have shown that this method yields negligible contact resistance and highly accurate conductivity values.[5]

The measured composite membrane resistance (R_m) is given by

$$R_m = R_{s1} + R_{pf} + R_{s2} \tag{1}$$

where the R_s's are the resistances of the thin polyheterocyclic surface layers, and R_{pf} is the parallel sum of the resistances of the polyheterocyclic fibers that run through the membrane. It is easy to show that R_{s1} and R_{s2} are much smaller than R_{pf}.[6] Furthermore, since the number of fibers in the membrane is known,[7] the conductivity of a single fiber can be calculated from R_m.

Figure 2 shows the effect of fiber diameter on conductivity along the fiber axis. The widest fibers investigated have conductivities roughly equivalent to those of conventional, electrochemically synthesized PP and PMT (10–100 ohm^{-1} cm^{-1}).[1b,c] Conductivity increases gradually with decreasing fiber diameter for fibers with diameters of hundreds of nm (Figure 2). Conductivity increases dramatically when the fiber diameter approaches mesoscopic values (i.e., tens of nm^2). The conductivities of the 30-nm diameter fibers are over an order of magnitude higher than the conductivities of the conventional polymers.[1b,c]

Alignment of the polymer chains (by stretching) has been shown to enhance conductivities in conductive polymers.[8] We propose that synthesis in the confined space of the mesoscopic pore causes the polymer chains to align along the pore axis. This alignment causes the conductivity along the axis to be higher than in conventional (nonaligned) films. We are currently conducting electron diffraction experiments on the mesoscopic fibers to see if experimental evidence for alignment can be obtained.

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Registry No. PP, 30604-81-0; PMT, 84928-92-7.

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(5) Conductivity values for homogeneous PP films were obtained by using this method and the more conventional four-point method; identical values were obtained. The four-point method cannot be used on these ultranarrow fibers.

(6) The surface layers are less than 200 nm thick and cover 100% of the surface area; the fibers are 10 μm long and occupy 1% (or less) of the surface area. Furthermore, for several membranes, we measured the resistance, scraped off the surface layers, and then remeasured the resistance; R_m values with and without the surface layers were identical.

(7) Determined electron microscopically, see: Cheng, I. F.; Whiteley, L. D.; Martin, C. R. *Anal. Chem.* **1989**, *61*, 762. Another question arises—does conductive polymer grow through the bulk of the host membrane? To answer this question, we attempted the heterogeneous synthesis on membranes, identical to Nuclepore, but without pores. Conductive polymer did not form in these, chemically identical, nonporous membrane.

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Conductive Polymer Bronzes. Intercalated Polyaniline in V_2O_5 Xerogels

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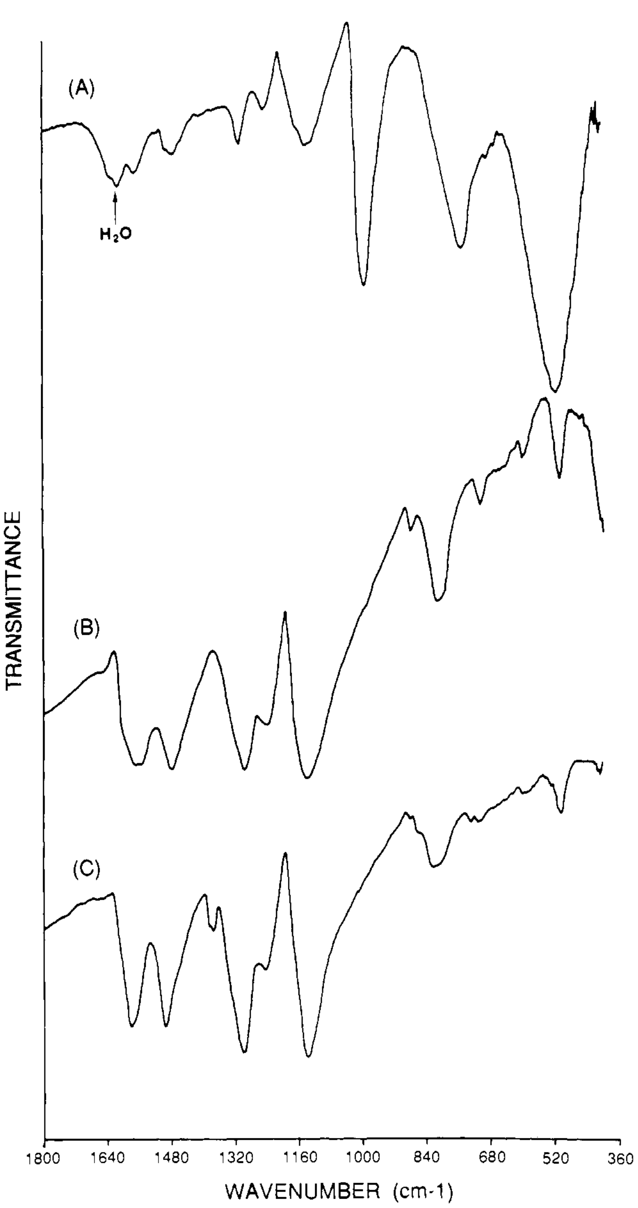

