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Topotactic Polymerization of Aniline in Layered Uranyl Phosphate

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Recently, we reported that conjugated polymers[1] such as polyaniline (PANI), polypyrrole, and polythiophene can be formed *in situ* by oxidative intercalation of their corresponding monomers in oxidizing layered hosts such as V_2O_5 xerogel[2] and FeOCl.[3] This chemistry is applicable provided the host material is sufficiently oxidizing to initiate the intercalative polymerization. In order to expand this field to other ordered host materials which have limited redox properties, we must find the proper conditions under which intercalated monomers can be polymerized, not necessarily by the host, but by external power.[4–6] Eventually, we hope to build up a general methodology to produce conjugated polymers in layered or spatially confined environments. In this communication, we report the successful polymerization of aniline in the galleries of uranyl phosphate using ambient oxygen.

Hydrogen uranyl phosphate $HUO_2PO_4\cdot 4H_2O$ (HUP) is a bright yellow layered material with an interlayer distance of 8.69 Å.[7] The layers consist of dumbell-shaped UO_2^+ ions with the uranium further coordinated by four equatorial oxygen atoms of four PO_4^{3-} tetrahedra forming two-dimensional sheets as shown in Figure 1. The galleries contain two water layers, hydrogen bonded to each other. The H^+ atoms in the galleries can be exchanged with cations or neutralized with bases. For example, HUP reacts with excess aniline in water to form a pale-yellow $(C_6H_5NH_3)UO_2PO_4\cdot 0.5H_2O$ (AUP) intercalation compound with an interlayer spacing of 10.46 Å.

Heating AUP in air at 130 °C results in a dramatic color change to black. FT-IR spectroscopy shows that the peaks due to anilinium ions gradually weaken and disappear and intense new broad peaks develop characteristic of PANI; see Figure 2. This solid-state conversion is complete in 3 weeks. The black crystalline product analyzes as $(PANI)_{0.94}UO_2PO_4\cdot 0.4H_2O$ (PUP) with an increased interlayer distance of 11.8 Å measured from the X-ray diffraction pattern shown in Figure 3. Scanning electron microscope (SEM) images, see Figure 4, show the platelike morphology of the host crystallites with no amorphous impurities. On the basis of the X-ray and FT-IR spectroscopic data, the structure of the host remains intact. By simple dissolution of the host layers of uranyl phosphate with excess 20% HCl, a black organic product is obtained which is PANI[8] on the basis of its FT-IR absorption spectrum. No shift is observed between the infrared frequencies of PUP and the extracted PANI salt. The presence of the 1576-cm^{-1} absorption indicates the existence of quinoid rings in the polymer.[9] However, a detailed examination of the infrared spectrum shows that the shape and frequency of each absorption are similar but not identical to those of bulk

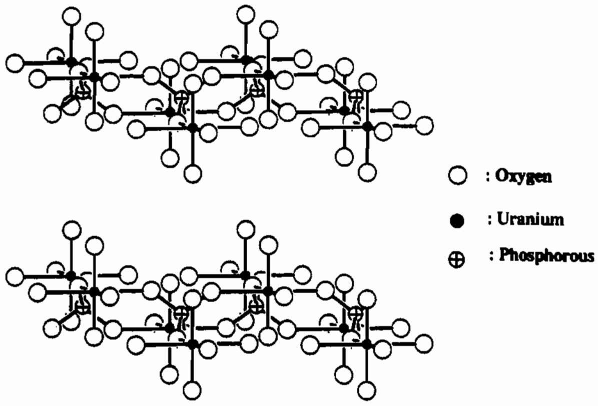

Figure 1. Structure of $HUO_2PO_4\cdot 4H_2O$.

