed with twenty-one 2,5,8-triamino-tris-*s*-triazine molecules, $C_{126}H_{21}N_{175}$, from a hydrogen content of only 0.6%.[2] [The preparation and structure models of melon have been reviewed by Bann and Miller.[3]] Redemann *et al.* also referred to the graphite-like carbon nitride in which the void between the three tris-*s*-triazine nuclei is filled by three carbons and one nitrogen atom.[2] The structure models of melon and the related carbon nitrides are depicted in Fig. 1. The above melon-based carbon nitrides have been forgotten as unconfirmed species. In order to prepare carbon nitride, the author reexamined Franklin's method; however, carbon nitride could not be prepared but a linear polymer of 2,5,8-triamino-tris-*s*-triazine was obtained. The chemical syntheses of the carbon nitrides by de-ammonation of melon are very difficult because of the weak basicity and limited thermal stability up to 500 °C, so this requires chemical modification of the starting materials with reactive functional groups. Recently, a new type of carbon nitride cross-linked with =CH– groups was prepared by pyrolysis of tri-functional tris-*s*-triazine derivatives.[4] This result suggests that the perfect carbon nitride cross-linked with –N< groups may be obtained by polycondensation of appropriate tri-functional derivatives. Prior to this work, several methods such as desalting, dehydration and deammonation polycondensation of various tris-*s*-triazine derivatives were attempted. Contrary to expectation, the product was not the perfect carbon nitride but a prototype one. Structural analysis elucidated that the prototype is similar to the symmetric triangular form of melon predicted by Redemann. Since melon-based C_3N_4 is regarded as having sufficiently large molecules of the prototype, this result suggests that the chemical synthesis of C_3N_4 is not impossible. In this work, the structure of the prototype, which was prepared by solid polymerization between the potassium salt and trichloride of tris-*s*-triazine, was reported.

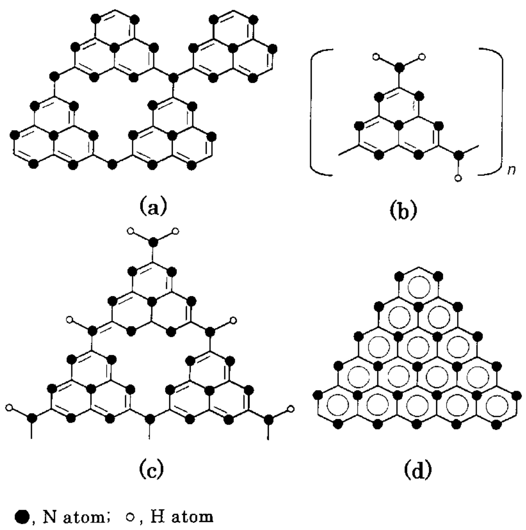

Fig. 1 The structure models of melon and the related carbon nitrides: (a) Franklin's model (the final deammonation polycondensate of melon); (b) Redemann's model (a linear form of melon); (c) Redemann's model (the symmetric triangular form of melon); (d) Redemann's model (graphite-like carbon nitride).

Experimental

The starting materials and carbon nitride were prepared according to the synthetic routes depicted in Fig. 2.

Deammonation polycondensate of 2,5,8-triamino-tris-*s*-triazine (melon)

Melon was prepared by heating ammonium thiocyanate according to ref. 5. The structure of melon was confirmed to be $[-C_6N_7(NH_2)(NH)-]_{10}$, a linear form of the decamer of 2,5,8-triamino-tris-*s*-triazine.[4]

2,5,8-Tricarbodiimide-tris-*s*-triazine potassium salt (potassium melonate)

Potassium melonate, $C_6N_7(NCNK)_3$, was prepared by the reaction of melon with molten potassium thiocyanate according to ref. 6.

