Synthesis of a New Graphite-like Layered Material of Composition BC_3N

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Treatment of poly(acrylonitrile) with boron trichloride at 400 °C or acrylonitrile with boron trichloride at 1000 °C yields a graphite-like semiconducting solid of composition BC_3N.

Thermal decomposition of poly(acrylonitrile) results in the formation of graphite by elimination of hydrogen and nitrogen. However, there appears to have been no report of the synthesis of graphite-like layered materials by chemically bridging linear polymer chains. As boron, carbon and nitrogen feature a formation of planar ring systems such as boron nitride and graphite, new B/C/N materials have been synthesized not only by gas-phase reactions as described by Badzian *et al.*[1] and Bartlett *et al.*[2–4] but also by the solid-phase pyrolysis of amine–boranes[5–8]. The features of the three neighbouring atoms (B, C, N) imply that boron is an appropriate chemical species for bridging linear, carbon and nitrogen-containing polymer chains.

A new graphite-like material (BC_3N) is formed as a black powder from interaction of white poly(acrylonitrile) powder with BCl_3 gas at 400 °C (reaction completion), followed by heat treatment under N_2, to remove HCl and crystallise the product, at 1000 °C. The reaction equation is as follows, see eqn. (1).

$$(\text{-}CH_2CHCN\text{-})_n + nBCl_3 \rightarrow (BC_3N)_n + 3nHCl \quad (1)$$

Elemental analyses, GC and alkali melting followed by inductively coupled plasma atomic absorption spectra for boron were used to determine the composition ($BC_{3.0\sim3.2}N_{0.8\sim1.0}$). The yield was almost quantitative based on eqn. (1).

X-Ray diffraction (Fig. 1) and electron diffraction data indicated a turbostratic structure for $(BC_3N)_n$ (*cf.* amorphous carbon which shows random orientation among planer layered sheets). The broad 00*l* ($2\theta = 24.5°$) and 10 ($2\theta = 43°$) diffractions suggested a small crystal unit for $(BC_3N)_n$ and some defects in the layered structure. The d-spacing in the direction of the *c*-axis was 0.36 nm.

$(BC_3N)_n$ can be also synthesized by chemical vapour deposition (CVD) reaction of acrylonitrile monomer and BCl_3. Acrylonitrile vapour carried by nitrogen gas interacts with BCl_3 in a hot zone (1000 °C) in the CVD apparatus, eqn. (2)

$$nCH_2{=}CHCN + nBCl_3 \rightarrow (BC_3N)_n + 3nHCl \quad (2)$$

Black plates are deposited in the hot zone inside a quartz reaction tube. Elemental analyses and X-ray powder diffraction data for the plates were almost the same as those of $(BC_3N)_n$ synthesized by the reaction (1). The fine black powder obtained, however, showed a composition of $BC_{5.8\sim6.0}N_{0.8\sim1.0}$, because of hybridization of $(BC_3N)_n$ and the presence of carbon produced by thermal decomposition of acrylonitrile.[9]

For reaction (2), B–C and B–N bonds could be made by the elimination of HCl from the reaction of Cl–B– and H–C– and an ionic interaction of B–N caused by formation of a $CH_2{=}CHCN{:}BCl_3$ adduct at the start of the reaction, respectively. The by-product adduct in reaction (2) was a white-gray powder. B–B and N–N bonds could not be easily made, because of an unfavourable reaction of Cl–B– and Cl–B– and a repulsion of lone pair electrons between nitrogen atoms, respectively. A possible atomic arrangement in the $(BC_3N)_n$ layers is now under investigation.

The four-probe basal-plane conductivity of $(BC_3N)_n$ plates synthesized by reaction (2) is 88.5 Ω^{-1} cm^{-1}, ten times lower than that of carbon plates prepared at 1000 °C by the CVD method and 10^5 times larger than that of $(B_xC_yN_z)_n$ prepared by the CVD reaction of BCl_3, C_2H_2 and NH_3.[3] The electron carrier might move on the conjugated C–C bonds which partly exist in the planer sheet of $(BC_3N)_n$. The conductivity increased in the range 25–700 °C, implying that $(BC_3N)_n$ behaves as a semiconductor and thermoelectric measurements under vacuum indicate $(BC_3N)_n$ is p-type, a low N:B ratio resulting in an overall electron deficiency (excess hole carriers) in the valence band of $(BC_3N)_n$. The activation

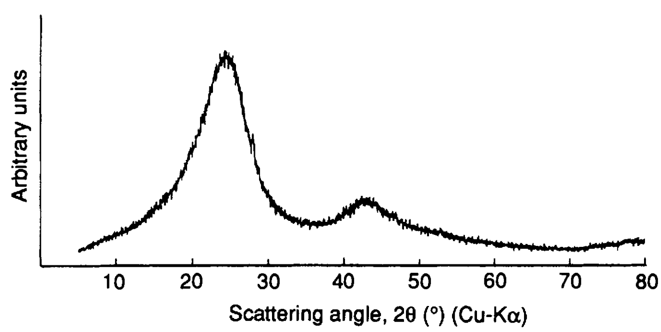

Fig. 1 X-Ray powder diffraction pattern of $(BC_3N)_n$ synthesized by the interaction of poly(acrylonitrile) with boron trichloride

energy was 6.29×10^{-3} eV, which was calculated from the relation between conductivity and temperature.

Received, 22nd January 1993; Com. 3/00414G

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