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Intercalative Polymerization of 3-Methyl- and 3,4-Dimethylpyrrole in the $VOPO_4$ Interlayer Space

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Finely powdered $VOPO_4 \cdot 2H_2O$ suspended in an ethanol solution containing 3-methyl- or 3,4-dimethylpyrrole leads to the intercalative polymerization of these pyrrole derivatives through the 2,5-coupling to yield $VOPO_4 \cdot (H_2O)_{1.4} \cdot (EtOH)_{0.2} \cdot (MeC_4HNH)_{0.65}$ and $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (Me_2C_4NH)_{0.6}$. The similar treatment of $VOPO_4 \cdot 2H_2O$ with pyrrole affords polypyrrole only on the $VOPO_4$ surface.

Pyrrole, thiophene, and aniline are well known to afford electrically conducting polymers by chemical or electrochemical oxidation.1,2) Although the conducting polymers are extensively studied for applications, their micro structures, such as chain conformation, packing, and cross-linking, have not been well clarified and remain uncontrolled. To elucidate their low-dimensional structures, polymerizations of pyrrole and aniline within restricted spaces of layered inorganic solids seem to be useful. However, polymerization in the interlayer spaces is difficult, generally polymers being formed on the surface of the layered solids to cover them. Only a few intercalative polymerizations of pyrrole, aniline, and bithiophene using layered $FeOCl$3,4) and $V_2O_5 \cdot nH_2O$,5,6) were reported, where factors necessary for the polymerization in layered spaces remained unclarified. Here we report intercalation/polymerization of 3-methyl- (3-Mepyrr) and 3,4-dimethylpyrrole (3,4-Me_2pyrr) in the $VOPO_4$-interlayer and compare it with the polymerization of pyrrole (Pyrr) which occurs only on the surface of $VOPO_4 \cdot 2H_2O$ solids, demonstrating an important role of β-methyl groups on the pyrrole ring for the intercalative polymerization process.

Finely powdered $VOPO_4 \cdot 2H_2O$7) suspended in an ethanol solution of 3-Mepyrr or 3,4-Me_2pyrr8) was stirred at 30 °C for 48 h to yield solid compounds analyzed as $VOPO_4 \cdot (H_2O)_{1.4} \cdot (EtOH)_{0.2} \cdot (MeC_4HNH)_{0.65}$ (1) and $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (Me_2C_4NH)_{0.6}$ (2). A similar reaction of suspended powders of $VOPO_4 \cdot 2H_2O$ with Pyrr in ethanol gave a solid compound analyzed as $VOPO_4\cdot(H_2O)_{1.8}\cdot(EtOH)_{0.2}\cdot(C_4H_2\text{-}NH)_{0.6}$ (3).[9)]

The reactions proceed in the redox process in which 3-Mepyrr and 3,4-Me_2pyrr are oxidized, followed by polymerization, and the $VOPO_4$ moiety is reduced producing the V(IV) sites. Both the compounds gave a broad, approximately isotropic powder ESR signal due to the V(IV) state (g = 1.96, the peak-to-peak linewidth = 9.9 and 14.1 mT for **1** and **2**, respectively). In accordance with this, a peak due to the $2p_{3/2}$ electrons of V(IV) nuclei was observed at 516.8 eV in the X-ray photoelectron spectra (XPS). X-Ray diffraction (XRD) measurements revealed that the layered structure of the $VOPO_4$ matrix is preserved in these compounds. The (001) and (200) reflections were clearly observed, which correspond to increased interlayer spacings of 12.3 and 13.8 Å along the *c*-axis for **1** and **2**, respectively. The observed net layer-expansion of 8.7 and 9.7 Å from layered anhydrous $VOPO_4$ (4.1 Å)[10)] suggests inserted monolayers of poly-3-Mepyrr and poly-3,4-Me_2pyrr ordering their molecular planes approximately perpendicular to the $VOPO_4$ layer. These arrangements are compatible with that of poly-Pyrr found for $FeOCl\cdot(\text{poly-Pyrr})_{0.34}$.[3)] The IR spectra of **1** and **2** show the formation of poly-3-Mepyrr and poly-3,4-Me_2pyrr and no evidence of free 3-Mepyrr and 3,4-Me_2pyrr, as illustrated in Fig. 1-a for **2**. The intercalated poly-3-Mepyrr and poly-3,4-Me_2pyrr can be isolated from **1** and **2** by dissolving the $VOPO_4$ framework into a 1 mol dm^{-3} NaOH aqueous solution, followed by the treatment of the solid by an excess HCl solution. The IR spectra of the compounds are very close to those of poly-3-Mepyrr and poly-3,4-Me_2pyrr prepared by oxidation of 3-Mepyrr and 3,4-Me_2pyrr through the Fe(III) ion in H_2O-toluene,[11)] as shown in Fig. 1-b and c for **2**. The similar reaction of Pyrr with finely powdered $VOPO_4\cdot2H_2O$ in ethanol in the suspended

