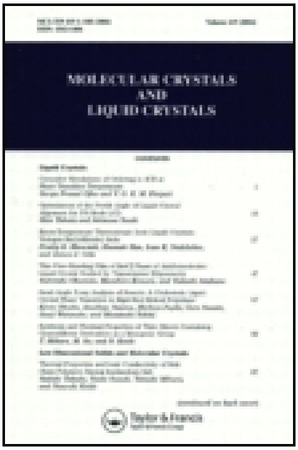

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$(SN)_x$ and $(CN)_x$—The Search for Intrinsic Polymeric Metals

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$(SN)_x$ and $(CN)_x$—The Search for Intrinsic Polymeric Metals

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Only one example of an intrinsic polymeric metal exists—polysulfur nitride—$(SN)_x$. The history of its discovery and its chemical and physical properties are reviewed. Another intriguing possibility as an intrinsic metal is $(CN)_x$. A ladder polymer having this formula has been hypothesized but probably has never been prepared. However, the homopolymer of cyanogen is an interesting material in and of itself and can be thermally converted to graphite fibers. Transition metal complexes of the homopolymer can also be prepared and converted to metallic and superconducting composite fibers.

$(SN)_x$ AND $(CN)_x$—THE SEARCH FOR INTRINSIC POLYMERIC METALS

Historical introduction

After the discovery of high conductivity in organic molecular complexes, it was evident to many of the early workers in the field that it would be important to extend the idea of complexing to polymer systems. A number of papers appeared on the conductivity of complexes of polymers with the ubiquitous iodine molecule,[1,2] as well as many other small molecule acceptors including TCNQ.[3] Indeed, many of the current ideas about doped polymers have their antecedents in this period—e.g. polyphenylene complexes,[1] processability in polymer complexes such as copoly(styrene,1-butyl-2-vinlpyridinium TCNQ)[3] to name but two examples.

It was also intriguing to consider the possibility of extended polymeric conjugated systems that were intrinsic metals—it was, of course, known that graphitic undoped layers are metallic in the basal plane, and that graphite intercalates could show a superconducting transition, albeit at very low temperatures.[4]

We looked for clues in the early literature, and a review by Goehring in 1956 of the chemistry of $(SN)_x$[5] lead us back to the work, in 1910, of Frank Playfair Burt of University College, London.[6] Burt was attempting quantitative analysis of the vapor formed by heating tetrasulfurtetranitride (S_4N_4), and while passing the vapor through silver gauze, observed the formation in his tubes of a thin film which appeared blue in transmission, and bronze-colored with a metallic luster in reflection. He also observed large single crystals of the compound. he states ". . . . A weighable quantity was finally obtained by accident. Nitrogen sulfide [S_4N_4] was being sublimed in a vacuum over quartz wool heated to about 300°; . . . . . . among a variety of products were some large, bronze colored crystals, which deposited in the connecting tubing leading to the pump." An average single crystal weighed about 4 milligrams. A final interesting historical note: Burt used quill tubing to attach his glass tubing to the vacuum pump, and it was in the quill tubing that he found his single crystals and thin films of polymer. (Perhaps someone should study epitaxy and crystal growth on quills!)

Burt's work lay dormant until the '50's when Becke-Goehring (her early work published under her maiden name Goehring) undertook detailed studies of the chemistry of S_4N_4, S_2N_2, and $(SN)_x$.[5] After reading her papers, my colleagues and I prepared $(SN)_x$ powder in 1962[7a] and found that the highly conducting material showed a very small activation energy (<0.02 eV). We speculated that conductivity might be metallic in this system. We did not succeed in preparing crystals of $(SN)_x$ until 1973.[7b] We will review the chemistry and physics of $(SN)_x$ starting with this work.

