Articles

Synthesis, Structure, and Characteristics of the New Host Material [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$

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A polymer [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$ has been prepared by the reaction of C$_3$N$_3$Cl$_3$ and NH$_3$ or C$_3$N$_3$Cl$_3$ and C$_3$N$_3$(NH$_2$)$_3$. An electron diffraction study suggests that this polymer has a hexagonal structure similar to that of graphite. A structural model for this polymer has been proposed on the basis of X-ray, electron diffraction, IR, ESCA, and specific gravity measurements. A hole surrounded by three amino radicals in the unit cell of this structure suggests the potential activity of this polymer as a host material. Interaction of the polymer with AlCl$_3$, ZnCl$_2$, or MgCl$_2$ at 500 °C has resulted in the formation of a material which can be converted at 900–1000 °C into AlN, ZnCN$_2$, or MgCN$_2$, respectively. The triazine ring in this polymer imparts good thermal stability and photoluminescent characteristics.

1. Introduction

Graphite has been known as an excellent host material because of its layered structure and ability to stabilize many chemical species between the layers. Recent interest has increased in the syntheses of new graphite-like host materials such as B/C/N,[1–10] B/C,[4] or C/N compounds.[4,7,9–14]

Since the *s*-triazine ring (C$_3$N$_3$) has a 6π-electron system which is analogous to benzene, it is expected that a conjugated polymer of *s*-triazine would tend to form a layered structure like that of graphite. Also the *s*-triazine ring would probably make the polymer thermodynamically stable so that the polymer could be an excellent host material. However, only a few attempts[13,14] have been made to prepare a layered material containing the *s*-triazine ring without decomposing the ring contained in the starting material.

In this paper, the preparation of a polymer [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$ containing *s*-triazine rings is reported. A possible layered structure of this polymer is proposed on the basis of X-ray diffraction, electron diffraction, IR, ESCA, and specific gravity measurements. The reaction mechanism for the formation of this polymer, some of its characteristics, and reactions with metal chlorides have also been investigated.

2. Experimental Section

Starting Materials. Cyanuric trichloride (C$_3$N$_3$Cl$_3$, Hayashi Pure Chemical Ind., purity >95%), melamine (C$_3$N$_3$(NH$_2$)$_3$, Hayashi Pure Chemical Ind., >95%), NH$_3$ (99.9%), N$_2$ (99.99%), boron trichloride gas (BCl$_3$, Sumitomo Seika, 99.99%), aluminum chloride (AlCl$_3$, Hayashi Pure Chemical Ind., >98%), zinc chloride (ZnCl$_2$, Hayashi Pure Chemical Ind., 99.9%), zinc metal (Zn, Hayashi Pure Chemical Ind., >99%), and magnesium chloride (MgCl$_2$, Hayashi Pure Chemical Ind., >99%) were used without further purification. The cyanuric trichloride and the melamine were verified by X-ray diffraction[15] and IR spectroscopy.[16]

Preparation of the Polymer [(C$_3$N$_3$)$_2$(NH)$_3$]$_n$. *Example 1: C$_3$N$_3$Cl$_3$ + NH$_3$.* A quartz glass tube 40 mm

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(16) *Aldrich Library of Infrared Spectra, Ed. III* No. C-9, 550-1 for C$_3$N$_3$Cl$_3$, No. M265-9 for C$_3$N$_3$(NH$_2$)$_3$.

in inner diameter and 1000 mm in length was used as a reactor. Cyanuric trichloride (15.0 g, $C_3N_3Cl_3$) was placed in the middle section of the tube. The reaction system was flushed with N_2. A mixture of NH_3 (50 mL/min) and N_2 (100 mL/min) was passed through the reaction tube at room temperature. The feed of the mixed gas was continued for 1 h. The flow of the mixed gas was continued, while the middle section of the tube was then heated in an electric furnace at a rate of 1 °C/min up to 400 °C, and this temperature was maintained for 2 h. N_2 alone was then passed through the tube, the temperature in the middle section of the tube was raised to 500 °C, and this temperature was maintained for 1 h. The main product was formed in the hot zone (the place where the cyanuric trichloride was placed), and the byproduct NH_4Cl was formed in the cool zone.

Example 2: $C_3N_3Cl_3 + C_3N_3(NH_2)_3$. Cyanuric trichloride (6.0 g) and 4.1 g of melamine were mixed and placed in the middle section of the reaction tube used in example 1, and N_2 gas was continuously passed through the tube. The temperature of the reaction tube was raised at a rate of 1 °C/min to 500 °C, and this temperature was maintained for 1 h. The product was formed in the hot zone.

Reactions of the Polymer with Metal or Metal Chloride. *Example 3:* $[(C_3N_3)_2(NH)_3]_n + AlCl_3$ *(500 °C).* $[(C_3N_3)_2(NH)_3]_n$ powder (1.00 g) obtained in the example 1 and 0.66 g of $AlCl_3$ were mixed in a drybox and placed in the middle section of the reaction tube used in example 1, and the reaction was carried out by the same method as example 2 thereafter.

Example 4: $[(C_3N_3)_2(NH)_3]_n + AlCl_3$ *(1000 °C).* The powder obtained in the example 3 (1.00 g) was placed in the middle section of the reaction tube used in example 1, and the reaction system was flushed with N_2. The flow of N_2 (50 mL/min) was continued, while the temperature of the reaction tube was raised at a rate of 5 °C/min to 1000 °C, and this temperature was maintained for 1 h. The product was formed in the hot zone.

Examples 5 $([(C_3N_3)_2(NH)_3]_n + ZnCl_2$ *(900 °C)), 6* $([(C_3N_3)_2(NH)_3]_n + Zn$ *(900 °C)), and 7* $([(C_3N_3)_2(NH)_3]_n + MgCl_2$ *(900 °C)).* The reaction of $[(C_3N_3)_2(NH)_3]_n$ powder (1.00 g) obtained in example 1 and $ZnCl_2$ (0.68 g), Zn powder (0.33 g) or $MgCl_2$ (0.47 g), respectively, was carried out at 900 °C by the same method as example 4.