Figure 1. FT-IR spectra of (A) $(C_6H_4NH)_{0.44}V_2O_5 \cdot 0.5H_2O$ (I) (The bands occurring below 1000 cm^{-1} are due to the V_2O_5 framework.); (B) authentic sample of polyaniline hydrochloride as prepared chemically by a literature procedure;[15c] and (C) material isolated by dissolving the V_2O_5 framework in 2% aqueous NaOH and then acidified with HCl. Similar spectra were obtained upon dissolution of I with aqueous HCl. Samples were run as KBr pellets.

It is well-known that organic molecules such as aniline, pyrrole, and thiophene yield, upon chemical or electrochemical oxidation, technologically promising, robust, electrically conductive polymers.[1,2] Progress in elucidating the real structure of these materials is hampered by their invariably amorphous nature.[3] Furthermore, owing to their limited processability, even oriented specimens for important anisotropic studies are rare or lacking. In this communication we report the successful in situ intercalation/polymerization of aniline in layered $V_2O_5 \cdot nH_2O$ xerogels[4,5]

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(1) (a) Electrical and Magnetic Properties of Low Dimensional Solids; Gillespie, R. J., Day, P., eds.; Proceedings of a Royal Society Discussion Meeting, The Royal Society: London, 1986. (b) See, for example: Proceedings of the Conference on Electronic Processes in Conducting Polymers; Vadstena, Sweden, August 1986 [*Synth. Met.* **1987**, *21*]. (c) Marks, T. J. *Science* **1985**, *227*, 881–889.

(2) (a) For a recent review of the field, see: Proceedings of the International Conference on Science and Technology of Synthetic Metals (*ICSM'88*); Aldissi, M. Ed.; *Synth. Met.* **1989**, *27–29*, references therein. (b) Handbook of Conductive Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol 1 and 2.

(3) Delabouglise D.; Garreau, R.; Lemaire, M.; Roncali, J. *New J. Chem.* **1988**, *12*, 155–161.

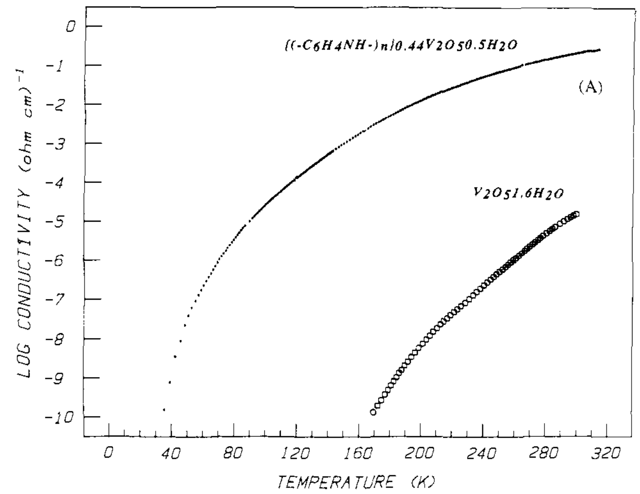
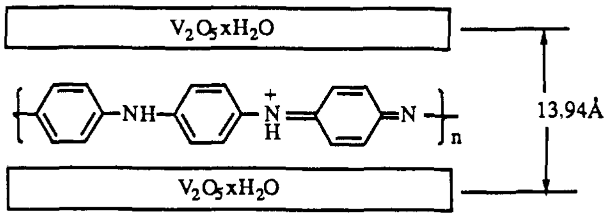


Figure 2. Four probe variable temperature electrical conductivity data of free standing films of $(C_6H_4NH)_{0.44}V_2O_5{\cdot}0.5H_2O$ (I) and pristine $V_2O_5{\cdot}1.6H_2O$ xerogel.