Another intriguing candidate as an intrinsic metal in the early literature was a poly (cyanogen)—$(CN)_x$. A polymer derived from heating metal cyanides was first prepared by Gay-Lussac in 1816.[8] Several efforts were made to examine CN derived polymers in the 50's and 60's; our attention was drawn to the system by a theoretical analysis of the band structure of a number of heteroatom polymers by Whangbo, Hoffman and Woodward in 1976, in which they calculated the band structure of $(CN)_x$, and predicted metallic behavior.[9] In the second part of this article, we will discuss our current work on $(CN)_x$, graphite fibers derived from $(CN)_x$ and metal graphite composites based on $(CN)_x$-transition metal complex decomposition.

$(SN)_x$ CHEMISTRY

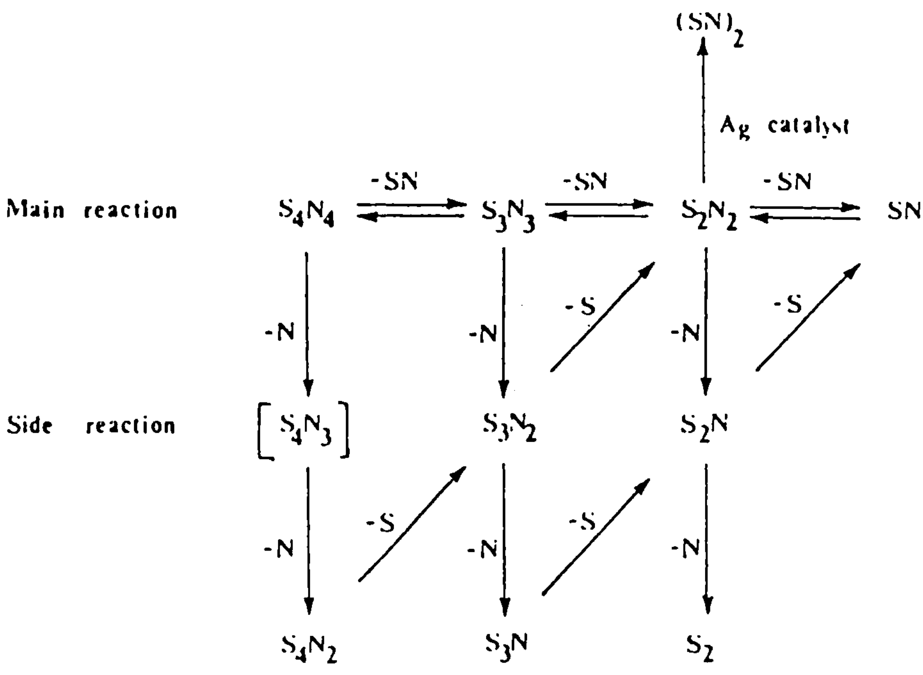
1. Standard method—thermolysis of S_4N_4 to S_2N_2 and polymerization to $(SN)_x$

This method has been discussed fully in our review in 1979.[10] A modification has been described by Kaneto, Yoshino and Inuishi[11] in which the vacuum systems used by other workers is modified so as to eliminate ground glass joints. The reaction consists of the thermal splitting of S_4N_4 over a silver wool catalyst to yield S_2N_2, a clear, colorless, cyclic dimer, which undergoes topochemical polymerization to $(SN)_x$. Our earlier review also discusses the crystal structures of monomer and polymer, and speculations regarding the reaction mode. A recent mass spectral study by Bezenyei, Eigendorf and Frost[12] adds some more information regarding the mechanism of the polymerization. They focus on the importance of a dark brown crystalline monomer with a molecular weight of 92. This monomer had been found, in our earlier work, to polymerize to $(SN)_x$ crystals much more rapidly than S_2N_2.[12]

Bezenyei *et al.*[12] suggest the following unifying mechanism. Typically S_4N_4 fragments to cyclic dimer S_2N_2. Some S_2N_2 transforms to a *linear* oligomer (also a dimer) $(SN)_2$. Polymerization then involves the reaction of linear oligomer with SN monomer (a paramagnetic dark red crystalline material which can also be isolated under certain conditions). The SN monomer originates from the cyclic dimer S_2N_2. This mechanism seems to account for not only the usual polymerization but for variations in kinetics of polymerization, the nature of isolated intermediates, and the many observations of colored species during the process. The complete fragmentation scheme suggested by these authors is shown below.