Characterization of the Products. The chemical compositions of the products were established by the usual combustion in oxygen followed by gas chromatography for carbon, hydrogen, and nitrogen; by alkali melting followed by ICP atomic absorption spectra for aluminum, zinc, and magnesium and by the Ag^+ titration method for chlorine.

X-ray diffraction data were obtained by using a diffractometer (Shimdzu XD-5) with Ni filtered Cu Kα radiation. The scan speed was 1° (2θ)/min.

Transmission electron micrographs and electron diffraction data were obtained by a transmission electron microscope (JEOL JEM-2000FX).

IR absorption spectra were measured by the KBr method and obtained by an infrared spectrophotometer (Perkin-Elmer 983G).
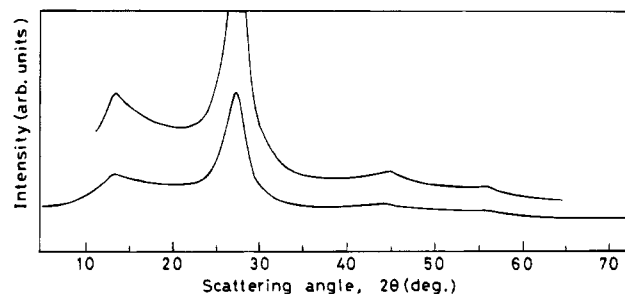
Figure 1. X-ray powder diffraction pattern of $[(C_3N_3)_2(NH)_3]_n$.

ESCA was performed on a Shimadzu ESCA 750 electron spectrometer with Mg Kα radiation. The binding energies of the elements were corrected by placing the C_{1s} peak of contaminating carbon, which was introduced by the oil vapor of the high-vacuum pump, at 284.6 eV.
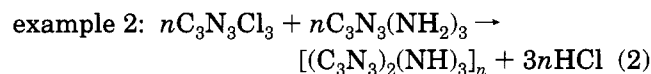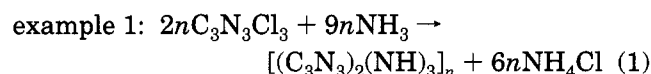
Specific gravity was measured by a He pycnometer (Shimadzu 1320) as well as a toluene pycnometer.

DTA and TGA were carried out by DTA-TG thermal analyzer (Rigaku CN8078B2) under air at a heating rate of 10 °C/min.

Photoluminescent spectra were obtained by a spectrophotometer (Hitachi 650-10). The spectra were essentially the same between those before and after a calibration by using a rhodamine B solution.

3. Results and Discussion

3.1. Structure and Characteristics of the Polymer $[(C_3N_3)_2(NH)_3]_n$. *Product $[(C_3N_3)_2(NH)_3]_n$ of Examples 1 and 2.* The products obtained by example 1 ($C_3N_3Cl_3 + NH_3$) and example 2 {$C_3N_3Cl_3 + C_3N_3(NH_2)_3$} were yellowish white powders and were insoluble in water and common organic solvents. Elemental analyses yielded the following results: Found (example 1): C 36.0, N 62.4, H 1.6 (wt %). Found (example 2): C 35.2, N 62.7, H 2.0 (wt %). Calc ($C_6H_9N_3$): C 35.8, N 62.7, H 1.5 (wt %). The composition was $C_6N_{8.9}H_{3.4}$ and $C_6N_{9.2}H_{4.1}$, respectively. The yields were 71% and 63%, which were calculated on the basis of the source $C_3N_3Cl_3$, by assuming the general formula $C_6N_9H_3$ and each reaction as follows:

example 1: $2nC_3N_3Cl_3 + 9nNH_3 \rightarrow$
$$[(C_3N_3)_2(NH)_3]_n + 6nNH_4Cl \quad (1)$$

example 2: $nC_3N_3Cl_3 + nC_3N_3(NH_2)_3 \rightarrow$
$$[(C_3N_3)_2(NH)_3]_n + 3nHCl \quad (2)$$

X-ray Diffraction of $[(C_3N_3)_2(NH)_3]_n$. Figure 1 shows the X-ray diffraction pattern of the obtained polymer $[(C_3N_3)_2(NH)_3]_n$. The *d* value determined from the maximum intensity diffraction peak of 2θ = 27.1° is 0.33 nm, which is close to the interlayer spacings of graphite (0.335 nm) and h-BN (0.333 nm). In addition, the weak and broad diffraction peaks at around 44.5° and 56° (2θ) are similar to the (100) and (004) diffraction peaks of graphite, respectively.

