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Polycondensation/pyrolysis of tris-*s*-triazine derivatives leading to graphite-like carbon nitrides

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Polycondensation/pyrolysis of 2,5,8-tricarbodiimide-tris-*s*-triazine and its derivatives gave hexagonal graphite-like pseudo carbon nitrides, $CH_{0.3-0.08}N_{1.0-0.63}$, composed of tris-*s*-triazine nuclei. The materials were stable up to 600–800 °C under an inert atmosphere depending on their nitrogen content.

Graphite-like heterocyclic materials such as g-C_3N_4 have attracted much attention for their potential as ceramic semiconductors and as precursors of super hard materials. One of the g-C_3N_4 materials, a hexagonal and planar C_3N_4 combined with sp^2 bonds, was recently proposed and prepared from melamine.[1–3] The material is formally depicted as the final de-ammonation product of melamine. In 1922, Franklin had already introduced the concept of graphite-like C_3N_4.[4] He suggested in his work on ammonium carbamate that C_3N_4 might be obtained as the final de-ammonation product by heating "melon" [an ill-defined polymer, first observed by Berzelius and named by Liebig, that is left after the ignition of mercury thiocyanate (see Fig. 1 for the structure of melon)]. Melon, however, underwent complete decomposition at the high temperatures required for losing ammonia. Franklin carried out extremely cautious heating of mercury thiocyanate to obtain impure specimens of carbon nitride. Later, Redemann and Lucas assigned two structures to melon, a linear form from the de-ammonation polycondensation of 2,5,8-triamino-tris-*s*-triazine and a symmetric triangular form from de-ammonation ring-closure of three molecules of 2,5,8-triamino-tris-*s*-triazine.[5] They deduced, from a hydrogen content of only 0.6%, that Franklin's carbon nitride may be the latter, cyclic, form of the polymer condensed with twenty-one molecules of 2,5,8-triamino-tris-*s*-triazine, $C_{126}H_{21}N_{175}$. The void between the three tris-*s*-triazine nuclei is filled by three carbons and one nitrogen atom.[5] The above melon-based carbon nitrides have been forgotten for a long time as unconfirmed species. In the 1990s, the chemistry of carbon nitrides has attracted interest in connection with super hard β-C_3N_4.[6,7] Despite numerous attempts using chemical vapor deposition and its modifications, most cases resulted in the deposition of amorphous carbon nitrides with small nitrogen contents. The hitherto known precursors and intermediates liberated nitrogen molecules at 400–500 °C without graphitization, which hindered the preparation of nitrogen-abundant carbon nitrides. In this work, melon-based graphite-like pseudo carbon nitrides were prepared for the first time by polycondensation/pyrolysis of several tris-*s*-triazine derivatives. The heat resistance of the carbon nitrides obtained is discussed from a structural viewpoint.

Experimental

Several tri-functional tris-*s*-triazine derivatives used in this work were prepared from melamine and thiocyanates according to the synthetic routes depicted in Fig. 1.

Tricyanomelamine potassium salt 1

A mixture of melamine (63 g) and potassium thiocyanate (145.5 g) was placed into a porcelain evaporating dish, heated to *ca.* 500 °C on a hot plate until all volatile products were expelled, then placed in an oven and heated to 630 °C for 1 h. After leaving to cool, the white cake produced was broken into small pieces, dissolved with boiling water and filtered under suction. The filtrate contained the tricyanomelamine potassium salt and 2,5,8-tricarbodiimide-tris-*s*-triazine potassium salt (potassium melonate) in approximately equal amounts. Isolation of each compound was carried out by fractional crystal-