Scheme I

Complete fragmentation scheme for the thermal decomposition of S_4N_4 in the presence of silver wool.[12]



2. Other methods of preparation

Because the preparation of $(SN)_x$ is somewhat tedious, there have been several attempts to find alternate routes. Banister *et al.*[14] document these attempts, and discuss in detail an effective route to $(SN)_x$ powder: reaction of $(NSCl)_3$ and Me_3SiN_3, initially at −18° in acetonitrile (24 hours), followed by 24 hours at room temperature.[15] $(SN)_x$ particles form, are allowed to settle and are filtered off and dried in vacuo. The $(SN)_x$ is then purified by (tedious) solvent extraction. Sublimation *occasionally* produced crystals, but the process could not be controlled. This method remains, then, a route to powdered $(SN)_x$ clearly of lower purity than crystals from topochemical polymerization.

Another interesting approach is the electrochemical synthesis of $(SN)_x$ from the electrolysis of S_5N_5Cl in liquid SO_2.[16] The patent literature generalizes this method to other salts and other solvents.[17] The cathodic deposit consisted, in the original paper by Banister *et al.*,[16] of microcrystalline polymer on the front side and a thin continuous blue film on the reverse side.

3. $(SNBr_{0.4})_x$

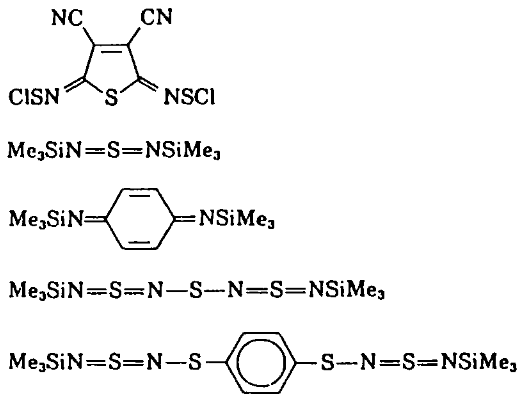
The very high conductivity reported for this material[18,19] has made it a target for synthesis by other methodologies. Note that a brominated $(SN)_x$ was first reported in 1896.[20] Demant and Dehnicke report its preparation from the reaction of $(NSCl)_3$ with $BrSiMe_3$ in dichloromethane solution at −60°; no measurements have as yet been reported on material prepared in this manner.[21]

4. SN polymers with integrated organic groups in the main chain

Several groups have attempted to prepare stable or processable SN containing polymers by incorporating other groups in the main chain. Scherer *et al.*[22] introduced *p*-phenylene groups. Wolmershaeuser *et al.*[23] reacted a variety of difunctional sulfuryl chlorides with *bis*-trimethylsilyl capped SN compounds. Chien and Zhou[24] also reported a series of SN polymers with heterocyclic spacer groups very similar to the work of Wolmerhaeuser *et al.* All of the prepared compounds are not very conducting; many can have their conductivities improved by doping. None show promise of processability. Typical reactions are given below.[24]

Scheme II

Some attempts at integrating organic groups in the main chain of an —SN—polymer by reaction of A with B-E.[24]



5. Summary remarks

We now know more about the mechanism of the solid state polymerization forming $(SN)_x$. Groups around the world have learned how to grow very fine crystals. Other groups have shown us how to prepare $(SN)_x$ films electrochemically, and have developed alternate synthetic pathways, albeit not very promising from the point of view of high purity materials. Attempts to prepare novel polymers with other groups in the main chain in addition to SN have unfortunately not yielded any materials of interest in terms of their electronic properties.

$(SN)_x$ PHYSICAL PROPERTIES

A large number of workers participated in the development of a thorough understanding of the physical properties of $(SN)_x$ both experimentally and theoretically. The ten years from 1973 when the metallic nature of the conductivity was first discovered[7] was a period of intense interest and substantial progress so that our understanding of $(SN)_x$ was rather complete by 1983. An excellent summary of the physical properties was published in 1985.[11] There is no need to repeat the details given in that report, and the period since 1985 has been essentially inactive. We will here give only the briefest summary of the properties of $(SN)_x$.

