# Electrochemical Synthesis of Poly(sulphur nitride)

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Poly(sulphur nitride) can be synthesized electrochemically, in liquid sulphur dioxide, from cyclopenta-azathienium chloride, $S_5N_5Cl$ (prepared by a new method from $S_5N_5FeCl_4$ and CsF).

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Poly(sulphur nitride), a quasi-one dimensional polymer, is of considerable current interest on account of its metallic properties (*e.g.* superconductivity below 0.3 K).[1] A variety of synthetic methods is available. Most preparations of crystalline $(SN)_x$ proceed *via* a solid state polymerization of $S_2N_2$,[2,3] and improved routes to this dimer have recently been described.[4]

Several solution preparations (involving azides) have also been reported.[5]

As far as we are aware, an electrochemical synthesis of poly(sulphur nitride) has not previously been achieved. We report here the electrochemical reduction of $S_5N_5Cl$ in liquid sulphur dioxide; $S_4N_4$ was the main co-product. The purified polymer consisted of 5—10 $\mu$m microcrystals. Electrolyses of $S_5N_5AlCl_4$ and $S_5N_5FeCl_4$ in acetonitrile also gave $(SN)_x$.

Cyclopenta-azathienium tetrachloroferrate(III) was prepared either from iron powder and $(NSCl)_3$ in nitromethane, or from $S_4N_4$, $(NSCl)_3$, and $FeCl_3$ in thionyl chloride solution.[6] It has been reported[7] that cyclopenta-azathienium chloride, $S_5N_5Cl$, prepared by heating (65 °C) $S_4N_4$ and $(NSCl)_3$ and recrystallized from anhydrous formic acid has a m.p. of 96 °C and decomposes at room temperature. We prepared $S_5N_5Cl$, in liquid $SO_2$, at 18 °C from $S_5N_5FeCl_4$ and CsF (molar ratio 1 : 3). Co-products ($S_4N_4$ and CsCl) were removed by extraction with acetonitrile in which $S_5N_5Cl$ is only sparingly soluble. Purified $S_5N_5Cl$ can be stored in an inert atmosphere without decomposition. On heating in a sealed capillary (under $N_2$) it failed to melt but darkened slightly and above 87 °C slowly produced $(NSCl)_3$ which condensed further up the capillary. The decomposition of $S_5N_5Cl$ became rapid above *ca.* 90 °C; the residue (largely $S_4N_3Cl$) exploded above *ca.* 170 °C without melting. The products of the decomposition were identified by Raman spectroscopy. $S_5N_5Cl$ is moderately soluble in liquid $SO_2$ (*ca.* 0.03 g/g $SO_2$ at 18 °C). Like $S_4N_4$ and $(SN)_x$ it detonates on percussion, however it is less sensitive to shock than $S_4N_4$. Hydrolysis of $S_5N_5Cl$ occurs only slowly in air to give a black mixture, containing $S_4N_4$, $(NH_4)_2SO_4$, and $(SN)_x$. All operations involving air sensitive materials were carried out in a glove box and all glassware was freshly heated to *ca.* 500 °C either in an annealing oven or by a hand torch.

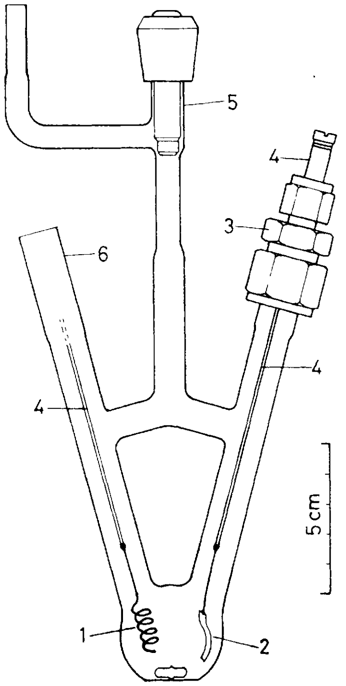

**Figure 1.** Electrolytic cell for liquid $SO_2$; 1,2 auxiliary/working electrodes, 3 Swagelok ½ to ¼ inch reducing union, 4 monel leads, 5 Rotaflo valve, 6 ½ inch o.d. precision tubing.

The electrolysis was carried out in a simple undivided cell (Figure 1). The working electrode was Pt foil (4.0 $cm^2$ area). The auxiliary electrode was coiled Pt wire (0.5 mm diameter). A Swagelok ½ to ¼ inch reducing union fitted with poly(tetrafluoroethylene) ferrules was used as a pressure lead-through for each electrode. $S_5N_5Cl$ (0.160 g, 0.60 mmol) and a magnetic stirring bar were put into the cell in the glove box; the cell was assembled and removed from the box. Sulphur dioxide (21 g) was condensed in *via* a metal vacuum line. On warming to room temperature the $S_5N_5Cl$ dissolved to give a pale yellow solution of *ca.* $4.1 \times 10^{-3}$ mol $dm^{-3}$ concentration. The cell was placed into a thermostated bath (at −1 °C) above a magnetic stirrer and was connected to a stabilized d.c. source. The current was adjusted to 4.0 mA (*i.e.*, nominal current density 1.0 mA $cm^{-2}$); the potential measured across the electrodes was 2.6 V. For the first 10 min the reaction pro-