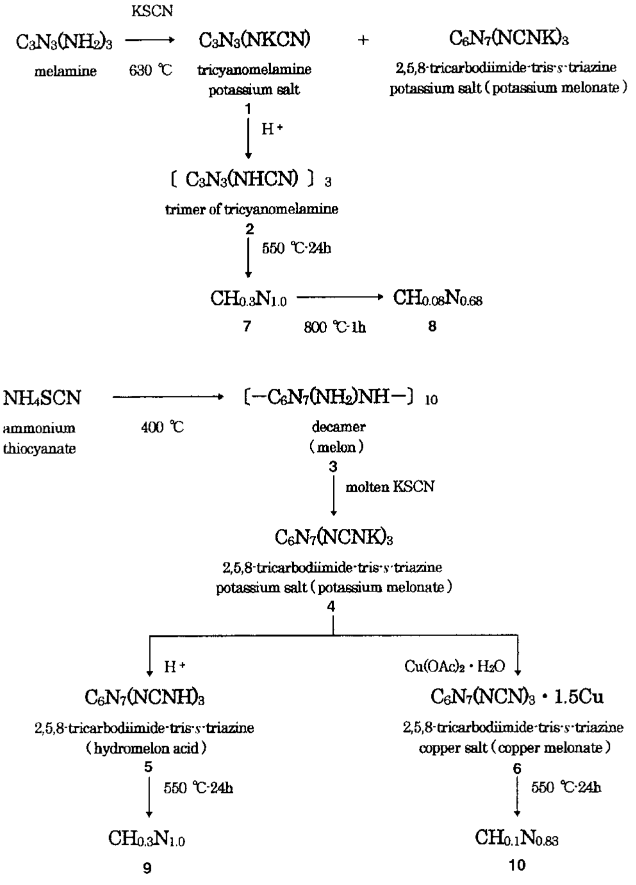

Fig. 1 Schematic diagrams showing the preparation of tri-functional tris-*s*-triazine derivatives leading to graphite-like carbon nitrides.

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lization. The expected compound precipitated after potassium melonate, yield 23.7 g. Recrystallization from water gave pure white needles. Anal. Calcd. for $K_3C_6N_9$: C, 22.84; N, 39.96; K, 37.20. Found: C, 22.83; H, 0.01; N, 39.97%; IR: 3051 w (broad), 2166 s, 1529 s, 1512 sh, 1406 s, 1244 w, 1028 vw, 808 w, 590 w, 523 w cm^{-1}.

Tricyanomelamine trimer **2**

Neutralization of an aqueous solution of the above compound with HCl at room temperature gave a white precipitate of a trimer of tricyanomelamine in quantitative yield. Anal. Calcd. for $C_{18}H_3N_{18}$: C, 35.82; H, 1.49; N, 62.69. Found: C, 35.87: H, 1.50; N, 62.63%. IR: 3506 w, weak multiplet over 3200–2500 cm^{-1}, 2210 s, 1674 m, 1620 sh, 1566 s, 1477 sh, 1389 s, 752 w cm^{-1}, laser-desorption MS: *m*/*z* 603 (M^+).

De-ammonation polycondensate of 2,5,8-triamino-tris-*s*-triazine (melon) **3**

Melon was prepared by heating ammonium thiocyanate, according to the method reported by Liebig (ref. 8). NH_4SCN (100.0 g) was placed into a porcelain evaporating dish and heated to *ca.* 300 °C on a hot plate until boiling ceased and all volatile products were expelled, then placed in an oven and heated to 400 °C for 2 h. A yellow solid remained. This was boiled in water, washed with 10% KOH, boiled in 35% HCl for 10 min, washed with water and vacuum-dried at 150 °C. A yellow powder of the de-ammonation polycondensate of 2,5,8-triamino-tris-*s*-triazine (melon) was obtained (9.2 g). Anal. Calcd. for $C_{60}N_{91}H_{33}$: C, 35.52; H, 1.63; N, 62.85. Found: C, 35.57; H, 1.60; N, 62.73%. The found N : C atomic ratio, 1.512, agrees very well with the value of 1.517 calculated for ten degrees of polymerization (a linear chain form of the decamer). Density: 1.68 g cm^{-3}. X-Ray powder diffraction data: orthorhombic: $a_o = 0.7396$ nm, $b_o = 2.0924$ nm, $c_o = 1.2954$ nm and $V_o = 2.004$ nm^3. From the density and the unit cell volume the estimated total weight of atoms in the unit cell is 2027 g which is equal to the molecular weight of the decamer. Laser-desorption mass spectrum: *m*/*z* 202, 403, 604 and 1006. Signals appeared at intervals of 201 *m*/*z* [corresponding to the $C_6N_7(NH_2)(NH)$ segment] in the range 1000 *m*/*z*.