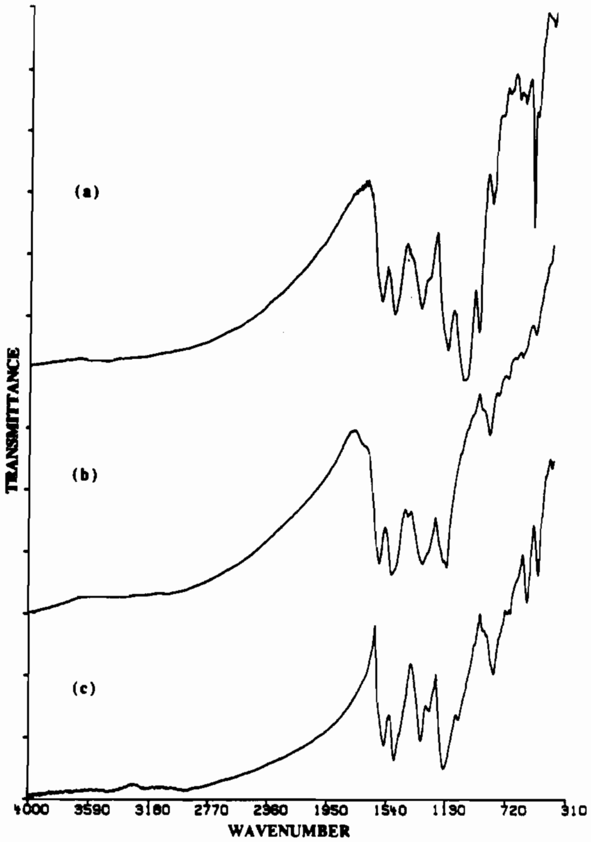

Figure 2. Infrared spectra (KBr) of (a) $(PANI)_{0.94}UO_2PO_4\cdot 0.4H_2O$, (b) extracted polyaniline salt, and (c) chemically synthesized polyaniline salt.

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(1) (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vols. 1 and 2. (b) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans.* **1986,** *82,* 2385. (c) Kanatzidis, M. G. *Chem. Eng. News* **1990,** *68,* 36.

(2) (a) Kanatzidis, M. G.; Wu, C.-G.; Marcy, H. O.; Kannewurf, C. R. *J. Am. Chem. Soc.* **1989,** *111,* 4139. (b) Wu, C.-G.; Kanatzidis, M. G.; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R. *Polym. Mater. Sci. Eng.* **1989,** *61,* 969. (c) Kanatzidis, M. G.; Wu, C.-G.; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R. *Chem. Mater.* **1990,** *2,* 222.

(3) (a) Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J. *J. Am. Chem. Soc.* **1987,** *109,* 3797. (b) Kanatzidis, M. G.; Wu, C.-G.; Marcy, H. O.; Kannewurf, C. R. *Adv. Mater.* **1990,** *2,* 364.

(4) Enzel, P.; Bein, T. *J. Phys. Chem.* **1989,** *93,* 6270–6272.

(5) (a) Day, P.; Ledsham, R. D. *Mol. Cryst. Liq. Cryst.* **1982,** *86,* 163–174. (b) Tieke, B. *Mol. Cryst. Liq. Cryst.* **1983,** *93,* 119–145.

(6) (a) Pillion, J. E.; Thompson, M. E. *Chem. Mater.* **1991,** *3,* 777. (b) Enzel, P.; Bein, T. *Chem. Mater.* **1992,** *4,* 819.

(7) (a) Morosin, B. *Phys. Lett.* **1978,** *65A,* 53. (b) Shilton, M. G.; Howe, A. T. *J. Solid State Chem.* **1980,** *34,* 137. (c) Lloyd, M. H.; Bischoff, K.; Peng, K.; Nissen, H. U.; Wessicken, R. *J. Inorg. Nucl. Chem.* **1976,** *38,* 1141.

(8) (a) MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W.-S.; Mu, S.-L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985,** *121,* 173. (b) Snauwaert, P.; Lazzaroni, R.; Riga, J.; Verbist, J. J. *Synth. Met.* **1987,** *21,* 181.