Electron Diffraction Study of $[(C_3N_3)_2(NH)_3]_n$. Figure 2 shows an electron micrograph (a) and an electron diffraction pattern (b) for the polymer. Although ring diffraction was usually observed, diffraction spots could also be observed for a crystalline portion of the sample.
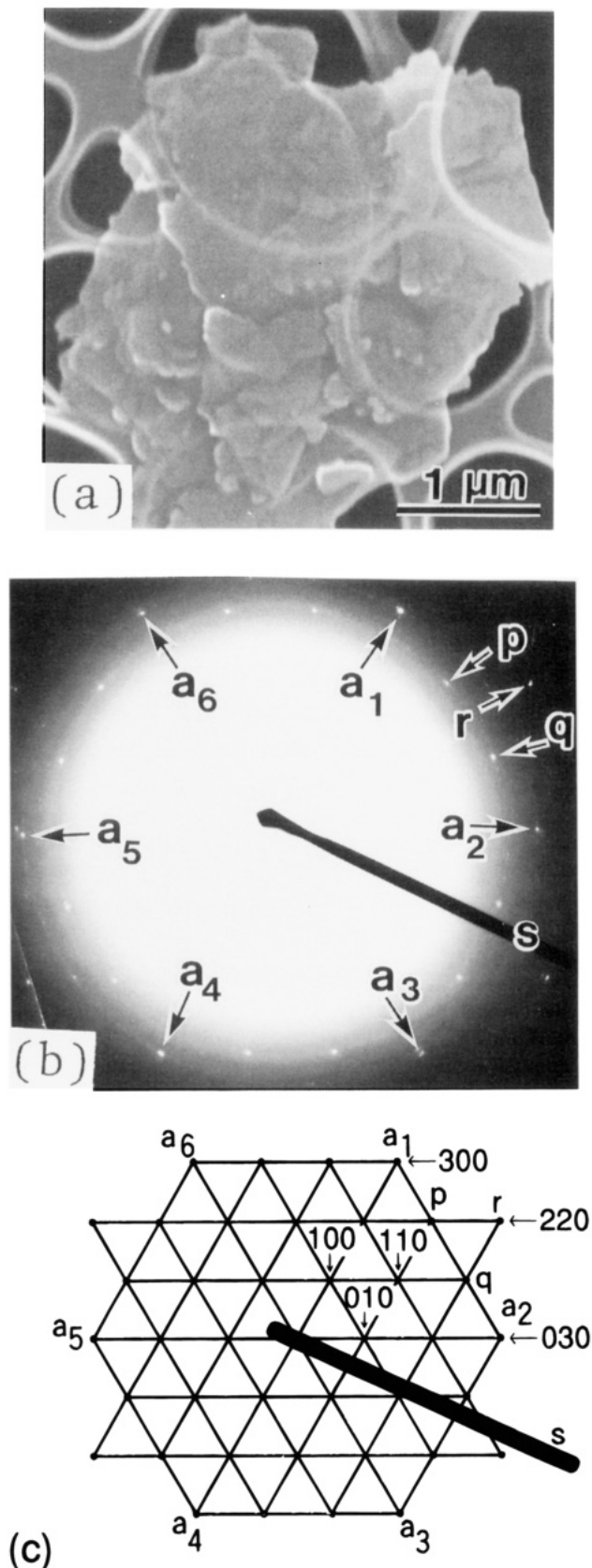
Figure 2. Electron diffraction pattern and transmission electron micrograph of [(C_3N_3)_2(NH)_3]_n: (a) transmission electron micrograph (TEM); (b) electron diffraction pattern; (c) schematic illustration of the diffraction pattern. Indices of a_1, a_2, p, q, and r are 300, 030, 210, 120, and 220, respectively.

The diffraction spots, in this case, can be clearly seen in the outer part of the diffraction pattern (b). Low-angle diffraction spots could not be clearly seen on the

photograph due to the interruption caused by the direct beam as well as their weak intensities. The low-angle diffraction spots must exist on the intersections of lines which are formed by connecting diffraction spots in the outer part, as is schematically illustrated in Figure 2c. The sample was arranged in such a way that an electron beam was incident perpendicular to the ab plane of [(C_3N_3)_2(NH)_3]_n. A group of diffraction spots a_1-a_6 in Figure 2b shows a 6-fold rotating symmetry, a group of spots a_1, p, q, and a_2 are on a straight line, and a group of spots p, q, and r makes a regular triangle. From the schematic illustration in Figure 2c, the spot r can be indexed as the 220 reflection whose d spacing is 0.2057 nm. The lattice constant a and d_{100} are, therefore, 0.823 nm (=4 × 0.2057 nm) and 0.713 nm {=0.823 × cos(π/3)}, respectively.

A dark-field image for the 002 diffraction and (00l) diffraction pattern of the polymer are shown in Figure 3. In this region, the c axis should be parallel to the photograph (arrow in Figure 3 (left)). A d spacing of 0.33 nm was obtained from the 002 diffraction, which coincides with the X-ray diffraction data described above. Diffuse and weak spots could be observed on the horizontal line through a center spot (000) of the original negative film for Figure 3 (right) and can be indexed as 220 whose d spacing (0.201 nm) fit to the d_{100} of graphite. The reason d_{220} could be observed will be discussed later (stacking sequence of [(C_3N_3)_2(NH)_3]_n).

It is concluded on the basis of the electron diffraction study that the polymer has a similar hexagonal structure as that of graphite.

IR Study of [(C_3N_3)_2(NH)_3]_n. Figure 4 shows the infrared absorption spectrum for the polymer. The large absorption band in the range 1650−1250 cm^{-1} is attributed to the stretching vibration of the triazine ring and the absorption at 802 cm^{-1} to the deformation vibration of the same ring. Therefore, the IR spectrum indicates that in the obtained compound the triazine ring (six-member C_3N_3 ring) remains undecomposed.

The absorption band at 3180 cm^{-1} is attributed to the N−H stretching vibration. It is probable that the analyzed compound has hydrogen atoms directly bonded not to triazine rings but to nitrogen atoms outside the ring.

ESCA study of [(C_3N_3)_2(NH)_3]_n. Figure 5 shows ESCA spectra for the polymer. The C_{1s} spectrum (a) exhibits a sharp symmetric peak at 287.8 eV. The position of this peak is at higher energy than the peak at 284.6 eV which is due to C−C bonds (carbon contamination). That is, the peak at 287.8 eV indicates that the electronic density of the carbon is reduced by interaction with a more electronegative atom such as nitrogen and is positively charged. The N_{1s} spectrum (b) indicates the existence of somewhat negatively charged nitrogen atoms (in the triazine ring: peak at 398.5 eV) and a nitrogen atom in a slightly different state (−NH−: shoulder on the higher energy side of the peak). Thus the ESCA spectrum indicates that the structure includes two kinds of nitrogen atoms and only one kind of carbon atom.