2,5,8-Tricarbodiimide-tris-*s*-triazine potassium salt (potassium melonate) **4**

Compound **4** was prepared by the reaction of melon with molten potassium thiocyanate according to ref. 9. Recrystallization from water gave pure snow-white felt-like needles. Anal. Calcd. for $K_3C_9N_{13}$: K, 28.80; C, 26.52; N, 44.68. Found: C, 26.50; H, 0.01; N, 44.65%. IR: 2187 m, 1651 s, 1499 s, 1448 s, 797 m, 573 vw cm^{-1}.

2,5,8-Tricarbodiimide-tris-*s*-triazine (hydromelon acid) **5**

Neutralization of an aqueous solution of potassium melonate with HCl at room temperature (ref. 9) gave a milky precipitate of 2,5,8-tricarbodiimide-tris-*s*-triazine (hydromelon acid) in quantitative yield. Anal. Calcd. for $C_9H_3N_{13}$: C, 36.86; H, 1.02; N, 62.12. Found: C, 36.86; H, 1.02; N, 62.10%. IR: 3356 w, 2193 m, 1670 ms, 1601 m, 1441 s, 1342 w, 1323 w, 787 w cm^{-1}.

2,5,8-Tricarbodiimide-tris-*s*-triazine copper(II) salt (copper melonate) **6**

To a stirred 300 ml clear hot solution of potassium melonate (12.0 g), a 100 ml solution of copper(II) acetate monohydrate (9.0 g) was slowly added, resulting in the immediate formation of a light blue precipitate. The precipitate was filtered with suction, washed with hot water and vacuum-dried at 40–50 °C overnight. A light blue powder of anhydrous copper(II) salt was obtained, yield 13.2 g (94%). Anal. Calcd. for $C_9N_{13}\cdot 1.5Cu$: C, 28.03; N, 47.23; Cu, 24.74. Found: C, 28.00; H, 0.02; N, 47.26; CuO (gravimetric analysis by oxidation), 30.53%. IR: 2187 m, 1636 s, 1420 s (very broad), 795 w, 559 vw cm^{-1}.

Pseudo carbon nitrides, $CH_{0.3}N_{1.0}$ **7** and $CH_{0.08}N_{0.63}$ **8**

CAUTION! Heat treatment of the above starting materials evolves NH_3, cyanogen and other harmful gases so the experiment must be provided with a vent which permits these gases to escape. Fig. 2 shows the apparatus used where the sample is heated in a gold crucible placed in a quartz glass tube under a stream of helium. Evolved gases are drawn through a flexible tube joined to the quartz glass tube, and a carbonaceous material remains in the apparatus.

Tricyanomelamine trimer **2** (10 g) was heated at 550 °C for 24 h. A deep-purple water soluble solid remained. Addition of conc. HCl to a solution of this material produced a colloidal precipitate. The precipitate was centrifuged, washed with water and vacuum-dried at 500 °C for 1 h. The remaining powder was repeatedly washed with boiling water and vacuum-dried at 200 °C. A deep-purple powder was obtained, yield 1.8 g (sample 1). Found: C, 44.31; H, 1.32; N, 52.90%. Density (ρ): 1.83 g cm^{-3}. Further annealing at 800 °C for 1 h left black powders (sample 4). Found: C, 57.26; H, 0.40; N, 42.14%. ρ: 1.98 g cm^{-3}.

Pseudo carbon nitride, $CH_{0.3}N_{1.0}$ **9**

Hydromelon acid (10 g) was treated in the same way as above. A deep purple powder was obtained, yield 1.8 g (sample 2). Found: C, 45.50; H, 1.28; N, 52.86%. ρ: 1.83 g cm^{-3}.