$(SN)_x$ shows metallic properties down to the onset of superconductivity. The resistivity ρ shows a temperature dependence $\rho \alpha T^n$ where $n = 1.9–2.3$[25–29] as is shown in Figure 1. A superconducting transition, first observed by Greene *et al.*,[30] occurs between 0.2 ~ 0.3 K. Both the width of the transition and T_c depend on sample quality. T_c decreases markedly with magnetic field, especially when applied ⊥ to the fiber axis and hence to the polymer chains. The magnetic field dependence is strong evidence for BCS superconductivity in $(SN)_x$. $(SN)_x$ is considered to be a quasi one-dimensional structure with sufficiently strong three-dimensional interchain interactions to suppress the Pierls instability normally expected in a linear chain structure.

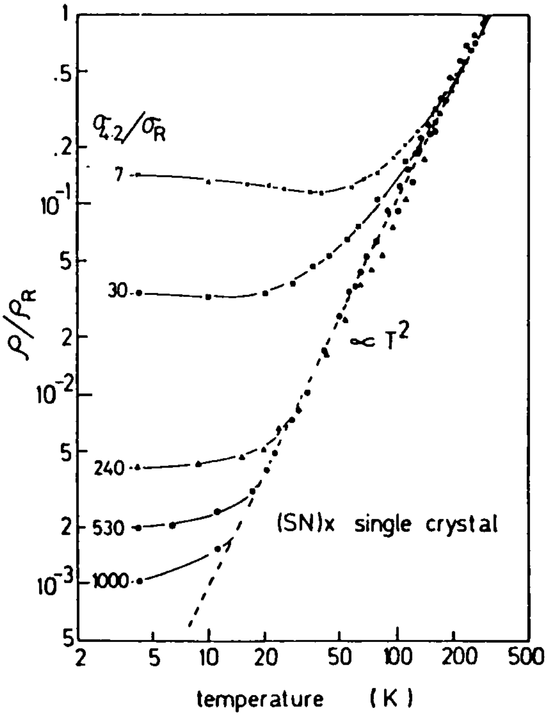


FIGURE 1 Temperature dependence of the electrical resistivity ρ/ρ_R along the *b* axis for various samples with different $\sigma_{4.2}/\sigma_R$ values.[11]

TABLE I

Electrical conductivities $\sigma_\parallel$ and $\sigma_\perp$, and carrier mobilities μ_{eff}, $\mu_\parallel$ and $\mu_\perp$ in $(SN)_x$ crystal (obtained from dc and magnetoresistance measurements).[11]

Temp. (K)	290	77	4.2	1.7
$\sigma_\parallel$ (S/cm)	1.5×10^3	3×10^4	1×10^5	1×10^5
$\sigma_\perp$	5	6	3	3
μ_{eff}	40	60	120	300
$\mu_\parallel$ (cm²/Vsec)	6.9×10^2	4.2×10^3	2.2×10^4	5.5×10^4
$\mu_\perp$	2.3	0.85	0.66	1.6

Magnetoresistance measurements and Hall effect measurements have allowed an assessment of the mobilities of charge carriers, summarized in Table I.[11] Negative magnetoresistance of $(SN)_x$ is observed below 4.2 K and at lower magnetic fields ($<3T$) and is most likely associated with defect structure.

$(SN)_x$ crystals display a shiny golden color in reflection along the fiber axis and a black color across the fiber axis, obviously associated with the intrinsic anisotropy of the electronic properties. The measurements of optical reflectance[31–33] all were susceptible to analysis by the Drude approximation and fit very well, as can be seen in Figure 2.