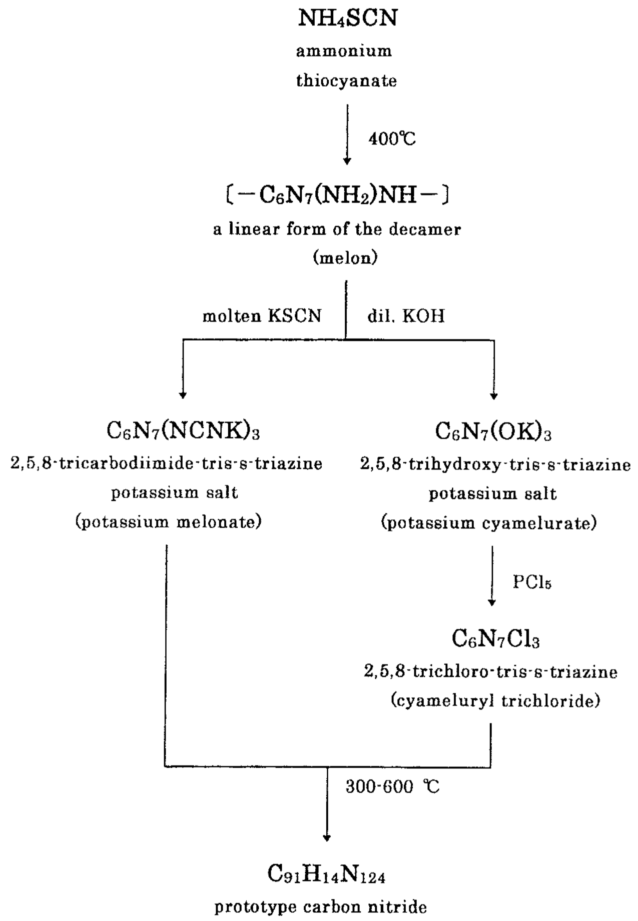

Fig. 2 Schematic diagram showing the preparation of the prototype carbon nitride.

2,5,8-Trihydroxy-tris-*s*-triazine potassium salt (potassium cyamelurate)

Potassium cyamelurate, $C_6N_7(OK)_3$, was prepared by alkali hydrolysis of melon in a boiling 3 M KOH solution according to ref. 6.

2,5,8-Trichloro-tris-*s*-triazine (cyameluryl trichloride)

Cyameluryl trichloride, $C_6N_7Cl_3$, was prepared by chlorination of potassium cyamelurate with phosphorus pentachloride according to ref. 7.

Prototype carbon nitride

Potassium melonate (1.5 g) and cyameluryl trichloride (1.0 g) were mixed homogeneously, placed into an autoclave and heated on a temperature program of 300 °C for 24 h, 500 °C for 4 h and finally 600 °C for 1 h. A yellow solid was taken out of the autoclave, granulated, boiled in water to remove unchanged starting material and byproducts, purified by boiling with 35% HCl, washed with hot water and vacuum-dried at 150 °C. A pale yellow fine powder was obtained, yield 1.1 g. Anal. Calcd. for $C_{91}H_{14}N_{124}$: C, 38.42; H, 0.49; N, 61.08. Found. C, 38.43; H, 0.50; N, 61.06%. Density: 1.80 g cm^{-3}.

Measurements

X-Ray powder diffraction was conducted with Cu-Kα radiation generated at 40 kV and 200 mA in the 2θ range 4–100° and at a scanning speed of 0.05° min^{-1}. The powder pattern was smoothed using a smoothing program, *LOW PASS FILTER*, installed in a machine to determine the precise peak positions. The best fit indexing of the diffraction pattern was carried out by computational analysis of the peak positions using an optimization program, "*DICVOL*91".[8] The mass spectra were run on a matrix-assisted laser-desorption mass spectrometer. Ionization was performed with a Nd–YAG laser (355 nm) without matrix. Density was measured by the sink–float method in a dibromomethane–ethanol solution whose density was determined pycnometrically.

Results and discussion

The IR spectrum of the carbon nitride material showed extraordinarily high absorbance of the 1240 and 1319 cm^{-1} peaks which are generally assigned to ν(C–N) of aromatic secondary and tertiary amines, respectively, in comparison with the spectrum of a linear form of the decamer of 2,5,8-triamino-tris-*s*-triazine cited as the standard reference (Fig. 3). This suggests the material to be a planar structure of melon. The mass spectrum showed a fragment pattern having a repeating unit of 184 *m*/*z* such as *m*/*z* 186→370→554 and a repeating unit of 185 (184) *m*/*z* such as 201→386→570 (Fig. 4). These patterns were unobserved in the mass spectrum of a linear type of melon such as the decamer (the linear type always exhibits a repeating unit of 201 *m*/*z*, corresponding to $C_6N_7(NH_2)(NH)$, starting from 202 *m*/*z* due to the $C_6N_7(NH_2)_2$ fragment). The 184 *m*/*z* unit corresponds to a $C_6N_7(N)$ fragment. The N/C atomic ratio of 1.36 of the material determined from CHN analysis is slightly larger than the theoretical value of 1.33 for the melon-based C_3N_4, so the material is composed of $C_6N_7(NH)_{1.5}$ and $C_6N_7(N)$ units. A possible structure corresponding to the maximum *m*/*z* 2842 is depicted in Fig. 5. The structure is a triangular form and is given the formula $C_{91}H_{14}N_{124}$ consisting of fifteen tris-*s*-triazine nuclei cross-linked with N and NH groups. The NH group is found only along the periphery. This structure is similar to that of the symmetric triangular form of melon predicted by Redemann *et al.*[3] Most of the remaining mass peaks can be explained as fragments derived from the parent. A nitrile group at the vertex of a triangle is supported by the weak 2179 cm^{-1} peak of the IR spectrum. One might suppose another type of structure, $C_{90}H_{26}N_{126}$, in which five pieces of a cyclic structure consisting of three tris-*s*-triazine nuclei and three NH groups are linearly jointed with NH groups. However, this structure is improbable because in the mass spectrum there are no fragments having a repeating unit of 571 *m*/*z* corresponding to a $(C_6N_7)_3(NH)_3(H)(NH)$ unit. The well-ordered structure shown in Fig. 5 suggests the material to be crystalline. As expected, the material showed a polycrystalline X-ray powder pattern (Fig. 6; Table 1). As a result of indexing, the pattern was assigned to an orthorhombic system having a lattice constant of $a = 0.7104$ nm, $b = 1.6190$ nm and $c = 1.2893$ nm. The total weight of atoms in the unit cell