Pseudo carbon nitride, $CH_{0.1}N_{0.83}$ **10**

Copper(II) melonate (7.5 g) was heated at 550 °C for 24 h. A black powder containing metallic copper was obtained. The powder was boiled in a 10% HNO_3 solution to remove copper. After filtration the residue was boiled in a 0.1 M NaOH solution to remove NO_3^- ions, then filtered, washed with water and vacuum-dried at 500 °C for 1 h. The remaining powder was washed with boiling water and vacuum-dried at 200 °C. A fine

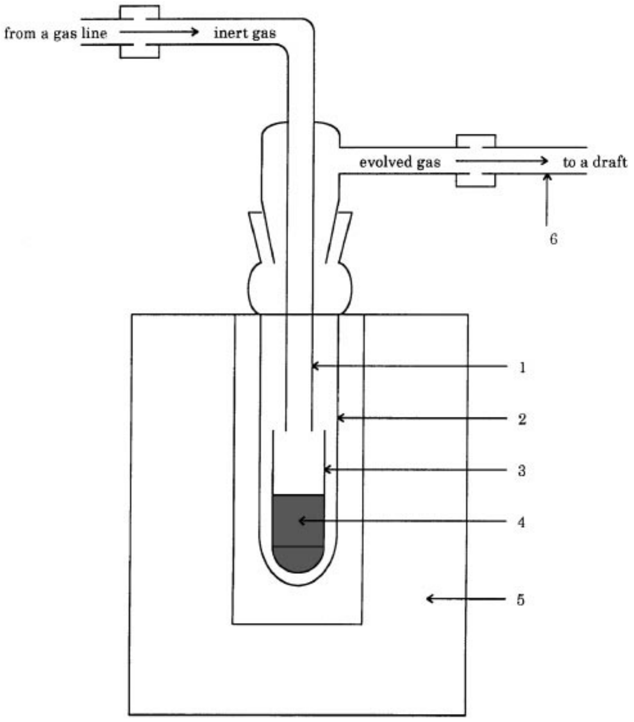

Fig. 2 The apparatus used for the polycondensation/pyrolysis of tris-*s*-triazine derivatives: 1, quartz tube for admitting an inert gas; 2, reaction chamber; 3, alumina tube; 4, sample; 5, heater; 6, vent.

black powder was obtained, yield 1.0 g (sample 3). Found: C, 50.31; H, 0.45; N, 48.72%. ρ: 2.02 g cm^{-3}.

Measurements

X-Ray powder diffraction was conducted in the 2θ range 4–100° with Cu-K$_\alpha$ radiation generated at 40 kV–200 mA at a scanning speed of 0.05° min^{-1}. Density was measured by the sink–float method in a dibromomethane–ethanol solution whose density was determined pycnometrically. Mass spectra were run on a matrix-assisted laser-desorption mass spectrometer. Ionization was performed with a Nd–YAG laser (355 nm) using a matrix of 2,5-dihydroxybenzoic acid. X-Ray photoelectron spectroscopy (XPS) was carried out using monochromatized Al-K$_\alpha$ X-ray radiation (1486.5 eV) and the photoelectrons were detected by a hemispherical analyzer operating at a pass energy of 23.5 eV. The binding energy was calibrated on the reference Au (4f$_{7/2}$) peak at 83.98 eV, and XPS curve fitting was performed with a non-linear least-squares fitting program using a mixed Gaussian–Lorentzian product function. Thermogravimetry was carried out in a stream of argon in the range 23–1200 °C at a heating rate of 20 °C min^{-1}. Graphite was used for comparison and checking the inert atmosphere. Because of leaks in the sample chamber, the TG curve in the range 1000–1200 °C was influenced by combustion.

Results and discussion

CHN analysis observed carbon, nitrogen and small amounts of hydrogen for samples 1 and 2, and trace amounts of hydrogen for samples 3 and 4. The IR spectra showed three to four broad peaks in the range 1600–1200 cm^{-1} but no appreciable peaks above 2500 cm^{-1} (Fig. 3). All the peaks can be explained on the basis of tris-*s*-triazine polymers such as melon: 2140–2200 cm^{-1}, C≡N and N=C=N stretching vibrations; 1610–1570 cm^{-1}, C=N and C=C stretching; 1500–1400 cm^{-1}, ring-stretching of aromatic amines; 1400–1200 cm^{-1}, stretching of aromatic amines. A similarity in the spectra and chemical compositions of samples 1 and 2 indicates both materials to have the same chemical structure. For samples 3 and 4, the simple IR patterns, lower wavenumber shifts of the C=N stretching band and nitrogen-deficient chemical compositions suggest an increase in length in the C=C and not in the C=N bonds.

