Communications to the Editor

Insertion of Poly(*p*-phenylenevinylene) in Layered MoO_3

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Poly(*p*-phenylenevinylene) (PPV) is one of a class of conjugated polymers which displays high electronic conductivity[1] and a large nonlinear optical susceptibility.[2] These properties are both highly dependent on the degree of polymer orientation and can be enhanced by orders of magnitude by alignment of the chains.[2,3] Efforts to induce orientation in conductive polymers have included polymerizing the monomers in dimensionally confined crystalline organic matrices.[4] PPV cnanot be introduced by this route, since the monomer does not undergo oxidative polymerization. It is prepared from a water-soluble polyelectrolyte precursor, which has been exploited to incorporate the polymer in amorphous glasses by sol-gel methods.[5]

Here, we report on the insertion of high molecular weight PPV into a layered oxide by intercalating the PPV precursor polymer between the layers of MoO_3 by ion exchange and converting it to PPV in situ. The resultant PPV-MoO_3 material has a high electronic conductivity. The method can also induce polymer chain alignment in the host through a guest-host template effect, since the precursor and the reduced molybdenum oxide sheets have opposite charges.

Preparation of the precursor to PPV, poly(*p*-xylylene-α-dimethylsulfonium chloride) **1**, gave an ionomer with an estimated M_w of 10^5 Da.[1] Reaction of aqueous ionomer solutions with colloidal dispersions of 0.5 wt % $[A(H_2O)_2]_{0.25}MoO_3$ (A = Na, Li)[6,7] in water yielded a material **2**, which analyzed as $[(C_8H_7)(S(CH_3)_2)_{0.75}]_{0.31}(H_2O)_{0.2}MoO_3$.[8] An $S(CH_3)_2/C_8H_7$ ratio below 1.0 indicates that partial elimination has occurred, which also occurs in the processing of PPV under these conditions (vide infra).[1] The 10 (0*k*0) reflections in the XRD pattern of a thin film of **2** (Figure 1) showed that a well-ordered material is obtained with an interlayer spacing of 13.3 Å. This is an increase of 6.4 over that of pristine MoO_3, in good agreement with the estimated dimensions of the phenyl ring of the polymer.[9,10] Therefore, the polymer chains are oriented with the aromatic ring plane perpendicular to the oxide sheets. FT-IR spectroscopy of **2** confirmed the presence of partially eliminated polymer **1** in the oxide lattice. Ionomer bands were observed at 2924, 2854, and 554 cm^{-1}, in addition to peaks at 3024 and 964 cm^{-1} characteristic of the conjugated form of PPV[11] and strong MoO_3 absorptions at 984 and 588 cm^{-1}. The intercalated ionomer could also be isolated by dissolving away the oxide lattice with acid. The FT-IR spectrum of this material showed the same bands (indicative of the ionomer and partially eliminated ionomer) as did the intercalated material and was identical to that of the ionomer itself processed under similar conditions.

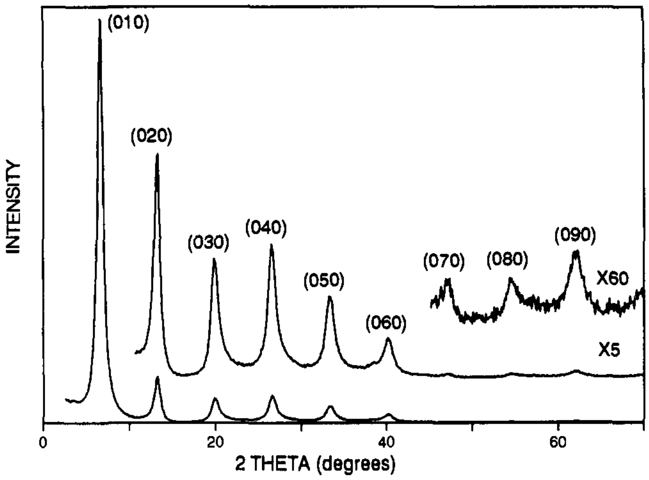

Figure 1. X-ray diffraction pattern (Cu Kα radiation) of an oriented film of **2**, $[(C_8H_7)(S(CH_3)_2)_{0.75}]_{0.31}(H_2O)_{0.2}MoO_3$. The intensity has been expanded by factors of 5 and 60 in the upper traces.