Note that both products obtained by example 1 (C_3N_3-Cl_3 + NH_3) and example 2 {C_3N_3Cl_3 + C_3N_3(NH_2)_3} are apparently the same material [(C_3N_3)_2(NH)_3]_n, as there was no significant difference between them according to the characterization described above.
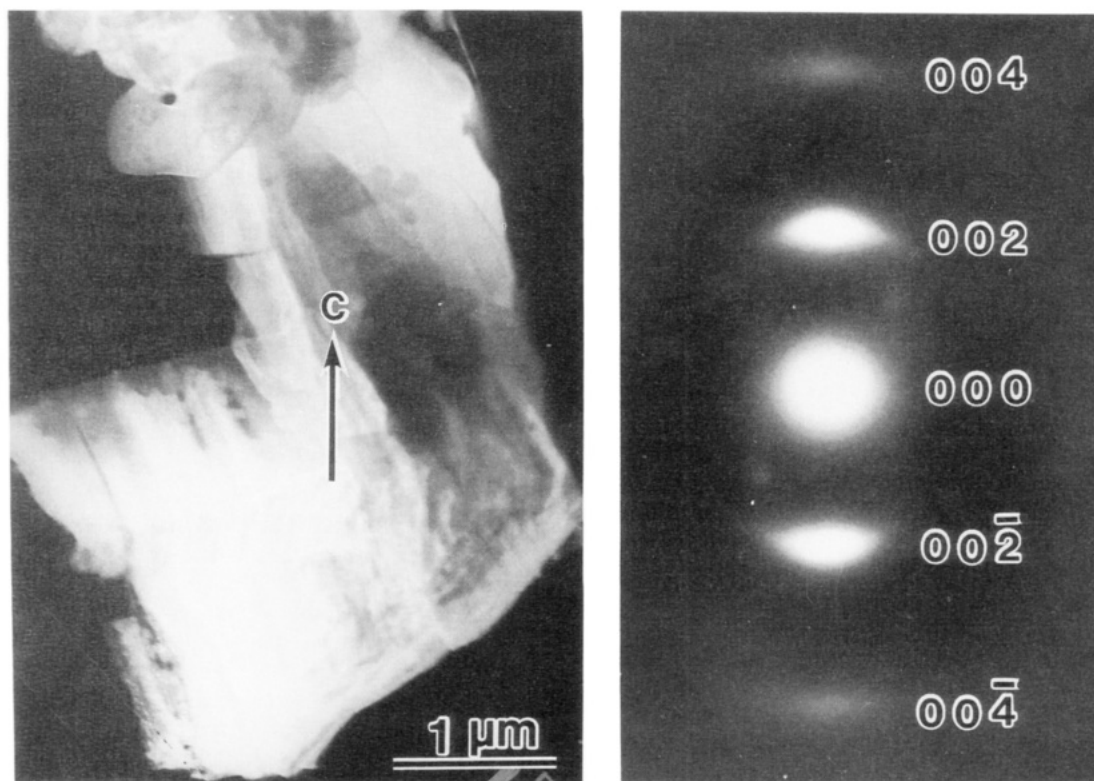
Figure 3. Dark-field image for 002 diffraction (left) and (00*l*) diffraction pattern (right) for $[(C_3N_3)_2(NH)_3]_n$.

Possible Structure (ab Plane) of $[(C_3N_3)_2(NH)_3]_n$. From the above results, a possible two-dimensional structure of the polymer $[(C_3N_3)_2(NH)_3]_n$ in which triazine rings are connected by amino chains ($-NH-$) is shown in Figure 6. This *ab* plane can be stacked in the direction of the *c* axis. The stacking sequence will be discussed later.

The composition ($C_6N_{8.9}H_{3.4}$ or $C_6N_{9.2}H_{4.1}$) showed a larger hydrogen content than the calculated value ($C_6N_9H_3$) for this polymer, probably because the edge part of the polymer contains H-rich groups such as $-NH_2$.

An important aspect is that the proposed structure contains a hole which is surrounded by three amino radicals in a unit cell of this two-dimensional *ab* plane. An estimated size of the hole is 0.40 nm in diameter. It is expected that this hole could allow incorporation of certain chemical species. Some examples are described in section 3.2 (reaction products of the polymer with metal or metal chlorides).

Stacking Sequence of $[(C_3N_3)_2(NH)_3]_n$. The weak diffraction peak at 13.5° (2θ) in Figure 1 indicates a *d* spacing of 0.66 nm which is almost twice the *d* spacing of the strong diffraction at 27.1° ($d = 0.33$ nm). Two explanations have been considered: (1) Two nearest-neighbor planes or two nearest-neighbor *d* spacings have slightly different electronic densities in the direction of the *c* axis. (2) Two nearest-neighbor *d* spacings have slightly different values. Both explanations can be respectively elaborated as follows:

(1) The hydrogen atoms of amino radicals in Figure 6 do not exist in the same plane made of carbon and nitrogen, because of the steric effect caused by the lone-pair electrons of the nitrogen atoms. The diffraction peak for the *d* spacing, 0.66 nm, described above suggests that these hydrogen atoms do not exist in one layered space but exist face to face in another layered
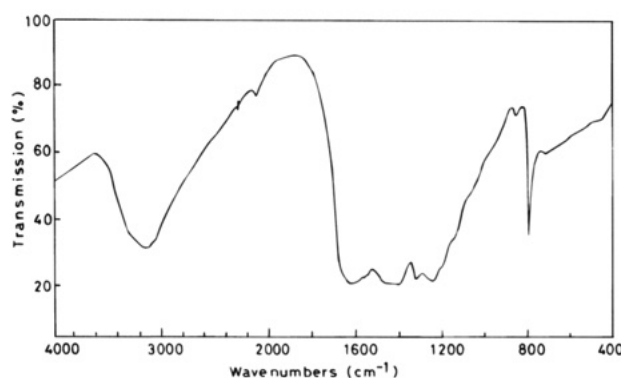

Figure 4. IR spectrum of $[(C_3N_3)_2(NH)_3]_n$.

space and these two layered spaces stack alternately (ABAB⋯, Figure 7). In this case, the one layered space has a smaller electronic density than that of the other layered space.

(2) Two layers (A and B) described above could interact with each other by N⋯H hydrogen bonds so that the stacking could be an ABAB⋯ sequence rather than AAAA⋯. The one layered space in which no hydrogen bond exists should have a slightly larger *d* spacing (by 2α in Figure 7) than that of the other layered space in which the N⋯H hydrogen bond makes a weak interaction between the two layers.