All the samples showed the same very broad XRD patterns similar to those of distorted turbostratic carbons (Fig. 4). Assuming the hexagonal system, the lattice constants of all the samples were $a = 0.2426$–0.2403 nm and $c = 0.6620$–0.6750 nm (Table 1). These values are very close to those of graphite (JCPDS 25-0284: $a = 0.2458$ nm, $c = 0.6696$ nm) but completely different from those of the melamine based g-C_3N_4.[2] The broad line-width at the (002) plane indicates there are many defects in the layered structure. However, the densities of all the samples were 1.83–2.02 g cm^{-3}. Considering that the structure of the hexagonal g-C_3N_4 phase contains many vacancies,[2] this result suggests the materials to be fairly compacted. Both results (which appear inconsistent with each other) can be explained assuming that these materials are disordered and do not form an extended planar structure. There may be steric hindrance preventing the tris-*s*-triazine nuclei lying in the same plane.

The reaction mechanisms leading to the carbon nitrides are not completely clear, however, the following results serve to determine the chemical structures of the materials. It was found that tricyanomelamine and hydromelon acid undergo polymerization at 284 and 335 °C, respectively, into the same yellow polymer of cyanomelon, –C_6N_7(NHCN)NH–C_6N_7(NCNNH$_2$)–NH–. The polymer was further polycondensed at 450–500 °C into brownish melon-polymers cross-linked with N=C=N and NH groups. On the other hand copper melonate was decomposed into brownish copper complexes of melon at 450–500 °C. These intermediates were further annealed to achieve perfect carbonization. Chemical decomposition of the carbon nitrides with 3 M KOH gave mainly 2,5,8-trihydroxy-tris-*s*-triazine derivatives but not cyanuric acid (2,4,6-triazinetriol). These results prove the materials to be melon-based carbon nitrides.

Mass spectrometric analysis of sample 1 gave an analytically feasible spectrum (Fig. 5). Continuous fragment patterns from

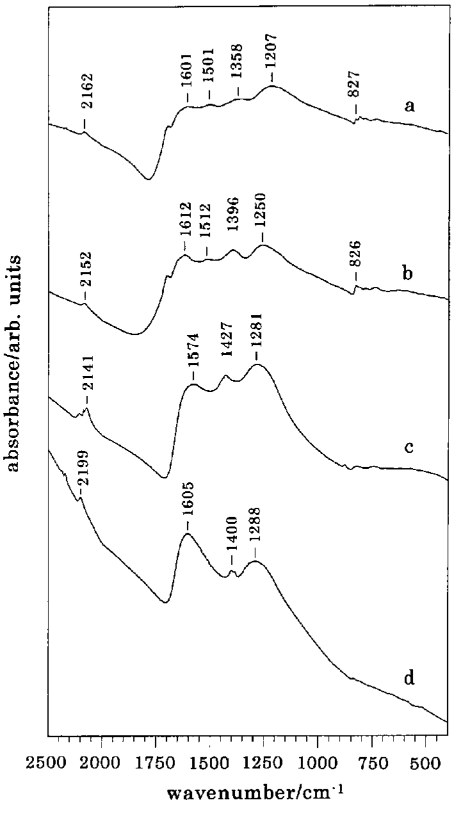

Fig. 3 IR spectra of the carbon nitrides: (a) CN$_{1.0}$ (sample 1); (b) CN$_{1.0}$ (sample 2); (c) CN$_{0.83}$ (sample 3); (d) CN$_{0.63}$ (sample 4).

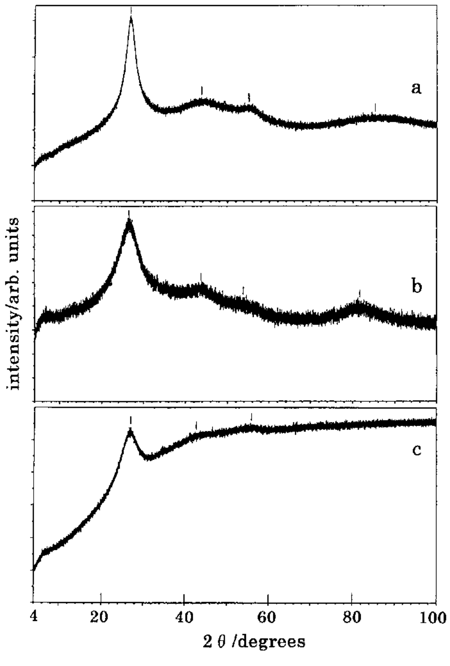

Fig. 4 X-Ray powder diffraction of the carbon nitrides: (a) CN$_{1.0}$ (samples 1 and 2); (b) CN$_{0.83}$ (sample 3); (c) CN$_{0.63}$ (sample 4).