The ionomer is converted to PPV by heating (100-250 °C) to eliminate HCl and $S(CH_3)_2$.[12] Thermal treatment of thin films of **2** at 260-280 °C (air or N_2) decreased the interlayer spacing to 12.5 Å (Δd = 5.6 Å), consistent with loss of $S(CH_3)_2$ from the ionomer and interlayer H_2O. FT-IR spectra of the polymer in the heated films (**3**) were obtained by dissolution of the MoO_3 matrix, as above. The substantially complete conversion to PPV is evident[13] from the almost complete disappearance of bands characteristic of the ionomer at 1425, 1314, and 1053 cm^{-1} and retention of the PPV bands at 962 (strong; trans-CH out-of-plane bending mode)[11] and 3024 cm^{-1}.

XPS spectra of thin films of **3** (heated at 270 °C for 2 h in air, followed by treatment at 200 °C, 10^{-3} Torr, 6 h) provided clear evidence for the formation of PPV in the lattice. These showed no evidence of any residual sulfur.[14] The S_{2s} peak was, however, observed in films of **2** at a binding energy of 166.0 eV, consistent with the $S(CH_3)_2^+$ group on the ionomer.[15] The C_{1s} high-resolution XPS spectrum of **3** (heated for 2 h in N_2) showed a complex

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[8] Anal. Calcd for $[(C_8H_7)(S(CH_3)_2)_{0.75}]_{0.31}(H_2O)_{0.2}MoO_3$: C, 18.46; H, 2.37; S, 3.85; Mo, 48.91. Found: C, 17.95; H, 1.75; S, 3.61; Mo, 47.25 (dried at 50 °C overnight).

[9] This is comparable to the Δd = 5.19 Å observed for $[\text{polyaniline}]_{0.44}V_2O_5$, for which the same chain orientation has been proposed.[4]

[10] We find that the insertion of the corresponding monomer, *p*-xylylenebis(dimethylsulfonium) dichloride gives an interlayer expansion of 6.3 Å.

[11] Bradley, D. D. C.; Friend, R. H.; Linderberger, H.; Roth, S. *Polymer* **1986**, *27*, 1709. FT-IR spectra of the heated films **3** were difficult to obtain due to the high IR reflectivity of these materials.

[12] The elimination reaction is complex. Most $S(CH_3)_2$ eliminates at about 115 °C; at 250 °C, only 2.5 wt % sulfur is reported to remain in PPV films.[1] We note that the conductivity of p-doped PPV reaches its maximum limit at 180 °C (see ref 1).

[13] In addition: (1) Pyrolysis mass spectra (up to 290 °C) identify H_2O and $S(CH_3)_2$ as the evolved products. No species with $m/e > 63$ were detected, thus ruling out the possibility of formation of $S(CH_3)_2O$ (via deoxygenation of the MoO_3 lattice). (2) TGA and DTA traces of **2** were very similar to that of the ionomer alone[1] and showed weight loss attributable to H_2O and $S(CH_3)_2$ in two very broad steps between 100 and 230 °C.

[14] The elimination of sulfur from thin films and small samples is virtually complete, as shown by XPS depth-profiling analysis (down to 500 Å) and the TGA data which showed approximately stoichiometric loss of $S(CH_3)_2$.

[15] $S(CH_3)_3I$ at 165.7 eV: Lindberg, B. J.; Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *1*, 277.

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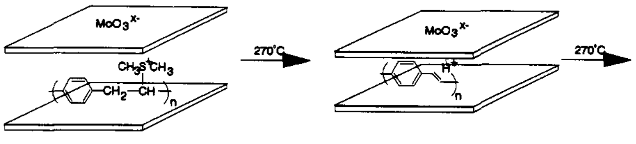
Scheme I



line shape. The spectrum was fit with three Gaussian peaks: B1 (78%) at 284.6 eV, B2 (16%) at 285.5 eV, and B3 (6%) at 287.1 eV. The first two bands are the same as those reported for pristine PPV.[16,17] The band at 287.1 eV has been attributed to electron-deficient sites on the chain created when the polymer is p-doped. The spectrum is identical to that obtained for PPV lightly p-doped either by electrochemical oxidation or with AsF_5.[16,17] We observed the same C_{1s} spectrum from **3** heat-treated in air, although in this case a fourth band was also visible at still higher binding energy (288.1 eV, 4% of the total intensity) which we ascribe to partial oxidation of the polymer chain.