An intensity calculation for the 00*l* X-ray diffraction peaks almost fits the model which is based on the two structural possibilities described above and has $\alpha = 0.03$ nm. The peaks at 13.5°, 27.1°, and 56.0° can be indexed as 001, 002, and 004, respectively.

The diffraction peak at 44.5° (2θ) in Figure 1 indicates a *d* spacing of 0.20 nm which is close to the d_{100} of graphite. This is probably due to the graphite-like structure made by the stacking sequence of ABAB⋯in which B is rotated by 60° against A in the *ab* plane for
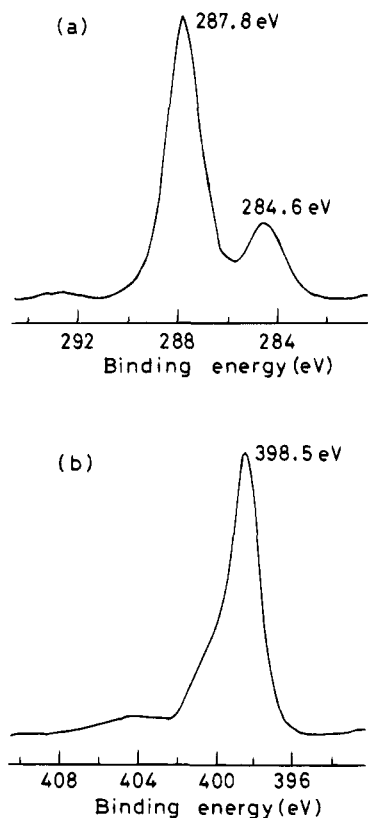
Figure 5. ESCA C_{1s} (a) and N_{1s} (b) spectra of $[(C_3N_3)_2(NH)_3]_n$. A peak at 284.6 eV is due to contaminating carbon which is used to correct the binding energies of the ESCA spectra.
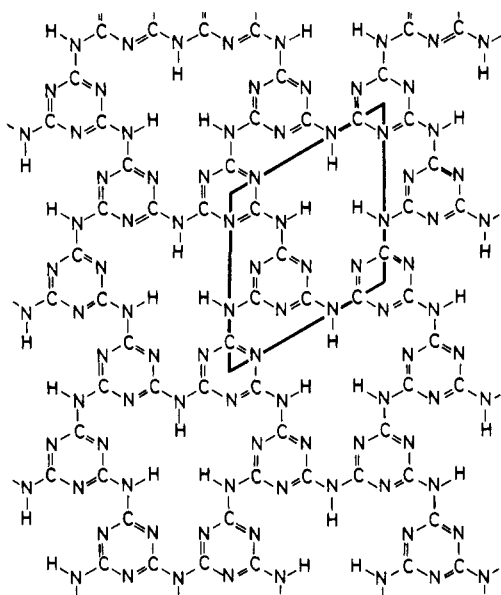

Figure 6. Possible structure model for a monolayer of graphite-like $[(C_3N_3)_2(NH)_3]_n$. The unit cell is shown by the bold line.

$[(C_3N_3)_2(NH)_3]_n$. In this case the peak at 44.5° (2θ) can be indexed as 220.

Further investigation of the structure for $[(C_3N_3)_2(NH)_3]_n$ is under study by solid-state NMR, EXAFS, and a comparison with other compounds containing s-triazine rings, such as melamine and its relatives.[17]

Specific Gravity and Theoretical Density of $[(C_3N_3)_2(NH)_3]_n$. The polymer powder had a specific gravity of
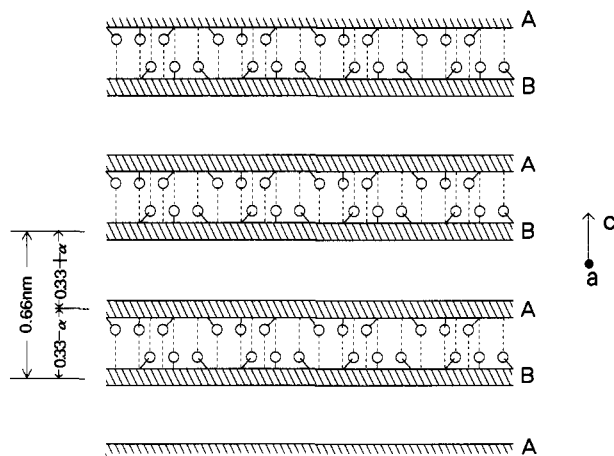
Figure 7. Stacking sequence in the direction of the c axis for $[(C_3N_3)_2(NH)_3]_n$: (O) hydrogen; (▨) planar sheet made of carbon and nitrogen.

1.6–1.8 which was measured by a toluene pycnometer and 1.70 by helium pycnometer. These values fit the theoretical density 1.77 g/cm³ which is calculated from the proposed structure (Figures 6 and 7), by using a C–N single bond length of 0.137 nm, a C–N conjugated bond length of 0.134 nm and a spacing between layers in the direction of the c axis of 0.660 nm.

Reaction Process of $[(C_3N_3)_2(NH)_3]_n$. Regarding the reaction in example 1 ($C_3N_3Cl_3$ + NH₃), an exothermic reaction occurred when NH₃ was introduced into the reaction system at room temperature. The products obtained at room temperature were $C_3N_3Cl_X(NH)_Y$ (X = 1 or 2, Y = 2 or 1, $X + Y$ = 3) and were identified by elemental analyses and IR spectra. These products polymerized at a higher temperature (100–400 °C) to form dimers, tetramers, and oligomers by elimination of HCl which reacted with excess NH₃ and produced NH_4Cl as a byproduct. The oligomers were finally converted to the polymer $[(C_3N_3)_2(NH)_3]_n$ at 500 °C by elimination of NH₃.

The following indicates a result of elemental analysis and composition of the product which was obtained at 200 °C for example 1 ($C_3N_3Cl_3$ + NH₃) and treated with water and acetone in order to eliminate NH_4Cl and monomers. Found: C 26.3, N 53.3, H 3.9, Cl 12.5 (wt %). Composition: $C_{6.2}N_{10.8}H_{11}Cl$. The analytical data fit the calculated value for the dimer $(C_3N_3)_2(NH)$-$(NH_2)_3Cl$: C 28.3, N 55.0, H 2.7, Cl 13.9 (wt %).