A large number of theoretical papers appeared calculating electronic band structures and discussing the origin of the suppression of the Pierls transition. The band structure proposed by Rudge and Grant[34] from OPW calculations and that proposed by Oshiyama and Kamimura[35] using the SCF-LCAO method show a similarity in the Fermi surface prediction. Rudge and Grant[34] view $(SN)_x$ as a semimetal in-

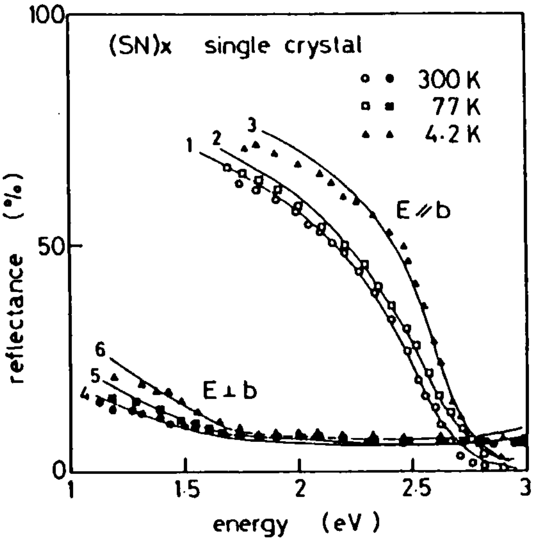


FIGURE 2 Reflectance spectra of $(SN)_x$ for $E \parallel b$ and $E \perp b$ at various temperatures; numbered solid curves represent the calculated curves.[11]

volving electron and hole pockets located at the Brillouin zone boundary; the Fermi surface consists of anisotropic tubes.

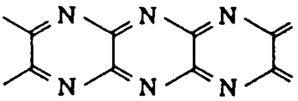
$(CN)_x$

1. Introduction

A polymeric compound called "paracyanogen" has been known since 1816.[8] Gay-Lussac noted the nitrogen-containing carbonaceous deposit upon heating mercuric cyanide to form cyanogen. A summary of early literature on forming the material and its chemical properties can be found in a paper by Bircumshaw *et al.*[36] These workers prepared the material from the decomposition of oxamide at 250–300°C in a sealed tube, as well as by the decomposition of mercuric or silver cyanide. Photopolymerization of cyanogen has been reported to occur[37,38] and Fabian succeeded in making thin (130 Å) films by uv polymerization of cyanogen vapor.[39] Reactive rf sputtering of carbon in nitrogen has resulted in "paracyanogen-like" films.[40] Brenner and Okamoto[41] prepared cyanogen from the reaction of KCN and PCl_5 and claimed the cyanogen so prepared polymerized spontaneously.

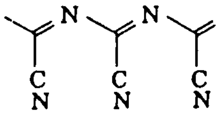
$$KCN + PCl_5 \rightarrow PCl_3 + 2KCl + 1/2(CN)_2$$

In general all of these methods yield intractable polymers, poorly characterized with poor or non-existent microanalysis. The favored structure is



It is for this structure that Whangbo, Hoffman and Woodward[9] predict a metallic conductivity. It is clear that none of the syntheses have really produced this structure. Conductivity measurements on the paracyanogens that have been prepared covered the range of conductivities from 10^{-8} to 10^{-13} $S^{-1}cm^{-1}$.

After several unsuccessful attempts at cyanogen polymerization, we found a route to a linear homopolymer via the electropolymerization of cyanogen.[43–45] This linear homopolymer we shall refer to as PCN. Its structure is given below.



2. Properties of PCN

PCN is an insulating solid showing high charge storage. Thus far we have done relatively little work on the properties of this insulating polymer itself, except for showing the ease of fiber formation and the ease of converting these fibers to carbon fibers. What we do know is the following:

(a) PCN has a high dipole moment. Dilute solution measurements give a dipole moment per monomer unit of 12 D (!), which is obviously much higher than the theoretical. This is a typical problem with cyanocarbon compounds which can show contributions by partial charge separation in the structures.[46] For example, the measured dipole moments of di- and tri- cyanovinyl benzenes are all much higher than the theoretical.[47]

(b) PCN forms fibers even when the molecular weight is as low as 500. This fiber formation is a typical property of higher molecular weight polymers, and one must expect that there is something "special" like strong dipole-dipole interactions between polymeric chains to lead to this easy fiber formation. Fibers can be formed simply by dipping a rod into a 40% by weight solution of PCN in tetrahydrofuran or dimethylformamide or mixtures thereof, and pulling out a fiber 10″ or more in length.