Table 1 Assignment of the X-ray powder diffraction patterns of carbon nitrides

Sample 1: $CN_{1.0}$, hexagonal				Sample 4: $CN_{0.63}$, hexagonal			
$a = 0.2426$ nm, $c = 0.6620$ nm				$a = 0.2403$ nm, $c = 0.6750$ nm			
$2\theta/°$	d_{obs}/nm	d_{calc}/nm	*hkl*	$2\theta/°$	d_{obs}/nm	d_{calc}/nm	*hkl*
26.912	0.3310	0.3310	002	26.385	0.3375	0.3375	002
43.724	0.2069[a]	0.2101	100	43.451	0.2081	0.2081	100
		0.2003	101	53.808	0.1702	0.1688	004
55.132	0.1664	0.1655	004	80.931	0.1187	0.1201	110
85.111	0.1139	0.1139	112				

[a] The observed *d*-value is between the calculated interplanar spacings of the (100) and (101) planes due to the overlap of both contributions.

m/*z* 555 to 1937 and no peaks next to *m*/*z* 3876 indicate that the sample is a double-structured polymeric material. The first intense *m*/*z* 555 peak is due to a mass of a segment block comprising a monomer, the signal at *m*/*z* 1937 at the edge of the continuous spectrum seems to be the mass of the monomer, and the next *m*/*z* 3876 peak is from a dimer. Considering the results of the CHN analysis, IR spectrum and chemical reactions, the fragment of *m*/*z* 555 must correspond to the structure, $(–C_6H_2N_7=CH–)_3$ ($M_w = 555$). Based on this, a possible structure of the material is shown in Fig. 6. The monomer possesses the triangular form condensed with ten tris-*s*-triazine nuclei, $C_{73}H_{26}N_{74}$ ($M_w = 1937$), which is just similar to the Redemann model of the symmetric triangular form of melon except for substituting a NH cross-linkage by a CH one. Coupling the monomer gives the structure of the dimer, $C_{146}H_{52}N_{148}$ ($M_w = 3874$). The end-groups, NH_2 and NHCN, of the monomer and dimer are derived from that of the raw material, so, *m*/*z* 1164 in the spectrum may correspond to the formula $C_{43}H_{19}N_{45}$ ($M_w = 1165$), in which a triangular form condensed with six tris-*s*-triazine nuclei is occupied with NH_2 at three vertices. The other fragments of *m*/*z* 614, 995, 1316, 1471, 1646 and 1834 can be explained by a combination of the $–C_6H_2N_7=CH–$ ($M_w = 185$) unit and the NH_2, NHCN and CN end groups, which would have been derived from the parent *m*/*z* 1937. On the other hand, the mass spectrum of sample 3 ($CN_{0.83}$) showed continuous fragment patterns having repeating units of *m*/*z* 426–432 (average 429), for example, *m*/*z* 250→679→1108, 1506→1932→2356→2786→3216→3646→4077→(4509)→4941 (Fig. 7). Since a N : C atomic ratio of 0.83 is

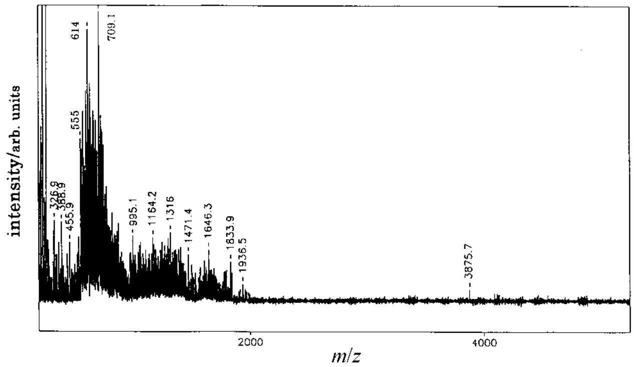

Fig. 5 Mass spectrum of the carbon nitride $CN_{1.0}$ (sample 1).