On the other hand, the reaction of example 2 {C_3N_3-Cl_3 + $C_3N_3(NH_2)_3$} occurred at temperatures higher than room temperature to produce dimers and oligomers. The reaction thereafter led a similar process to that of example 1 ($C_3N_3Cl_3$ + NH₃).

Figure 8 shows the reaction process for $[(C_3N_3)_2$-$(NH)_3]_n$ which can be deduced from the reaction in example 1. This process can also lead to the structure of $[(C_3N_3)_2(NH)_3]_n$ shown in Figure 6.

Thermal Stability of $[(C_3N_3)_2(NH)_3]_n$. Figure 9 shows the results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for this polymer in air. The polymer was stable at temperatures under 400 °C, and quickly decomposed over 500 °C exothermically. It has been reported that the melamine-related compounds show fire-retardative characteristics.[17] Such a thermal stability could be due to the stable s-triazine ring.
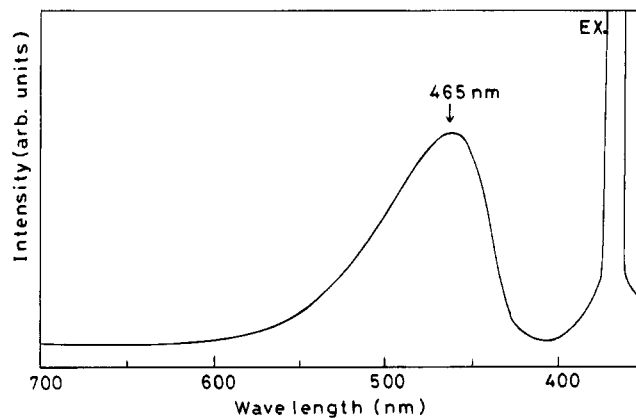
(17) Costa, L.; Camino, G.; Martinasso, G. *Am. Chem. Soc., Div. Poly. Chem. (Polym. Prepr.)* **1986**, *30*, 531.
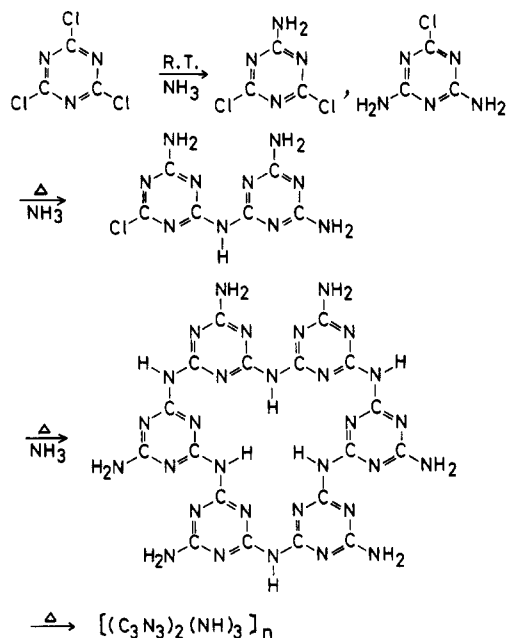
Figure 8. Reaction process of $[(C_3N_3)_2(NH)_3]_n$ for the C_3N_3-Cl_3-NH_3 system.
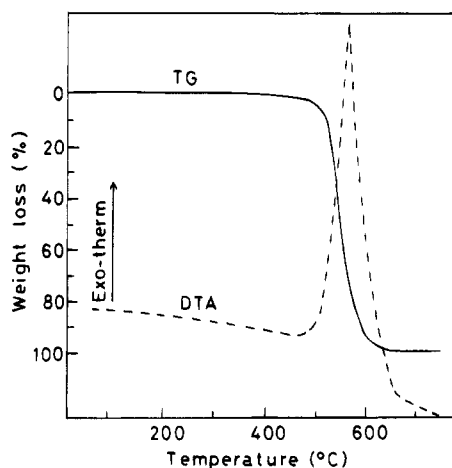

Figure 9. TGA and DTA curves of $[(C_3N_3)_2(NH)_3]_n$ measured in air. Heating rate: 10 °C/min.

Figure 10. Photoluminescent spectrum of $[(C_3N_3)_2(NH)_3]_n$. EX indicates excitation light of 365 nm from Hg lamp.

Photoluminescence of $[(C_3N_3)_2(NH)_3]_n$. This polymer exhibits strong photoluminescence at room temperature. Figure 10 shows a photoluminescent spectrum of $[(C_3N_3)_2-(NH)_3]_n$. The luminescent intensity was strongest under an exciting wavelength of 365 nm from a high-pressure
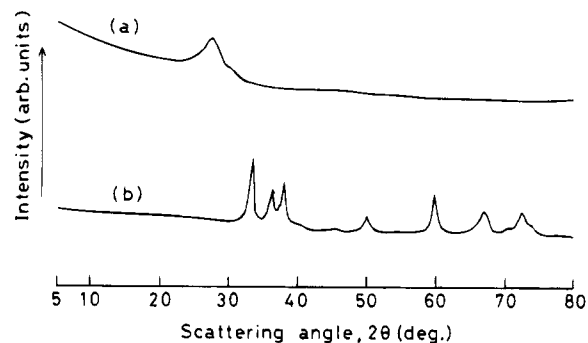
Figure 11. X-ray diffraction patterns of the intermediate product (a) and AlN (b) prepared by the reaction of $[(C_3N_3)_2-(NH)_3]_n$ with $AlCl_3$ at 500 and at 1000 °C, respectively.

mercury lamp. The luminescence was observed in a wide range (430–550 nm) and had a peak at 465 nm. A blue color could be seen by the naked eye. It has been reported that π-conjugated polymers such as poly-(phenylenevinylene)[18] and poly(3-hexylthiophene)[19] show photoluminescence based on their $\pi-\pi^*$ transitions and can be applied to light-emitting diodes.[20] Photoluminescence behavior was also observed for the intermediate products {the monomer $C_3N_3Cl_x(NH)_y$ ($X = 1$ or 2, $Y = 2$ or 1, $X + Y = 3$) prepared at room temperature and the dimer $(C_3N_3)_2(NH)(NH_2)_3Cl$ prepared at 200 °C in example 1 ($C_3N_3Cl_3$ + NH_3)} in a range similar to that of the polymer $[(C_3N_3)_2(NH)_3]_n$, although no luminescence was observed for the starting materials C_3N_3-Cl_3 and $C_3N_3(NH_2)_3$. These luminescent characteristics probably depend on the $\pi-\pi^*$ transition of the s-triazine ring which is analogous to that of the benzene ring.