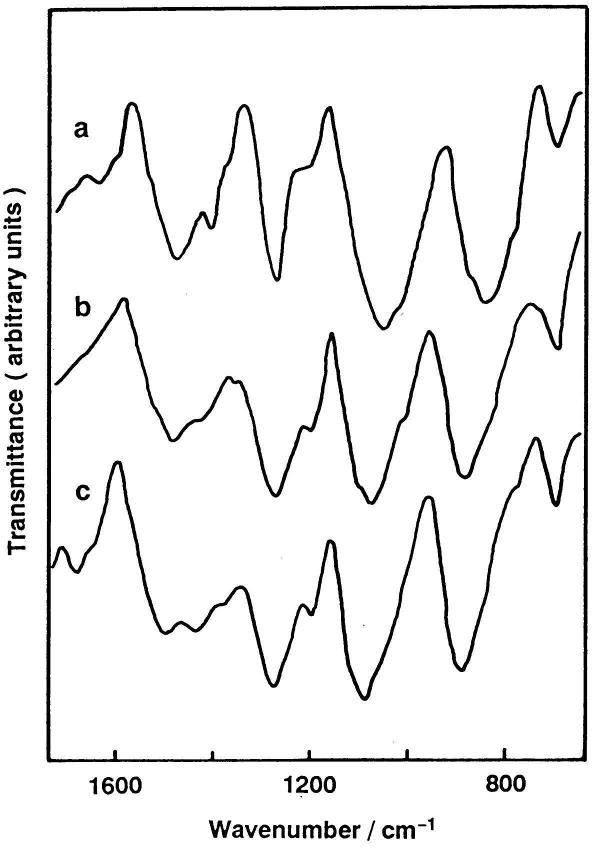

Fig. 1. IR spectra of (**a**) $VOPO_4\cdot(H_2O)_{1.8}\cdot(EtOH)_{0.2}\cdot(Me_2C_4NH)_{0.6}$ (**2**), (**b**) poly-3,4-Me_2pyrr prepared chemically by the literature method,[11)] and (**c**) solids isolated by dissolving the $VOPO_4$ moiety of **2** in a 1 mol dm^{-3} NaOH aqueous solution, followed by the HCl-treatment. Samples were measured in KBr disks.

condition afforded poly-Pyrr which has been identified by the IR spectrum. However, the $VOPO_4$ interlayer spacing determined from XRD was 6.5 Å. This finding suggests that no intercalation of the poly-Pyrr fragments occurs into the $VOPO_4$ framework, the polymer being on the surface of the $VOPO_4$ moiety.

Figure 2 shows the differential thermal analysis (DTA) curves of $VOPO_4 \cdot 2H_2O$, compounds **2** and **3**. The curve for $VOPO_4 \cdot 2H_2O$ indicates the release of two kinds of water molecules with the raise of temperature, while a broad DTA peak for **2** suggests the presence of water molecules which are released from the coordination to the vanadium ion owing to the intercalation of the polymer and located probably through hydrogen-bond in the $VOPO_4$ interlayer space. This is also the same for **1**. The curve for **3** also indicates the clear release of a water molecule at high temperature, which confirms that the interlayer space contains no polymer, but only water and a small amount of ethanol molecules.

3,4-Me_2pyrr is oxidized by the V(V) ion and polymerized only through the 2,5-coupling, resulting in a linear polymer which can intercalate into the restricted $VOPO_4$ interlayer space. The line shape of the XPS peak of carbon 1s electrons observed for **2** is rather symmetric, as illustrated in Fig. 3. On the other hand, the C 1s XPS peak of **3** shows a considerably broad structure at a higher energy side. This asymmetry

