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Preparation of Polypyrrole from Pyrrole by Using the Catalytic System of $VO(acac)_2$–$AlCl_3$–O_2

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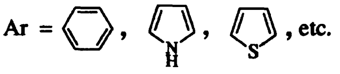
Polypyrrole was prepared by the oxidation of pyrrole with molecular oxygen in the presence of bis(acetylacetonato)(oxo)vanadium(IV) ($VO(acac)_2$) and aluminum chloride ($AlCl_3$) as a catalyst. The polymerization of pyrrole at 20 °C at a mole ratio of $VO(acac)_2/AlCl_3=1/1$ in acetonitrile under 1 atm of oxygen gave polypyrrole, 10^{-2} S cm^{-1} in electrocondutivity in 260% yield on the basis of the catalyst charged. The addition of pyridine to the system improved the electroconductivity of the polypyrrole produced. The reaction mechanism is discussed based on the UV-vis spectra of the reaction mixtures, the ESR spectra of the catalytic system, and the oxygen consumption during polymerization.

Electroconducting polymers have received much attention as a new materials. Many researchers have reported on their chemical[1—12] and electrochemical[12—14] preparation, structure[3,15] and properties[7,9,11] as well as their applications.[11,16—20] Especially, the oxidative polymerization of the corresponding simple monomers by various chemical methods is of great interest from a practical point of view, because chemical methods are quite useful for the mass production of conducting polymers.

Many methods have been developed to prepare conducting polymers from corresponding simple monomers. A typical preparation example is shown below, where high-valent transition metal compounds like iron(III) chloride are used as oxidants of the monomers.[7,8]

$$n\ \text{H-Ar-H} + 2n\ \text{MX}_m \longrightarrow \text{+Ar+}_n + 2n\ \text{M}'\text{X}_{m-1} + 2n\ \text{HX}$$



(1)

Here,

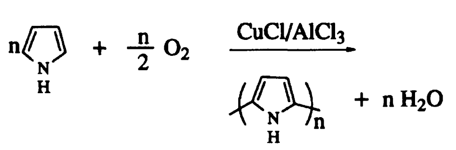
$M = Fe(III), Cu(II), etc.;$

$M' = Fe(II), Cu(I), etc.;$

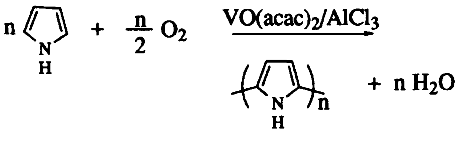
and $X = Cl^-, Br^-, etc.$

These methods have been called "catalytic methods." However, such reactions require the use of twice the molar amount of transition-metal salts as a reagent. It is therefore a great problem to safely dispose of such a large amount of low-valent metal salts, as well as a huge volume of hydrogen halide gas, both of which are by-produced during the reaction. These are the disadvantages of the industrial production of the conducting polymers by conventional chemical methods.

To solve these problems, we have already proposed a novel method for preparing conducting polymers from corresponding simple monomers by using a real catalyst and molecular oxygen as an oxidant.[1] For example, poly(p-phenylene) has been prepared from benzene by the $CuCl$–$AlCl_3$–O_2 catalytic system.[2] In this system, oxygen is consumed as an oxidant of benzene and no hydrogen chloride is produced as a by-product, although the conventional method, using $CuCl_2$ and $AlCl_3$, does produce a huge volume of hydrogen chloride gas as an essential by-product. The $CuCl$–$AlCl_3$–O_2 system is also of great use for producing polypyrrole from pyrrole in acetonitrile (cf. Eq. 2).[3]



(2)



(3)

We presently prepare polypyrrole from pyrrole by using $VO(acac)_2$[21] (Eq. 3) instead of CuCl in the previous system.[3] In a search for optimum preparation conditions, the effects of $AlCl_3$ in the catalytic system, oxygen as an oxidant, and pyridine as an additive, as well as the effect of reaction temperature, have been examined. On the basis of these results as well as the UV-vis and ESR spectra of the catalytic system, the reaction mechanism is briefly discussed.

Experimental

Materials Aluminum chloride was purified by sublimation under a vacuum. Pyrrole was distilled under a vacuum in a nitrogen atmosphere and kept under nitrogen until use. Acetonitrile was kept over a molecular sieve (3A) overnight and then distilled in the presence of blue sodium-benzophenone. All other chemicals waere used as received.