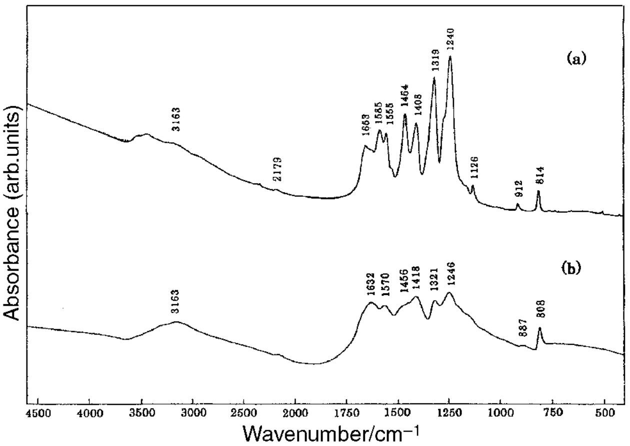

Fig. 3 IR spectra of the samples: (a) prototype carbon nitride; (b) a linear chain form of the decamer of 2,5,8-triamino-tris-*s*-triazine.

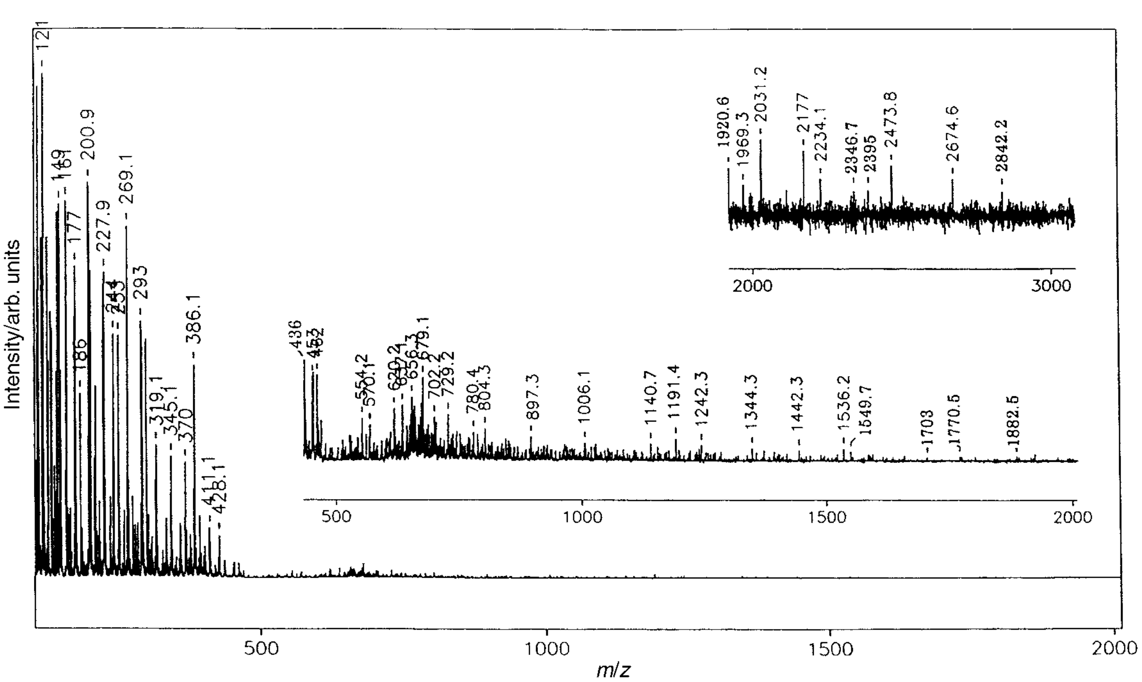

Fig. 4 Mass spectrum of the prototype carbon nitride.

which was estimated from a unit cell volume of 1.483 nm^3 and the density of 1.80 g cm^{-3} was 1608 g. Since the molecular structure in Fig. 5 is composed of a C_6N_8 unit having a symmetry number of three, the total weight should be an integral multiple of the weight (184 g) of C_6N_8. The total weight agrees fairly with 9 times the weight of C_6N_8, considering the true density of the material will be slightly larger than the specific gravity observed.