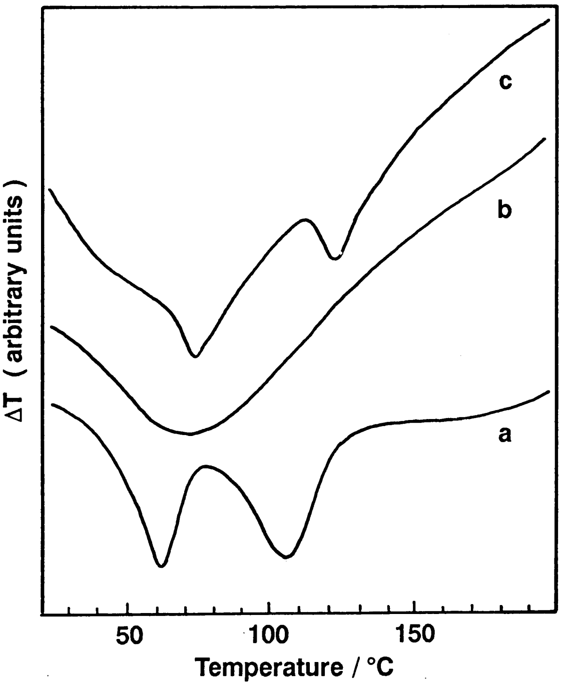

Fig. 2. DTA curves of (**a**) $VOPO_4 \cdot 2H_2O$, (**b**) $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (Me_2C_4NH)_{0.6}$ (**2**), and (**c**) $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (C_4H_2NH)_{0.6}$ (**3**).

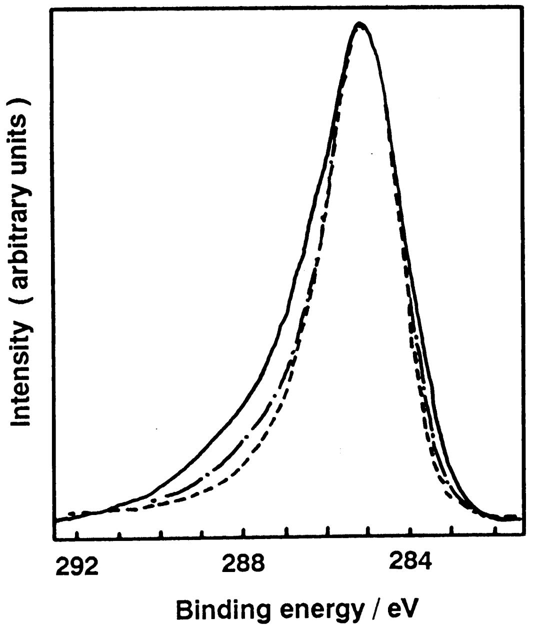

Fig. 3. C 1s XPS peaks of the polymers included in the $VOPO_4$ moieties: $VOPO_4 \cdot (H_2O)_{1.4} \cdot (EtOH)_{0.2} \cdot (MeC_4HNH)_{0.65}$ (**1**) (—·—·), $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (Me_2C_4NH)_{0.6}$ (**2**) (-------) and $VOPO_4 \cdot (H_2O)_{1.8} \cdot (EtOH)_{0.2} \cdot (C_4H_2NH)_{0.6}$ (**3**)(———).

on the higher energy side is ascribed to cross-linked or chain-terminating carbons as well as carbons in partially saturated ring.[12,13] In the polymerization of Pyrr, the 2,3-coupling was reported to occur as well as the 2,5-coupling.[12,13] This may result in the cross-linked structure of poly-Pyrr to afford broader C 1s XPS peaks. Branched, nonlinear configurations of poly-Pyrr formed on the surface of the $VOPO_4$ moiety seem to prevent its insertion into the interlayer space. Intercalation of poly-3-Mepyrr into the interlayer suggests the polymerization occurs essentially through the 2,5-coupling as well as that of 3,4-Me_2pyrr. In accordance with this, the broadness of the C 1s XPS peak of **1** is rather close to that of **2**.

Detailed studies on the intercalative polymerization of the pyrrole-derivatives are now in progress.

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9) Anal. **1**, Found: C, 17.96; H, 3.03; N, 3.61%. Calcd for $C_{3.7}H_{7.1}N_{0.65}O_{6.6}PV$: C, 17.70; H, 2.84; N, 3.68%. **2**, Found: C, 19.06; H, 3.82; N, 3.45%. Calcd for $C_{4.0}H_{9.0}N_{0.6}O_{7.0}PV$: C, 18.52; H, 3.50; N, 3.24%. **3**, Found: C,13.72; H, 3.00; N, 3.44%. Calcd for $C_{2.8}H_{6.6}N_{0.6}O_{7.0}PV$: C; 13.86; H, 2.72; N, 3.46%.

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