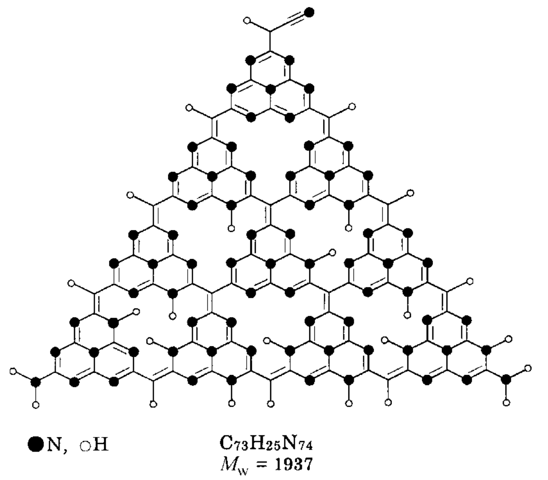

Fig. 6 Possible structure of the carbon nitride $CN_{1.0}$.

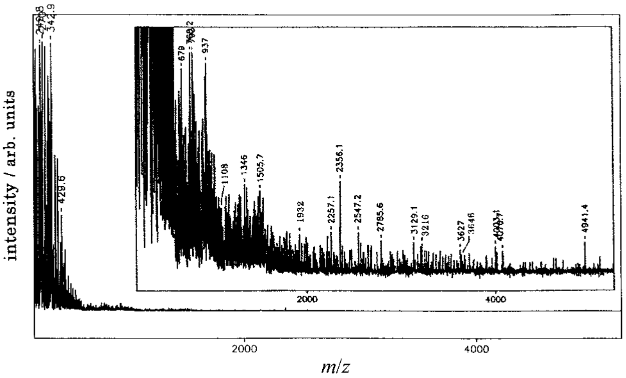

Fig. 7 Mass spectrum of the carbon nitride $CN_{0.83}$ (sample 3).

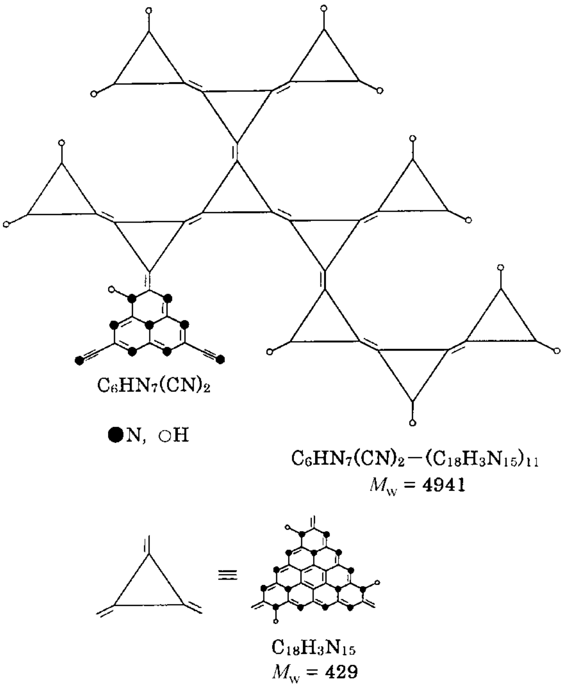

Fig. 8 Possible structure of the carbon nitride $CN_{0.83}$.

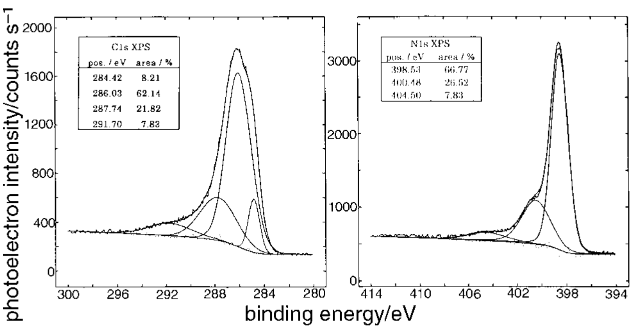

Fig. 9 XPS C 1s and N 1s spectra of the carbon nitride $CN_{0.83}$.