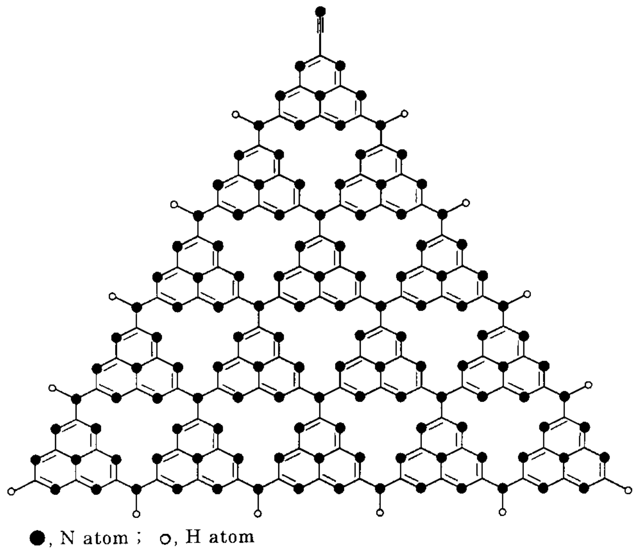

Fig. 5 Possible structure of the prototype carbon nitride, $C_{91}H_{14}N_{124}$. The structure is similar to that of the symmetric triangular form of melon predicted by Redemann.

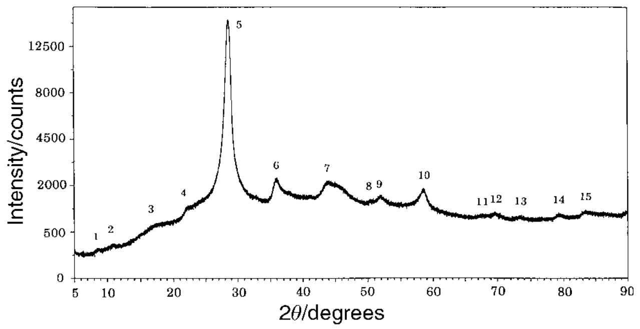

Fig. 6 X-Ray diffraction pattern of the prototype carbon nitride. Diffraction peaks are numbered.

Since the prototype shows a high thermal stablity for an organic material up to 600 °C, it may be used as a model compound for C_3N_4. Although the reaction system is simple, there is still room for improvement to obtain higher degrees of polymerization. At present, homogeneous liquid-phase polymerization is under study in several nonaqueous solvent systems instead of inhomogeneous solid polymerization.

Conclusion

Solid polymerization of potassium melonate and cyameluryl trichloride in an autoclave was carried out. The structure of the material obtained was investigated by elemental analysis, IR spectroscopy, mass analysis and X-ray powder diffraction. As a result, it was found that the material is a triangular form of prototype carbon nitride, $C_{91}H_{14}N_{124}$, condensed with fifteen 2,5,8-triamino-tris-*s*-triazine molecules. This type of compound

Table 1 Interplaner spacings/nm for the prototype carbon nitride

Peak number	2θ/ degrees	Observed *d* values	Calculated *d* values	Difference	Orthorhombic *hkl*
1	8.757	1.0090	1.0086	−0.0004	011
2	10.920	0.8095	0.8095	±0.0000	020
3	16.600	0.5336	0.5340	+0.0004	120
4	21.956	0.4045	0.4048	+0.0003	040
5	28.670	0.3111	0.3111	±0.0000	202
6	35.999	0.2493	0.2489	−0.0004	106
7	43.924	0.2060	0.2057	−0.0003	313
8	50.602	0.1802	0.1799	−0.0003	334
9	51.934	0.1759	0.1759	±0.0000	410
10	58.470	0.1577	0.1577	±0.0000	442
11	67.828	0.1381	0.1382	+0.0001	512
12	69.647	0.1349	0.1349	±0.0000	503
13	72.828	0.1296	0.1295	+0.0001	551
14	79.351	0.1207	0.1207	±0.0000	554
15	83.566	0.1156	0.1157	+0.0001	630

Orthorhombic: $a = 0.7104$ nm, $b = 1.6190$ nm, $c = 1.2893$ nm.

is similar to the symmetric triangular form of melon predicted by Redemann.

Acknowledgement

This research was performed under the auspices of the Japan Fine Ceramics Center Foundation, the Frontier Carbon Technologies, contracted by the New Energy and Industrial Technology Development Organization whose sponsorship is gratefully acknowledged.

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