(c) When PCN is heated, an exothermic event occurs at approximately 300°C, after which weight loss upon heating becomes appreciable. N_2 evolution peaks at about 500°C. The exothermic event involves the disappearance of $-\text{C}{\equiv}\text{N}$ as judged by the ir spectrum, so that cyclization is believed to occur followed by elimination of nitrogen as networks of graphitic-like structures form. In this respect the carbonization and graphitization is similar to that hypotheszed for poly(acrylonitrile) (PAN) fiber[48] carbonization and also to recent work on carbon films from cyanoacetylene.[49]

(d) Fibers formed from PCN can be converted to carbon fibers by heat treatment and compared favorably with those prepared commercially from PAN or pitch.

(e) Carbon fibers made from PCN thermalization contain significant amounts (3%) of nitrogen when heat treated to 1800°C, at which point they show a metallic temperature dependence of their conductivity.

(f) PCN can form complexes with metals such as Ta, Nb, Al, Cu, etc. Complexes of $-\text{C}{\equiv}\text{N}-$ containing polymers with metal salts have been previously reported.[50,51]

3. Metallic carbon fibers derived from PCN at 1800°C

PCN fibers heat treated to 1800°C are metallic. Since this result is so unusual, we are currently in the midst of a detailed evaluation of the properties of fibers produced under these conditions. We have prepared some fibers that show a metallic temperature dependence of the conductivity, conductivity increasing continuously from room temperature to 77 K by a factor of 1.2. We have prepared other fibers which show a weakly activated temperature dependent conductivity down to about 10 K (⟨.0004 eV⟩) followed by an *increase* in conductivity with decreasing temperature down to 1.2 K.

Such low temperature increases in conductivity have been previously observed in some benzene derived graphite fibers heat treated to 2900°C and in graphite whiskers, where the onset of the metallic-like dependence is at about 100 K.[52] These authors interpret the high temperature resistivity as being dominated by phonon scattering, whereas at low temperature, impurity and defect scattering affects the conductivity. They argue that such behaviour is an indication of a high degree of ordering of the graphite.

A metallic temperature dependent conductivity is usually only seen in carbon fibers which are processed at temperatures close to 3000°C. For example, recently Yashujima *et al.*[53] reported that poly(phenyleneoxadiazole) derived fibers showed a metallic-like temperature dependence at low temperature, but only when heat treated to 2800°C or above. Therefore it seems most plausible to suspect that the presence of nitrogen in our PCN samples processed at 1800°C may be responsible for their unique behaviour. To the best of our knowledge, there are no theoretical analyses of the anticipated behaviour of a nitrogen rich graphite with which to compare our preliminary results.

4. Carbon-metal composites derived from PCN[54]

Carbon fibers have very desirable thermal and mechanical stability, and can be fabricated into continuous filaments. Such properties would clearly be desirable in a superconductor or in a metal-carbon composite. To this end, carbon fibers coated by chemical vapor deposition with niobium carbonitride (NbCN) films have been studied extensively because the fiber substrate allows processing while the NbCN has desirable superconducting properties (18.2 K transition, high critical field parameter).[55] Since PCN complexes with transition metals, we realized we had a route to composite carbon fibers with transition metals and/or transition metal carbides by the decomposition of PCN-metal complexes.

In a typical experiment, $TaCl_5$ or $NbCl_5$ is dissolved in the concentration range of a few % to 25% by weight of polymer in a concentrated solution of the polymer (~30–40% by weight) in dimethylformamide. The solution is simply stirred at room temperature for a short period of time, usually 2–3 hours. Fibers of these transition metal-polymer complexes are handdrawn from the viscous solution with the tip of a glass rod. In this manner, fibers of a few inches to two feet in length can be easily prepared with a typical cross section of 10–50 μm.