Two (and four-probe) dc conductivity measurements on thin films of **3** revealed an increase in room-temperature conductivity (to $\sim$0.5 S cm^{-1}) of more than 1 order of magnitude greater than the alkali molybdenum oxide, $Na_{0.25}MoO_3$, and 2 orders of magnitude greater than similarly treated monomer-intercalated MoO_3.[10,18] Variable-temperature conductivity data show thermally activated charge-transport behavior characteristic of a semiconductor. Our data indicates that the increase in conductivity observed in the PPV–MoO_3 films does *not* arise from deoxygenation of the MoO_3 lattice.[19]

These data are consistent with the formation of p-doped PPV within the oxide layers. PPV is an insulator ($\sigma = 10^{-13}$ S cm^{-1}) and, hence, cannot directly increase the conductivity of the composite material. Conductivities for p-doped PPV films (e.g., with AsF_5), however, can exceed 10^3 S cm^{-1}.[1,3] We have proposed a series of events that *may* occur during the formation of PPV (Scheme I). Ion exchange, followed by mild heat treatment, initially forms $[HPPV]_xMoO_3$, in which the H^+ is probably coordinated to the MoO_3 lattice, but could also interact with the conjugated PPV chain. If H_xMoO_3 were formed, it would convert to MoO_3 at 150 °C by the evolution of H_2 (air) or to $MoO_{3-x/2}$ by the evolution of H_2O (vacuum, N_2).[20] This could not give rise to the observed conductivity: MoO_3 is an insulator, and we have determined the conductivity of substoichiometric $MoO_{3-x/2}$ to be $\sigma = 10^{-5}$ S cm^{-1} at room temperature. The proton could, however, oxidize the polymer chain by removal of an electron (hence forming a radical carbocation site on the PPV chain). This is analogous to p-doping PPV with H_2SO_4, which is known to produce a highly conductive form of the polymer.[1,3]

We have shown that a new type of intercalation reaction is possible, in which high molecular weight ionomers can be inserted between the layers of inorganic oxides by ion exchange. This is distinguishable from an imbibition process.[21] The ionomers enter the interlamellar gap as linear chain molecules to provide interleaved stacks of polymer/oxide which are well-ordered. This has yielded a novel nanocomposite of PPV and MoO_3 that is not obtainable by in situ polymerization.

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Supplementary Material Available: XPS spectra, FT-IR spectra, X-ray diffraction patterns, and conductivity data for **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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(18) The latter measurements were performed on thin films heat-treated under conditions identical to **3**, except for the ionomer-intercalated MoO_3 which was heated at 50 °C.

(19) XPS measurements on thin films of **2**, **3**, and Na_xMoO_3 all showed an O/Mo ratio of close to 3, and Mo_{3d} high-resolution spectra showed no significant difference in the Mo(V)/Mo(VI) ratio. If deoxygenation was responsible for the increased conductivity, we would also have expected it to occur in monomer-intercalated MoO_3.

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Synthesis of Reactive Homoleptic Tellurolates of Zirconium and Hafnium and Their Conversion to Terminal Tellurides: A Model for the First Step in a Molecule-to-Solid Transformation

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Compounds incorporating elements from groups 12 and 16 (so-called II–VI materials) are increasingly important due to their remarkable electronic properties.[1-13] The use of molecular species as precursors to these materials is particularly appealing,[14] since the products may be prepared in a variety of forms, including nanoclusters, thin films, and bulk solids; however, little is known of the pathway involved in the molecule-to-solid transformation.[15] The metal chalcogenolate starting materials are known to decompose to chalcogenides as in eq 1 (where M = Zn, Cd, Hg; E = S, Se, Te; and R = aryl, alkyl).

$$[M(ER)_2]_n \rightarrow [ME]_n + nER_2 \qquad (1)$$

We sought to monitor the progress of elimination reactions of this general type by using well-defined soluble model compounds. Here we report studies of homoleptic tellurolate derivatives of early transition metals where preliminary evidence suggests that these complexes undergo similar elimination reactions in the solid state. Analogous reactivity is also observed in homogeneous solution; in this case, however, we have been able to isolate and fully characterize the presumed M=Te intermediates. This chalcogenolate-to-chalcogenide transformation may be viewed as a homogeneous model for the first step in the thermal decomposition of a molecular compound to a solid-state material.

Using the synthetically versatile, sterically demanding $^{-}TeSi(SiMe_3)_3$ ("sitel") ligand, we prepared the brightly colored hom-

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