(9) (a) Ohsaka, T.; Ohnuki, Y.; Oyama, N. *J. Electroanal. Chem.* **1984,** *161,* 399. (b) Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T.; Kawagoe, T. *Macromolecules* **1988,** *21,* 1297. (c) Harada, I.; Furukawa, Y.; Ueda, F. *Synth. Met.* **1989,** *29,* E303.

0020-1669/93/1332-2989$04.00/0

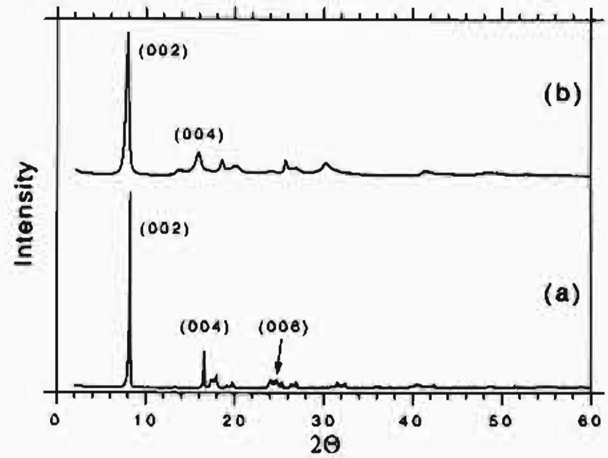

Figure 3. X-ray diffraction pattern of (a) $(C_6H_5NH_3)UO_2PO_4{\cdot}0.5H_2O$ and (b) $(PANI)_{0.94}UO_2PO_4{\cdot}0.4H_2O$.

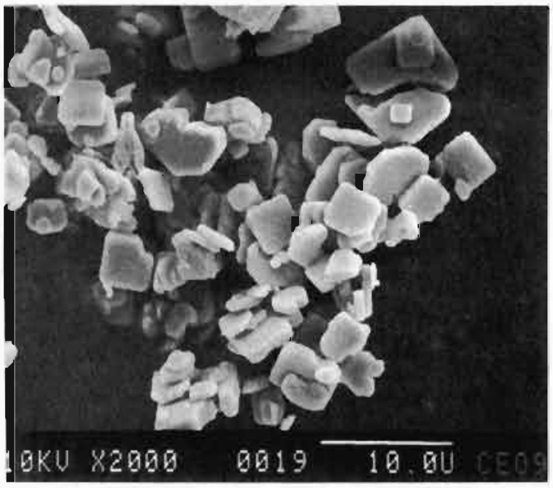

Figure 4. Scanning electron microscope photograph of crystallites of $(PANI)_{0.94}UO_2PO_4{\cdot}0.4H_2O$.

PANI.[10] These small but significant spectroscopic differences may be due to a small degree of crossing-linking of the polymer in the galleries. Any cross-linking probably occurs because of the relatively elevated temperature (130 °C) of the solid-state polymerization. A cross-linked version of PANI was observed earlier after thermal treatment of bulk PANI, and it is presumed to be a significant new member in the PANI family[11] with a two-dimensional structure. The electronic spectrum shows a broad absorption band ~800 nm which continues into the IR, similar to emeraldine salt.[12]

The diamagnetic uranyl phosphate host allows observation of the strong polaron signal of PANI by electron paramagnetic resonance spectroscopy. At 24 °C PUP shows a single sharp peak with a g value close to the free electron value ($g = 2.0023$) and 10-G peak width which is slightly broader than the reported value for bulk PANI ($\Delta H_{pp} \leq 3$ G).[13] Magnetic susceptibilities of AUP and PUP were measured as a function of temperature and are shown in Figure 5. As the reaction progresses, the diamagnetic AUP gradually becomes paramagnetic PUP due to the increasing amount of PANI in the galleries. The data for PUP slightly deviate from the Curie–Weiss law, which is attributed to the existence of temperature-independent Pauli susceptibility.[14]