3.2. Reaction Products of the Polymer with Metal or Metal Chlorides. *Product of Example 3.* A reaction of $AlCl_3$ with $[(C_3N_3)_2(NH)_3]_n$ at 500 °C.

During the reaction, HCl elimination was observed at 120 °C by means of IR spectroscopy of the gaseous products. The HCl elimination occurred strongly at 300 °C and had almost stopped by 500 °C.

The product weighed 1.22 g and was more yellowish than that of the starting material $[(C_3N_3)_2(NH)_3]_n$. Elemental analysis of the product gave the composition $C_6N_{9.5}H_{8.4}Al_{0.90}Cl_{0.30}$. The observed reaction and the composition of the product both suggest that almost 1 mol of aluminum atom was incorporated into the structure of $[(C_3N_3)_2(NH)_3]_n$ at 500 °C.

An IR spectrum of the product was very similar to that of starting material $[(C_3N_3)_2(NH)_3]_n$, which suggests the product retained the main framework of $[(C_3N_3)_2-(NH)_3]_n$.

Figure 11a shows an X-ray diffraction pattern of the product. The 002 diffraction of $[(C_3N_3)_2(NH)_3]_n$ did not move in its position but broadened and weakened and the 001 diffraction almost disappeared. No diffraction ascribable to $AlCl_3$ or Al metal was observed. These X-ray diffraction results suggest that the Al may have been inserted into the hole in the unit cell of $[(C_3N_3)_2-(NH)_3]_n$, thereby making a similar layered structure as that of $[(C_3N_3)_2(NH)_3]_n$ without any expansion of the d

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spacing. The disappearance of the 001 diffraction is probably due to a larger electron density in the layer of the inserted compound (polymer with Al) than that of $[(C_3N_3)_2(NH)_3]_n$ and a destruction of the regularly ordered N$\cdots$H hydrogen bond in $[(C_3N_3)_2(NH)_3]_n$. Also the broadening of the diffraction peaks suggests a reduction of the crystalline size of the polymer.

The purpose of this reaction was to obtain the insertion compound of aluminum $\{[(C_3N_3)_2(N)_3Al]_n\}$ from the reaction of $AlCl_3$ with the three H in the hole of the polymer, which is described as follows:

$$[(C_3N_3)_2(NH)_3]_n + nAlCl_3 \rightarrow [(C_3N_3)_2(N)_3Al]_n + 3nHCl \quad (3)$$
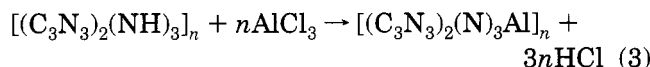
Although the elimination of hydrogen chloride could be observed, the single phase $[(C_3N_3)_2(N)_3Al]_n$ could not be obtained. The impurity chlorine, measured by elemental analysis for the product, cannot be inserted into the hole with aluminum without expansion of the layer distance as there is not enough room in the hole for Al + Cl molecule. The impurity chlorine might be due to regions of the structure which contain quaternary N such as $-NH_2{}^+Cl^--$ formed by a protonation of a $-NH-$ radical with HCl. The higher hydrogen content compared to the original polymer is probably due to the increase of $-NH_2$ terminals formed by the reduction of the crystalline size as well as the hygroscopic characteristics of the product.

Product of Example 4 $\{[(C_3N_3)_2(NH)_2]_n + AlCl_3$ at *1000 °C}. Formation of AlN*: The product weighed 0.15 g and was a white powder. The X-ray diffraction pattern (Figure 11b) and the following elemental analysis indicated the product was the well-known compound AlN. Found: Al 65.0, C 0.7, N 32.0, H 0.0 (wt %). Calc (AlN): Al 65.8, N 34.2 (wt %). This result shows the product of example 3 ($C_6N_{9.5}H_{8.4}Al_{0.90}Cl_{0.30}$) decomposed above 500 °C and formed AlN at 1000 °C.

AlN was also prepared by a direct reaction of $[(C_3N_3)_2(NH)_3]_n$ with $AlCl_3$ at 1000 °C as follows:

$$[(C_3N_3)_2(NH)_3]_n + nAlCl_3 \xrightarrow{1000\,°C} (AlN)_n + 3nHCl \quad (4)$$
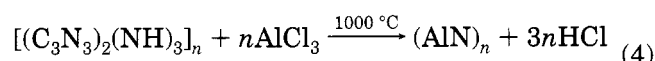
Products of Example 5 $\{[(C_3N_3)_2(NH)_2]_n + ZnCl_2\}$ and *Example 6* $\{[(C_3N_3)_2(NH)_2]_n + Zn\}$. When the reaction was stopped at 500 °C in example 5, the intermediate product showed a similar X-ray diffraction pattern and an IR spectrum as those of the product for example 3 $\{[(C_3N_3)_2(NH)_3]_n + AlCl_3$ at 500 °C}. No diffraction ascribable to $ZnCl_2$ or Zn metal was observed. The elemental analysis for this intermediate product gave a composition $C_6N_{9.1}H_{2.7}Zn_{0.90}Cl_{0.10}$. A Zn atom could also be inserted into the hole in the unit cell of $[(C_3N_3)_2(NH)_3]_n$ in a manner analogous to that of Al (example 3).