The fibers are heated in an inert gas stream in stages to 700°C. After this initial heating, they are transferred to a vacuum induction furnace and heated to 1800°C to complete the graphitization process. What results from this process are graphitic fibers showing room temperature conductivities of the order of 3000 $S\ cm^{-1}$. X-ray powder diffraction shows a clear match to TaC as well as a graphite peak. Scanning electronic microscopic investigation showed that the fibers are uniform and dense.

Table II gives data on the electronic conductivity, activation energy, and superconducting transition temperature T_c of several TaC-C fibers. Figure 3 is a plot of the resistivity vs. temperature through the superconducting transition with and without the application of a magnetic field of 2.0 KG normal to the fiber axis for two samples prepared by heating PCN fibers in contact with Ta. One of the two samples was tilted slightly with respect to the normal axis, and the critical field shows a dependence on orientation indicating the anisotropic character of the samples. The residual resistivity is $\sim 10^{-10}\Omega cm$, and the width of the transition is ~0.4 K. Thus, we have demonstrated the concept of creating carbon-metal composites via thermal processing for the case of carbon-tantalum carbide and carbon-

TABLE II

Properties of TaC-C Composite Fibers as a Function of Ta Content

Ta % by wt	T_c °K	ρ_{RT} Ωcm × 10^4	Ea eV
30[a]	9.8 − 10	3.0	−0.004
22	5.5 − 5.8	9.6	0.004
6	3.8 − 4	4.0	0.0005
2.5	1.2 − 2	2.8	0.0001

[a] These samples were prepared by heating PCN fibers in contact with Ta for 24 hours at 700° prior to heating the fibers to 1800°.

niobium carbide in the form of fibers. These fibers show normal state metallic conductivity and superconductive states whose transition temperature depends on the TaC or NbC concentration. Because of the abundance of nitrile ligands and lone pair nitrogen atoms in the backbone, it is anticipated that PCN will be quite versatile in forming other metal complexes as well.

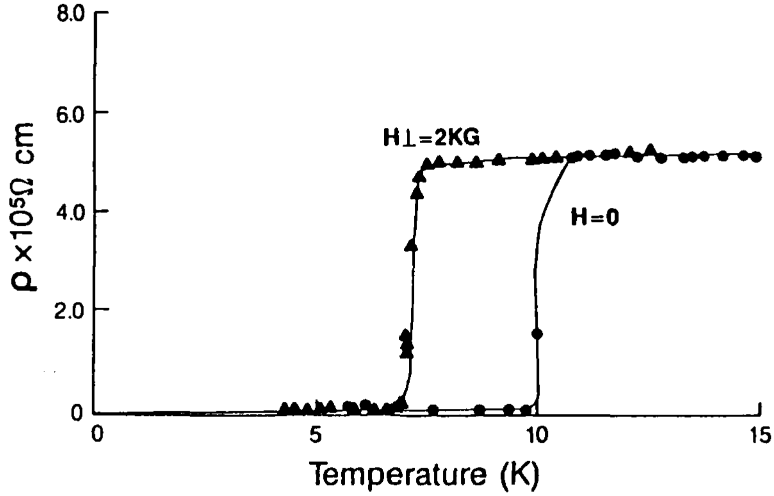


FIGURE 3 Resistivity of two samples of TaC-C fibers in the superconducting region with and without application of a 2 KG magnetic field perpendicular to the fiber axis.

CONCLUDING REMARKS

$(SN)_x$ remains the only example of an intrinsic polymeric metal. $(CN)_x$ is an interesting polymeric system, but the ladder polymeric structure, predicted to be a metal, has not yet been prepared. The linear homopolymer of cyanogen does afford interesting routes to metallic carbons and metallic and superconducting carbon-metal composites. The high temperature solid state chemistry leading to graphitic structures is an area of exploration that may produce a wide variety of highly stable, highly conducting materials.

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