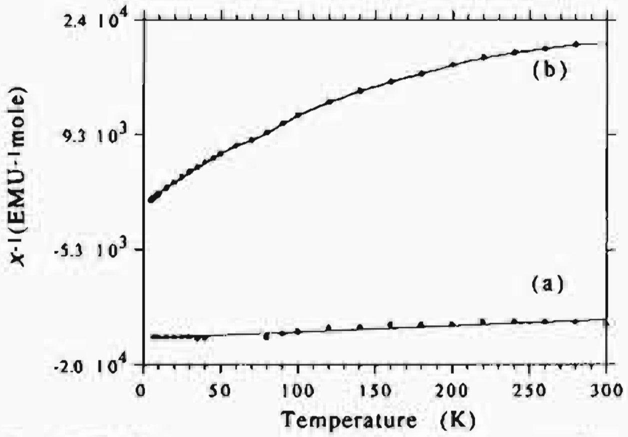

Figure 5. Variable-temperature magnetic susceptibility data of (a) $(C_6H_5NH_3)UO_2PO_4{\cdot}0.5H_2O$ and (b) $(PANI)_{0.94}UO_2PO_4{\cdot}0.4H_2O$. The data of PUP have been corrected for diamagnetic contributions.

The thermal gravimetric analysis of PUP in air reveals three major weight loss processes, one below 100 °C, attributed to loss of water, a second beginning from about 250 °C up to 450 °C, and a third starting at 600 °C. The latter two weight-loss steps are assigned respectively to PANI decomposition and conversion to $(UO_2)_2(P_2O_7)$.[15]

PANI obtained from PUP is partially (~50%) soluble in *N*-methyl-2-pyrrolidinone (NMP). Molecular weight studies using gel permeation chromatography (GPC)[16] on the soluble fraction show one elution band whose maximum corresponds to a molecular weight of 5000 ($M_w/M_n = 1.5$). The MW is much lower than that obtained for bulk PANI[11c,17] (~80 000) and it reflects the fact that the PANI was formed in a structurally and kinetically confined environment.

Pressed pellets of PUP show no measurable conductivity ($<10^{-10}$ S/cm). This behavior is similar to that of the PANI/zeolite system[4] in which the conjugated polymer is embedded in an insulating three-dimensional host and cannot be accessed electrically. Isolated from PUP, the polymer has a room-temperature conductivity of 10^{-5} S/cm, consistent with the presence of cross-linking.[18]

The use of oxygen is key to the polymerization of anilinium. Other oxidants such as $(NH_4)_2S_2O_8$, $FeCl_3$, and H_2O_2 yield polyaniline outside the HUP host as determined by X-ray diffraction and SEM examination. We believe the reason for the successful polymerization of anilinium in the galleries of HUP

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(10) (a) Observed vibrations of extracted polyaniline: 1576, 1492, 1280, 1118, and 815 cm^{-1}. (b) The vibrations of polyaniline salt prepared chemically by $(NH_4)_2S_2O_8$ are as follows: 1560, 1481, 1292, 1109, 797 cm^{-1}.

(11) (a) Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth. Met.* **1991**, *41–43*, 765. (b) Rodrigue, D.; Snauwaert, P.; Demaret, X.; Riga, J.; Verbist, J. J. *Synth. Met.* **1991**, *41–43*, 769. (c) Scherr, E. M.; MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Tang, X.; Druy, M. A.; Glatkowski, P. J.; Cajipe, V. B.; Fischer, J. E.; Crorhack, K. R.; Jozefowicz, M. E.; Ginder, J. M.; McCall, R. P.; Epstein, A. J. *Synth. Met.* **1991**, *41–43*, 735. (d) Epstein, A. J.; MacDiarmid, A. G. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Ed.; Plenum Press: New York, 1990; pp 303–315.

