Photopolymerization of S_2N_2 to $(SN)_x$

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Summary S_2N_2 single crystals grown in tetrahydrofuran solution can be photopolymerized in their mother liquor at temperatures as low as −65 °C to produce $(SN)_x$ with an electrical conductivity of *ca.* 2000 Ω^{-1} cm^{-1}, increasing by a factor of 250 at 13 K.

ALTHOUGH the thermal, topochemical polymerization of S_2N_2 crystals to $(SN)_x$ was first observed in 1910 by Burt,[1] it was not until 1973 that the electrical properties of $(SN)_x$ 'single crystals' were measured for the first time by Walatka, Labes, and Perlstein,[2] initiating a large number of studies of the 'metallic' and superconducting properties and the chemistry of $(SN)_x$.[3] Crystals of S_2N_2 are normally grown from the vapour phases at 0 °C and are allowed to polymerize thermally over a period of several months at room temperature. We have found that the polymerization of S_2N_2 single crystals grown in tetrahydrofuran (THF) solution can be photoinduced at temperatures as low as −65 °C to yield crystals having conductivities comparable to high quality $(SN)_x$ obtained from the thermal polymerization. The electrical conductivity σ of photopolymerized $(SN)_x$ crystals is *ca.* 2000 Ω^{-1} cm^{-1} at room temperature, increasing by a factor of 250 at 13 K. Superconducting properties of these crystals are currently being examined.

S_2N_2 monomer was prepared by Patton's method.[4] Solutions of S_2N_2 in $LiAlH_4$-dried THF were prepared at pressures of *ca.* 5×10^{-7} Torr by condensing a weighed sample of S_2N_2 onto a known volume of THF cooled to −196 °C. The crystal-growing ampoule was then placed in a light-tight container. The ampoule bath temperature was lowered at a programmed rate of 1 °C h^{-1} to the photopolymerization temperature. During this time smooth-facetted clear colourless crystals were formed (observed by using a Wratten no. 25 red filter). The crystals were irradiated with an 18-W tungsten microscope illuminator.

Darkening of the crystals was observed within *ca.* 30 s after commencing illumination. Within 5 min the crystals were opaque black. The crystals were then thermostated at −35 °C. Within several weeks the characteristic golden lustre of fully polymerized $(SN)_x$ crystals was observed. However, the crystals were maintained at −35 °C for 6 months to complete polymerization. Failure

to do so results in portions of the crystal remaining unpolymerized. Similar observations regarding incomplete polymerization have been made on vapour-grown $(SN)_x$.[5]

After removal of solvent *in vacuo*, the crystal-growing ampoule was pressurized with He at 0 °C. The crystals were then annealed for 2 h at 75 °C. Satisfactory elemental analyses were obtained for $(SN)_x$ (S and N; absence of C and H). *Crystal structure:* monoclinic space group $P2_1/c$; $a = 4{\cdot}161(5)$; $b = 4{\cdot}434(1)$, $c = 7{\cdot}589(9)$ Å; $\beta = 109{\cdot}52(7)°$. The unit cell parameters are essentially the same as those of vapour phase-grown $(SN)_x$, and are comparable to those reported earlier.[5,7]

Whereas S_2N_2 crystals are colourless, their solution in THF is a light yellow colour at −20 °C or lower. Photopolymerization was found not to be initiated by wavelengths > 500 nm, and therefore the absorption region 320—500 nm of the solution appears to be the active region. It was also observed that S_2N_2 vapour-grown crystals do not photopolymerize under comparable conditions, nor is any polymer formed from a saturated S_2N_2 solution in the absence of crystals. These observations are consistent with a picture of photopolymerization being initiated at the S_2N_2–THF solid–solution interface.

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[1] F. P. Burt, *J. Chem. Soc.*, 1910, 1121.
[2] V. V. Walatka, M. M. Labes, and J. H. Perlstein, *Phys. Rev. Letters*, 1973, **31**, 1139.
[3] For a recent review, see G. B. Street and R. L. Greene, *IBM J. Res. & Dev.*, 1977, **21**, 99.
[4] R. L. Patton, Ph.D. Thesis, University of California, Berkeley, California, (1969).
[5] C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Amer. Chem. Soc.*, 1975, **97**, 6358.
[6] Galbraith Laboratories, Inc., Knoxville, Tennessee.
[7] P. Love, G. H. Myer, H. I. Kao, M. M. Labes, W. R. Junker, and C. Elbaum, Conference on Synthesis and Properties of Low-Dimensional Materials, June 13—16, 1977, New York Academy of Sciences, to be published, *Ann. New York Acad. Sci.*, 1978.