Chart I



to yield films of a novel, conducting polymer/oxide bronze, a layered, molecular composite.[6] It is demonstrated here for the first time that the redox intercalation of aniline results in the conductive protonated form of polyaniline. It should be noted that pyrrole and 2,2′-bithiophene were shown earlier to intercalatively polymerize in FeOCl.[7]

The reaction of aniline with films of $V_2O_5{\cdot}nH_2O$[8] is slow; however, on swelling with water, rapid color change from dark red to bluish black occurs followed by the appearance of metallic luster. The reaction proceeds at room temperature and yields a free standing quasi-flexible film, which after thorough washings with acetone, analyzes for $(C_6H_4NH)_{0.44}V_2O_5{\cdot}nH_2O$, (I). This is a redox reaction in which the aniline monomer is oxidatively polymerized, and the V_2O_5 layers are reduced generating V^{4+} centers. X-ray diffraction experiments reveal that the layered nature of the V_2O_5 matrix in this material is preserved. Seven (00*l*) reflections are observed, corresponding to a new interlayer spacing of 13.94 (1) Å.[9,10] The observed 2.39 Å net layer expansion represents the removal of one water layer (ca. 2.8 Å) from the intralamellar space followed by the insertion of a monolayer of polyaniline.[11] Thus the contribution of the guest species to the interlayer distance in I is 5.19 Å, comparable to that found in $(\text{pyridine})_{0.50}TaS_2$. In the latter, pyridine and pyridinium ions are intercalated with their C_2 axis parallel to the TaS_2 slabs.[12,13] A similar model can be advanced for I as shown in Chart I. Consistent with this model, the (00*l*) reflection is the most intense in the X-ray diffraction pattern. Additional support for this model derives from the corresponding intercalation compound with 2,5-dimethylaniline for which a larger interlayer spacing is observed at 14.57 (1) Å. Infrared spectroscopy of I clearly shows polyaniline and no evidence of anilinium ion or free aniline (see Figure 1). The intercalated polyaniline can be isolated from I by dissolving the V_2O_5 skeleton either in 20% HCl or 2% NaOH solutions and unequivocally identified by its infrared spectrum.[14] Such infrared spectral identification of the various polyaniline forms has been used extensively in the literature and shown to be valid and straightforward.[15]

Consistent with the presence of the protonated (conductive) form of polyaniline intercalated in the $V_2O_5{\cdot}nH_2O$ xerogel are the electrical transport studies on free standing films of I, which show a dramatic increase in conductivity by four orders of magnitude with respect to pristine xerogel with a room temperature value of $\sim 0.5\ \Omega^{-1}\ \text{cm}^{-1}$. Variable temperature measurements (from 5 to 300 K) show a corresponding decrease in conductivity with falling temperature, characteristic of thermally activated behavior, Figure 2. This behavior is similar to that observed for the protonated polyaniline polymer.[16] Variable temperature thermoelectric power measurements agree with corresponding data on protonated polyaniline and suggest the presence of a metallic density of states. The Seebeck coefficient, S, is relatively small $\sim -30\ \mu V/\text{deg}$ and negative. As T decreases, S decreases toward zero, consistent with expectations of metal-like n-type conductivity. Although analogous thermoelectric power data on pristine $V_2O_5{\cdot}xH_2O$ xerogels could not be measured due to their high resistivity, studies on their electrical properties by Livage et al. have shown that they are semiconducting with features typical of thermally activated small polaron transport.[17]

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(8) (a) $V_2O_5{\cdot}nH_2O$ xerogels are prepared by ambient temperature drying of gels formed from the polycondensation of vanadic acid. This polycondensation occurs spontaneously in freshly prepared solutions of vanadic acid with a concurrent increase in viscosity which eventuates in a sol-gel transition. The dried gels exemplify an extreme and dramatic type of layer faulting in which successive layers are displaced and rotated parallel but otherwise more or less randomly with respect to each other. This is termed a random layer or turbostatic structure. Interlayer spacing: 11.55 Å. (b) Lemerle, J.; Nejem, L.; Lefebvre, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 17–20.

(9) (a) Scanning electron microscopy (SEM) of free standing films of I show a smooth, continuous, and homogeneous surface morphology with no evidence of what might be interrreted as phase separation. (b) Thermal gravimetric analysis (TGA) experiments under flowing argon show that after an initial loss of water a thermally resistant component exists with no appreciable volatility up to 250 °C.

(10) As in the pristine xerogel no (*hkl*) or (*hk*0) reflections are observed in I, confirming the random orientation of the V_2O_5 slabs perpendicular to the stacking axis.[4a,8a]

(11) This aqueous monolayer amounts approximately to 1 equiv of H_2O and contributes 2.8 Å to the interlayer spacing of the pristine xerogel. The residual H_2O in I is probably interspersed with polyaniline in the V_2O_5 intralamellar space, being either hydrogen bonded to layer oxygen atoms or coordinated to $V^{5+/4+}$ centers.

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(13) The $(\text{pyridine})_{0.30}V_2O_5{\cdot}H_2O$ has been reported to contain intercalated pyridinium ions with a similar interlayer spacing of 13.0 Å. (b) Ruitz-Hitzky, E.; Casal, B. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1597–1604.