(12) (a) Ohira, M.; Sakai, T.; Takeuchi, M.; Kobayashi, Y.; Tsuji, M. *Synth. Met.* **1987**, *18*, 347. (b) Bloor, D.; Monkman, A. *Synth. Met.* **1987**, *21*, 175. (c) Epstein, A. J.; MacDiarmid, A. G. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 165–173.

(13) (a) Salaneck, W. R.; Liedberg, B.; Inganas, O.; Erlandsson, R.; Lundstrom, I.; MacDiarmid, A. G.; Halpern, M.; Somasiri, N. L. D. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 191. (b) Javadi, H. H. S.; Laversanne, R.; Epstein, A. J.; Kohli, R. K.; Scherr, E. M.; MacDiarmid, A. G. *Synth. Met.* **1989**, *29*, E439.

(14) (a) MacDiarmid, A. G.; Chiang, J.-C.; Richter, A. F.; Epstein, A. J. *Synth. Met.* **1987**, *18*, 285. (b) Epstein, A. J.; Ginder, J. M.; Zuo, F.; Bigelow, R. W.; Woo, H.-S.; Tanner, D. B.; Richter, A. F.; Huang, W.-S.; MacDiarmid, A. G. *Synth. Met.* **1987**, *18*, 303. (c) Genies, E. M.; Boyle, A.; Lapkowski, M..; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139.

(15) (a) Pekarek, V.; Benesova, M. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1743. (b) Pekarek, V.; Vesely, V. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1151.

(16) A Shimadzu LC-10A HPLC system with a PLgel 5 μm mix column was used. The MW was measured at 75 °C by using NMP (containing 0.5 wt % LiCl) as an eluent. The elution rate was 0.2 mL/min. Polystyrene of known molecular weights was used as a standard.

(17) (a) Abe, M.; Ohtani, A.; Umemoto, Y.; Akizuki, S.; Ezoe, M.; Higuvhi, H.; Nakamoto, K.; Okuno, A.; Noda, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1736. (b) Genies, E. M.; Noël, P. *Synth. Met.* **1992**, *46*, 285.

(18) Genies, E. M.; Lapkowski, M.; Penneau, J. F. *J. Electroanal. Chem.* **1988**, *249*, 97.

by oxygen is kinetic and related to gallery access by oxygen and the mobility of anilinium ions. While oxygen gas can diffuse through the AUP and oxidize anilinium ions, larger, solvated oxidants such as $(NH_4)_2S_2O_8$, $FeCl_3$, etc. cannot. Instead, ion-exchange (e.g. NH_4^+, H_3O^+) is more favorable, which releases anilinium in solution to be polymerized outside of the host. Other aniline derivatives have also been intercalated into HUP such as *o*-toluidine, *o*-ethylaniline, 4-aminobiphenyl, etc. Surprisingly, none of them could be polymerized by O_2 at 130 °C or higher temperature. The investigation of other metal phosphate layered materials is in progress.[19]

In summary, we have shown that O_2 uniquely provides a valuable method to polymerize aniline inside nonoxidizing host materials. In addition, compared to other familiar oxidants, O_2 has the advantage of providing a clean reaction environment since the byproduct is either H_2O or H_2O_2, which escapes as gas at the reaction temperature. Thus, the ion-exchange problem associated with $(NH_4)_2S_2O_8$ is avoided. Disadvantages are higher temperature and longer reaction times which can lead to thermal degradation of the polymers.[20] Therefore, the polymerization must occur at optimum temperature to minimize the thermal decomposition. Lower polymerization temperatures may be possible by using ozone instead of oxygen.

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(19) Liu, Y.-J.; Kanatzidis, M. G. Unpublished results.

(20) (a) Kulkarni, V. G.; Campbell, L. D.; Mathew, W. R. *Synth. Met.* **1989**, *30*, 321. (b) Hagiwara, T.; Yamaura, M.; Iwata, K. *Synth. Met.* **1988**, *25*, 243.