Preparation of Polypyrrole. Typical experiments were carried out as follows: bis(acetylacetonato)-(oxo)vanadium(IV) ($VO(acac)_2$, 1.33 g (5 mmol)) and aluminum chloride ($AlCl_3$, 1.33 g (10 mmol)) were placed in a 50-cm^3 two-necked flask under dry nitrogen. Dry acetonitrile (13 cm^3) was added dropwise into the stirred mixtures. Stirring the mixtures for an hour resulted in a homogenous solution. Into this homogenous acetonitrile solution, pyrrole (1.68 g, 25 mmol) was added dropwise; the mixtures were stirred for an additional 2 h under nitrogen. The reaction was started by exchanging the atmosphere of nitrogen with oxygen while continuing to stir the mixtures. After 24 h of stirring under oxygen at the designed temperature, the reaction mixtures were poured into a 6 mol dm^{-3} hydrogen chloride aqueous solution to stop the reaction. Brownish-black precipitates were collected by filtration, and washed with a 6 mol dm^{-3} HCl aqueous solution, pure water, and then ethanol. The solid product, polypyrrole, was dried under reduced pressure at 80 °C overnight.

Measurements. The electroconductivity of polypyrrole was calculated as the volume resistivity on the basis of data measured by a four-probe method with a Mitsubishi Petrochemical Industry Roresta AP-400 electroconductive meter for compressed-disk samples of 10 mm in diameter and 1 mm in thickness. Ultraviolet and visible (UV-vis) absorption spectra were measured with a Hitachi 220 spectrophotometer for a sample diluted about 20 times from the solution used for the reaction. Electron spin resonance (ESR) spectrum measurements were carried out at room temperature with a JEOL JSE-PE-1X spectrometer for 0.05 cm^3 of the sample solution in a 5 mmϕ quartz tube. The consumption of oxygen was followed based on its volume using a gas burret.

Results and Discussion

Effect of Aluminum Chloride on the Reaction. A dispersed solution of bis(acetylacetonato)(oxo)vanadium (VO(acac)$_2$) and pyrrole in acetonitrile could not form polypyrrole by contact with oxygen at room temperature. However, the addition of aluminum chloride ($AlCl_3$) to the dispersed solution could form a homogeneous solution and produce polypyrrole as brown precipitates in considerably good yield by contact with oxygen. The structure of the produced polypyrrole was confirmed by a comparison of the IR spectrum with that of the authentic polypyrrole, prepared from pyrrole by oxidation with an excess amount of $FeCl_3$,[22] as well as by elemental analyses. When the charged ratio of pyrrole to the VO(acac)$_2$/$AlCl_3$ (1/2) catalyst was changed from 1 to 10, the yield of polypyrrole in an isolated amount increased upon increasing the ratio until 5, was then kept nearly constant. Thus, the VO(acac)$_2$–$AlCl_3$ complex actually works as a catalyst. The catalytic efficiency reaches nearly the maximum at a charged ratio of pyrrole to the vanadium complex of 5. This is probably because the water by-produced in the reaction (Eq. 3) could deactivate the $AlCl_3$ in the catalytic system. From the above results, the charged ratio of pyrrole to the vanadium complex was kept at 5 in all further experiments. The obtained results at various charged ratios of $AlCl_3$ to VO(acac)$_2$ in acetonitrile at 20 °C are summarized in Table 1. The yield of polypyrrole based on the charged pyrrole did not change with increasing the ratio of $AlCl_3$ to VO(acac)$_2$ from 1 to 2, but increased with increasing the ratio from 2 to 3.

In contrast with the above results, the reaction practically proceeded by the addition of only $AlCl_3$ without VO(acac)$_2$. In this case, however, only the addition polymerization product was obtained. The structure was estimated by the composition, calculated from the elemental analysis, as shown in Table 1, and supported by the characteristic IR absorption spectrum. The low electroconductivity of the polymeric product also supports this estimation. Thus, the conductivity has a tendency to decrease with increasing the mole ratio of $AlCl_3$ to VO(acac)$_2$. In elemental analysis, the number of hydrogens per nitrogen also has a tendency to increase with increasing the mole ratio of $AlCl_3$ to VO(acac)$_2$ from 1 to 3. This tendency could be attributed to contamination of the addition polymerization product and to the low molecular weight of the polymeric products obtained at the high mole ratio of $AlCl_3$ to VO(acac)$_2$. The high hydrogen content as well as the low processability could result in a low conductivity of the polymer prepared at a high mole ratio of $AlCl_3$ to VO(acac)$_2$. Although there is a disadvantage in low conductivity, the coexistence of $AlCl_3$ does, in fact, improve the yield of polypyrrole. In other words, $AlCl_3$ can activate the catalytic activity of VO(acac)$_2$ for the polymerization of pyrrole.