The intermediate product obtained at 500 °C for example 6, which employed Zn metal, showed a similar X-ray diffraction pattern to the product for example 3 $\{[(C_3N_3)_2(NH)_3]_n + AlCl_3$ at 500 °C} and the intermediate product for example 5 $\{[(C_3N_3)_2(NH)_3]_n + ZnCl_2$ at 500 °C}. A small amount of the starting materials (Zn metal) was also observed by X-ray diffraction.

The products obtained at 900 °C for examples 5 and 6 weighed 0.28 and 0.25 g, respectively, and both were
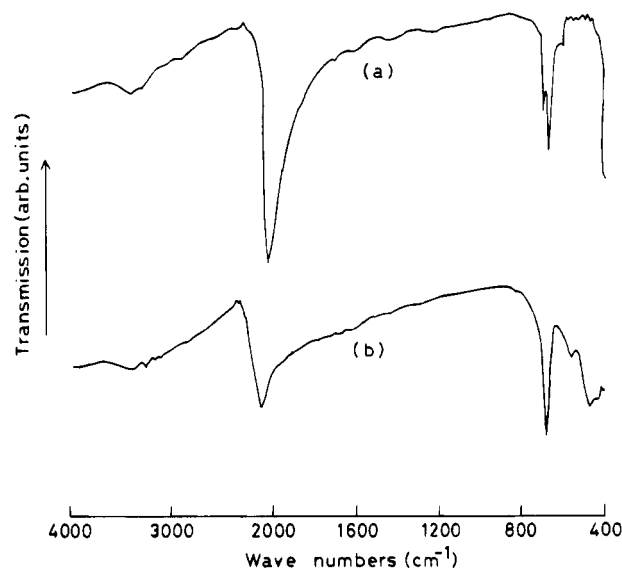
Figure 12. IR spectra of $ZnCN_2$ (a) and $MgCN_2$ (b) prepared by the reaction of $[(C_3N_3)_2(NH)_3]_n$ with $ZnCl_2$ (or Zn) and $MgCl_2$, respectively, at 900 °C.

grayish white powders. The X-ray diffraction pattern[21] and the following result of elemental analysis indicated that both products were the known compound $ZnCN_2$. Found (example 5): Zn 56.3, C 12.0, N 26.9, H 0.0 (wt %). Composition (example 5): $ZnC_{1.2}N_{2.2}$. Found (example 6): Zn 56.5, C 11.5, N 27.4, H 0.0 (wt %). Composition (example 6): $ZnC_{1.1}N_{2.3}$. Calc ($ZnCN_2$): Zn 62.0, C 11.4, N 26.6. The IR spectrum (Figure 12a) shows the strong band at 2030 cm^{-1} which corresponds to the stretching vibration of carbodiimide ($-N=C=N-$).

Product of Example 7 $\{[(C_3N_3)_2(NH)_2]_n + MgCl_2\}$. When the reaction was stopped at 500 °C, the intermediate product showed a similar X-ray diffraction pattern and an IR spectrum as those of the product for example 3 $\{[(C_3N_3)_2(NH)_3]_n + AlCl_3$ at 500 °C} and the intermediate product for example 5 $\{[(C_3N_3)_2(NH)_3]_n + ZnCl_2$ at 500 °C}. No diffraction ascribable to $MgCl_2$ or Mg metal was observed. The result of elemental analysis for the intermediate product gave a composition $C_6H_{9.3}H_{3.1}Mg_{0.94}Cl_{0.11}$. A Mg atom could also be inserted into the hole in the unit cell of $[(C_3N_3)_2(NH)_3]_n$ in a manner analogous to those of Al (example 3) and Zn.

The product obtained at 900 °C weighed 0.13 g and was a white powder. The following result of elemental analysis shows a composition close to that of $MgCN_2$ which is a new compound: Found: Mg 36.0, C 17.8, N 41.5, H 0.0 (wt %). Composition: $MgC_{1.0}N_{2.0}$. Calc ($MgCN_2$): Mg 37.8, C 18.7, N 43.6 (wt %). Although the following X-ray diffraction pattern could not be indexed, the IR spectrum (Figure 12b) was very similar to that of $ZnCN_2$ (Figure 12a). X-ray diffraction data: intensity d (nm) w 0.4671, w 0.2763, vs 0.2622, vw 0.2430, vw 0.2350, w 0.2201, w 0.2099, w 0.1996, m 0.1633, vw 0.1566, w 0.1542, vw 0.1497, vw 0.1487, w 0.1388, vw 0.1342, vw 0.1313, w 0.1262, vw 0.1215.

From these reactions of the polymer $[(C_3N_3)_2(NH)_3]_n$ with metal or metal chlorides, it is concluded that the polymer has potential activity as a new host material as well as a starting material for preparing nitrides or carbonitrides. The oxidation states for the metals

(21) *JCPDS Int. Centre for Diff. Data 1989*, Card No. 1-788 for $ZnCN_2$.

inserted in the polymer and other reactions of the polymer with metal halides will be investigated later.

4. Summary

A new graphite-like layered polymer $[(C_3N_3)_2(NH)_3]_n$ was prepared by the interaction of $C_3N_3Cl_3$ with NH_3 or $C_3N_3(NH_2)_3$. An electron diffraction study suggests that the polymer has a hexagonal structure similar to that of graphite. The proposed atomic arrangement in the layer of $[(C_3N_3)_2(NH)_3]_n$ is composed of s-triazine rings connected by amino radicals.

$[(C_3N_3)_2(NH)_3]_n$ was stable in air even at 400 °C, probably due to the stable 6π-electron system of s-triazine ring. The s-triazine ring also imparts unique photoluminescent characteristics. The polymer exhibited a strong photoluminescence in the range 430–550 nm (blue color) at room temperature.

The polymer $[(C_3N_3)_2(NH)_3]_n$ reacted with $AlCl_3$, $ZnCl_2$, Zn, or $MgCl_2$ at around 500 °C to produce a layered material containing the respective metal, which was converted at 900–1000 °C into AlN, $ZnCN_2$, or $MgCN_2$, respectively.

It can be concluded that this polymer is both a promising new host material and a useful starting material for preparing nitrides or carbonitrides.