Formation of Crystalline Epitaxial Films of the Metallic Polymer, $(SN)_x$, by the Thermal Decomposition of S_4N_4 Vapour

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Summary Films of the pure, metallic, crystalline covalent polymer, $(SN)_x$, may be deposited as parallel $(SN)_x$ chains on selected plastic surfaces from the vapour of S_4N_4 after it has been heated to *ca.* 275 °C.

WE have shown previously[1,2] that when crystals of $(SN)_x$, prepared by the solid state polymerization of S_2N_2, are heated at *ca.* 145 °C and the issuing vapours are pumped over a glass coldfinger at *ca.* 25 °C, golden films of $(SN)_x$ are deposited. If thin strips of polymers such as Mylar, Teflon, polyethylene, *etc.* were oriented by stretching and then attached to the cold finger, golden epitaxial crystalline films of $(SN)_x$ were obtained on the plastic substrates.[2] This was the first reported large-scale fully oriented epitaxial growth of any polymer. The films showed strong optical and electrical anisotropy.

Recent studies[3] suggest that the substance in the vapour from the heated $(SN)_x$, responsible for the production of the $(SN)_x$ films, is a reactive, possibly linear isomer of S_4N_4. If this were the case, it should be possible to produce such an isomer by the controlled thermal rearrangement of S_4N_4.

We report that when S_4N_4 is heated at 70 °C and the vapour is pumped over Pyrex or quartz wool at *ca.* 275 °C, golden films of $(SN)_x$ are deposited directly from the vapour phase on glass or polymer surfaces held at 10—30 °C. Elemental analyses of scrapings of the film from the glass surface agree with those expected for pure $(SN)_x$ and *X*-ray powder patterns show no lines characteristic of S_4N_4[4] or S_2N_2[5] in the $(SN)_x$. On occasions it is necessary to heat the films at 75 °C for several hours with pumping, to remove traces of unchanged S_4N_4.

The films on the plastic substrates are identical with those obtained by the sublimation of $(SN)_x$ and consist of essentially completely aligned parallel $(SN)_x$ polymer chains. This is shown by the fact that when examined under polarized light the films appear golden under light polarized parallel to the polymer chains and dark blue-grey under perpendicularly polarized light. *X*-Ray studies show that the films have the same crystal structure as $(SN)_x$[6] and that the $\bar{1}02$ plane of the crystal, which is parallel to the plane containing the $(SN)_x$ chains, is also parallel to the plane of the polymer substrate.

The nature of the gaseous species resulting from the thermal decomposition of S_4N_4 vapour which is responsible for the formation of the $(SN)_x$ is not yet known, although it is possible it may be the same reactive isomeric form of S_4N_4 postulated as being present in the vapour of subliming $(SN)_x$. The formation of a reactive gaseous species in this study, by the controlled heating of S_4N_4 vapour, is consistent with this hypothesis.

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