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The intercalation reaction reported here using layered $V_2O_5{\cdot}nH_2O$ xerogels is general. We have produced stable free standing films containing a variety of other important conducting polymers such as polypyrrole, polythiophene, and their derivatives.[18] It should be noted that this class of materials can be viewed not only as conducting polymer intercalation compounds but also as bronzes. I could be characterized as a *polymer bronze* by analogy to alkali metal[19] or molecular[5d,e] bronzes. It is conceivable that in molecular scale organic/inorganic composites the otherwise independent band structures of each component can interact/overlap, thus giving rise to a new set of properties not possible from either component separately.[20] They may provide theoretical models for oriented polymers and also be of potential value for uses as electrode materials. Work on the characterization and development of these materials is underway.

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[20] This point has been raised previously by Peter Day who attempted to prepare such materials via photopolymerization of appropriate intercalated monomers. The resulting materials however were nonconductive. See: Day, P. in ref 1, pp 117–131, and ref 6.

The Preparation of Large Semiconductor Clusters via the Pyrolysis of a Molecular Precursor

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The systematic preparation of nanometer size semiconductor clusters represents a significant challenge to synthesis chemistry. Recent efforts have included aqueous arrested precipitation,[1] organic[2] and inorganic[3] polymer-stabilized arrested precipitation, and precipitation in organized media such as zeolites,[4] lipid membranes,[5] vesicles,[6] and micelles.[7] Since molecular precursors have been used to prepare bulk solid-state compounds,[8] it seemed reasonable that the solution-phase thermolysis of the appropriate precursors would be an independent synthesis route to large clusters. In this communication we describe the preparation of nanometer-sized clusters of CdSe starting from either $Cd(SePh)_2$, **1**, or $[Cd(SePh)_2]_2[Et_2PCH_2CH_2PEt_2]$, **2**, we report the molecular structure of **2**, and we show that the mild solid-state pyrolysis of

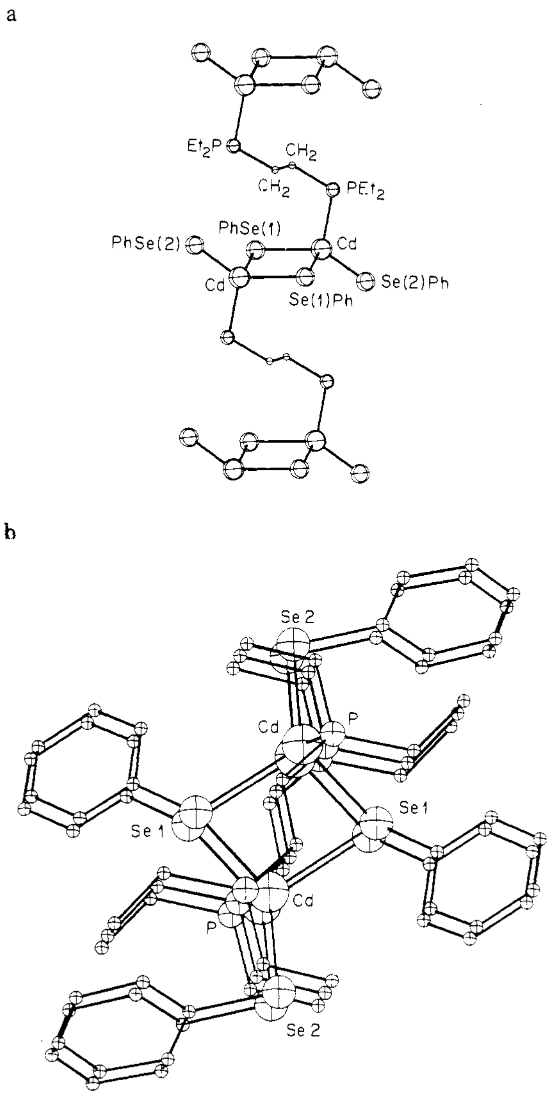

Figure 1. (a) ORTEP drawing of the backbone of $[Cd(SePh)_2]_2$-$[Et_2PCH_2CH_2PEt_2]$, with the phenyl and ethyl groups removed for clarity. Significant distances are as follows: Cd–Se(1), 2.735 (3) Å; Cd–Se(1a), 2.678 (3) Å; Cd–Se(2), 2.564 (3) Å; Cd–P, 2.582 (7) Å. Significant angles are as follows: Cd–Se(1)–Cd, 83.55 (9)°; Se(1)–Cd–Se(1a), 96.45 (10)°; Se(1)–Cd–Se(2), 114.02 (11)°; Se(1)–Cd–P, 99.59 (17)°; Cd–Se(1)–C(Ph), 104.2 (7)°; Cd–Se(2)–C(Ph), 97.5(7)°. (b) View of the polymer down the *c*-axis, illustrating the stacking of the Cd_2Se_2 cores.

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