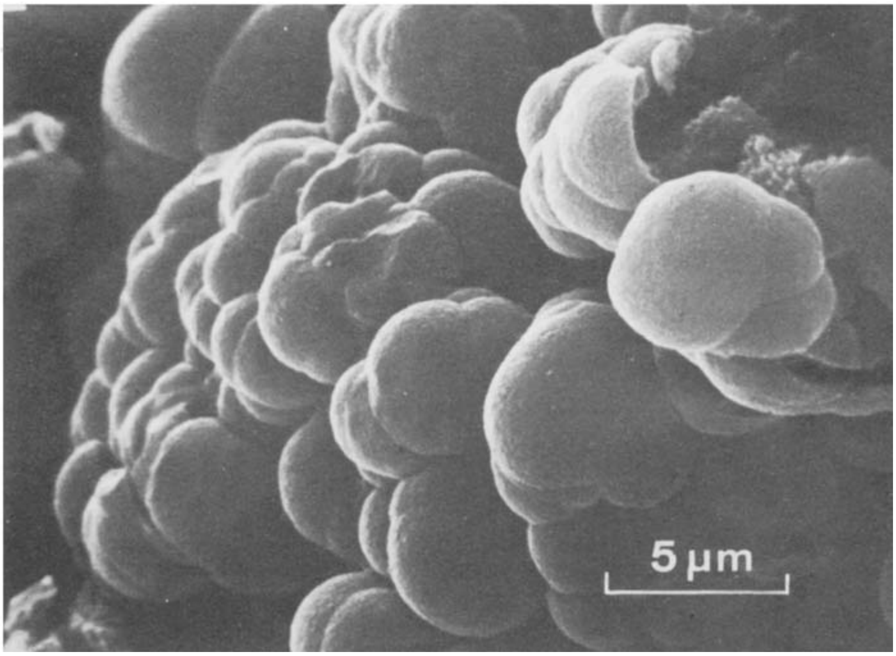

**Figure 2.** An s.e.m. photograph of the cathodic deposit of $(SN)_x$; magnification 5000×.

ceeded without stirring and an even black film formed almost immediately on the cathode's front surface (*i.e.*, facing the anode) together with a brown turbid cloud in the electrolyte. After ten minutes the stirrer was turned on, the turbidity disappeared and a steady growth ensued. Throughout the electrolysis (4 h) the current and the potential remained remarkably stable (fluctuations *ca.* 2%) and no gas evolution occurred. The solid residue at the bottom of the cell after evaporation of the solvent was a mixture of $S_5N_5Cl$ (as a major component) and $S_4N_4$. The cathodic deposit on the front side was microcrystalline $(SN)_x$ interspersed with minute $S_4N_4$ crystals. The reverse side of the cathode was coated with a continuous thin blue layer of $(SN)_x$. The $S_4N_4$ was removed by sublimation at 60 °C *in vacuo* ($\leqslant 10^{-6}$ Torr). Under an optical microscope (40 ×) the fragmented deposit of the purified polymer appeared composed of bright gold highly reflecting microcrystals of 10 $\mu$m average size (and a very few needles, up to 0.5 mm in length). These microcrystals were stacked in zig-zag chains arranged at right angles with respect to the electrode surface. Almost identical growth features with 4—5 $\mu$m crystallites resulted from another experiment carried out at a higher current density (7.5 mA $cm^{-2}$) and under somewhat different conditions: 0.5 mm diameter coiled Pt wire as cathode, 8.0 mA, 3.0 V, concentration $4.8 \times 10^{-3}$ mol $dm^{-3}$. A scanning electron microscope (s.e.m.) (JEOL—T20 instrument) photograph (Figure 2) of the product $(SN)_x$ shows the stacks of rounded crystals viewed obliquely down the chain-like stacks.

The final $(SN)_x$ was identified by chemical analysis, i.r. spectra,[8] and *X*-ray powder diagram data.[2,9] Poly(sulphur nitride) was also prepared electrochemically from $S_5N_5FeCl_4$ and $S_5N_5AlCl_4$ both in acetonitrile [*e.g.*, 0.105 g $S_5N_5AlCl_4$ in 40 $cm^3$ acetonitrile, at 0.9 mA, 26.5 V for 7 h, giving 23.8 mg $(SN)_x$, *i.e.* 2.1 (SN) units per unit charge].

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## References

1 M. M. Labes, P. Love, and L. F. Nichols, *Chem. Rev.*, 1979, **79**, 1.

2 C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, 1975, **97**, 6358.

3 A. J. Banister and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1980, 731.

4 T. Chivers, A. W. Cordes, R. T. Oakley, and P. N. Swepston, *Inorg. Chem.*, 1981, **20**, 2376; H. W. Roesky and J. Anhaus, *Chem. Ber.*, 1982, **115**, 3682.

5 F. A. Kennett, G. K. MacLean, J. Passmore, and M. N. S. Rao, *J. Chem. Soc., Dalton Trans.*, 1982, 851.

6 A. J. Banister, A. J. Fielder, R. G. Hey, and N. R. M. Smith, *J. Chem. Soc., Dalton Trans.*, 1980, 1457; A. J. Banister and H. G. Clarke, *Inorg. Synth.*, 1977, **17**, 188.

7 L. Zbořilová and P. Gebauer, *Z. Anorg. Chem.*, 1981, **483**, 44.

8 J. W. Macklin, G. B. Street, and W. D. Gill, *J. Chem. Phys.*, 1979, **70**, 2425.

9 A. J. Banister, Z. V. Hauptman, J. Passmore, P. S. White, and C. M. Wong, in preparation.