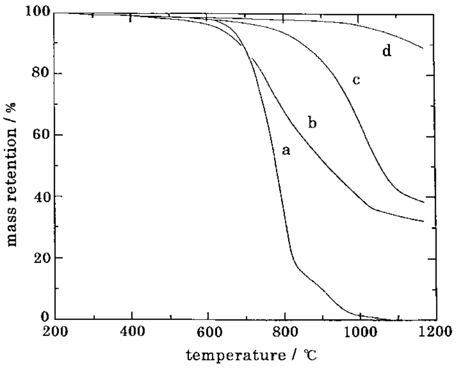

Fig. 10 Thermogravimetry of the carbon nitrides measured in a stream of argon: (a) $CN_{1.0}$ (samples 1 and 2); (b) $CN_{0.83}$ (sample 3); (c) $CN_{0.63}$ (sample 4) and (d) graphite.

arithmetically equal to the ratio given by eliminating six nitrogen atoms from three tris-*s*-triazine nuclei, the repeating units would be the fused structure with three tris-*s*-triazine nuclei, $C_{18}H_3N_{15}$ ($M_w = 429$). A possible structure for this material is depicted in Fig. 8. The structure was qualitatively supported by XPS C 1s and N 1s spectra (Fig. 9). The binding energy of 284.8 eV was in the range assigned to carbon rings such as benzene and graphite.[10] Based on the XPS database,[11] the peaks at 286.0 and 400.5 eV and those at 287.7 and 398.5 eV were attributed to the binding energy due to >C=C–N< and >C=N– bonds, respectively. The small peaks at 291.7 and 404.5 eV are due to adsorbed contaminants, since the peaks were diminished by Ar^+ ion-beam sputtering. Such a fused structure is reasonable considering cyclopolymerization reactions known for carbodiimide, cyanamide and nitrile groups. The high density of the material also supports the possibility of this structure. An extension of this type of cyclopolymerization presents pyramidal structures such as fused with six tris-*s*-triazine nuclei $C_{37}N_{24}$, ten nuclei $C_{63}N_{34}$, fifteen nuclei $C_{96}N_{45}$ and so on. The mass spectrum of sample 4 ($CN_{0.63}$) is not investigated at present but the chemical composition is approximated as $C_{37}N_{24}$.

All the samples showed high heat-resistance over 600 °C (Fig. 10). Samples 1 and 2 were rapidly decomposed above 700 °C and completely disappeared at 1000 °C; samples 3 and 4 had improved heat-resistance and left a residue even at 1000 °C. Sample 4 in particular was stable up to 800 °C and kept 40% of its initial weight at 1200 °C. That is, the heat resistance of the carbon nitrides tends to decrease with an increase in the nitrogen content. The melon based C_3N_4 as described in the introductory section is formally depicted as the final de-ammonation product of melon. It will be natural to deduce that such a cross-linked structure is less heat-resistant than the perfectly fused structure of graphite. The high heat-resistance of the nitrogen-deficient samples is due to the largely fused structures.

The starting materials prepared are the tri-functional monomers capable of cyclopolymerization/cross-linking. whose property enabled the preparation of the heat-resistant intermediates stable at severe temperatures during carbonization. Complete determination of the structures of the carbon nitrides is difficult at present because of their infusible and insoluble properties and very distorted crystal structures.

Conclusion

A graphite-like carbon nitrides of composition CN_x ($x = 1.0$–0.63) were prepared by polycondensation/pyrolysis of several tri-functional tris-*s*-triazine derivatives. All the carbon nitrides were composed of the tris-*s*-triazine nuclei. The structures were different depending on the raw materials used. Tricyanomelanine and 2,5,8-tricarbodiimide-tris-*s*-triazine (hydromelon acid) gave a hexagonal material cross-linked with aromatic Ar=C<groups. The copper salt of hydromelon acid gave a fused structure with three tris-*s*-triazine nuclei. In TG the carbon nitrides were heat-resistant up to 600–800 °C and tended to become more labile with an increase in the nitrogen content.

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