In order to investigate the effect of $AlCl_3$ upon VO(acac)$_2$, the UV-vis spectra of the VO(acac)$_2$ solution were measured with and without $AlCl_3$. The results are shown in Fig. 1. The absorption at 590 nm, which is attributed to the d–d transition of the original VO(acac)$_2$, disappears and a new peak at 840 nm appears upon the addition of an equimolar or twice molar amount of $AlCl_3$ to VO(acac)$_2$. Although VO(acac)$_2$, itself, is not very soluble in acetonitrile, the addition of $AlCl_3$ into the dispersion of VO(acac)$_2$ in acetonitrile solubilizes the VO(acac)$_2$, resulting in a clear solution having an absorption peak at 840 nm. This suggests the formation of a new complex of VO(acac)$_2$ due to the coordination of $AlCl_3$. The absorbance at 840 nm was followed by

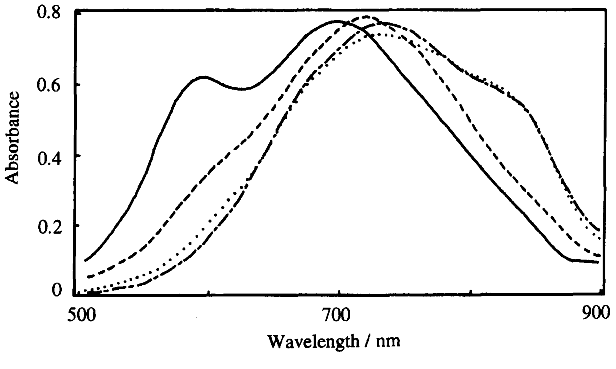
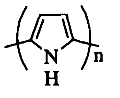


Fig. 1. UV-vis spectra of VO(acac)$_2$ (——), and VO(acac)$_2$–$AlCl_3$ (1 : 1; –·–, 1 : 2; ····, and 1 : 3; - - -) in acetonitrile. [VO(acac)$_2$]$=1.67\times10^{-5}$ mol dm^{-3}.

Table 1. Effect of $AlCl_3$ on the Polymerization of Pyrrole[a)]

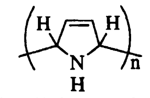
Molar ratio[b)]		Yield[c)]	Composition	Conductivity
$VO(acac)_2$	$AlCl_3$	%		σ/S cm^{-1}
1	0	1.1	—	—
1	1	51.8	$C_{4.07}H_{3.45}NCl_{0.25}O_{0.78}$	2.1×10^{-2}
1	2	49.0	$C_{4.25}H_{3.62}NCl_{0.25}O_{0.39}$	1.2×10^{-4}
1	3	75.7	$C_{4.29}H_{3.64}NCl_{0.30}O_{0.68}$	—
0	1	26.0	$C_{4.72}H_{6.73}NCl_{0.33}O_{0.73}$	$<10^{-10}$

a) Reaction conditions; Temp: 20 °C, Time: 24 h, Solvent: acetonitrile. b) Molar ratio: $VO(acac)_2$: pyrrole=1 : 5. c) Based on pyrrole.



Oxdative polymer

$n = \infty$; C_4H_3N



Additive polymer

$n = \infty$; C_4H_5N

varying the amount of $AlCl_3$ added to the same amount of $VO(acac)_2$ suspended in acetonitrile. The results are illustrated in Fig. 2. The continuous variation results suggest the formation of an $AlCl_3/VO(acac)_2=1/2$ or 1/1 complex. However, the absorption spectrum of the solution of $AlCl_3/VO(acac)_2=1/2$ still has a peak at 590 nm due to the original $VO(acac)_2$ without complexation. The peak at 590 nm can disappear at a ratio of $AlCl_3/VO(acac)_2=1/1$. The addition of a three-times molar amount of $AlCl_3$ makes the peak at 840 nm also fade out. This can probably be attributed to the formation of another complex of $VO(acac)_2$ with three moles of $AlCl_3$. Although the structures of these complexes are not yet obvious, the additon of $AlCl_3$ to $VO(acac)_2$ should form complexes which could increase the yield of polypyrrole. Thus, the complex formation of $VO(acac)_2$ with $AlCl_3$ improved the catalytic activity, resulting in an increase in the yield of polypyrrole.

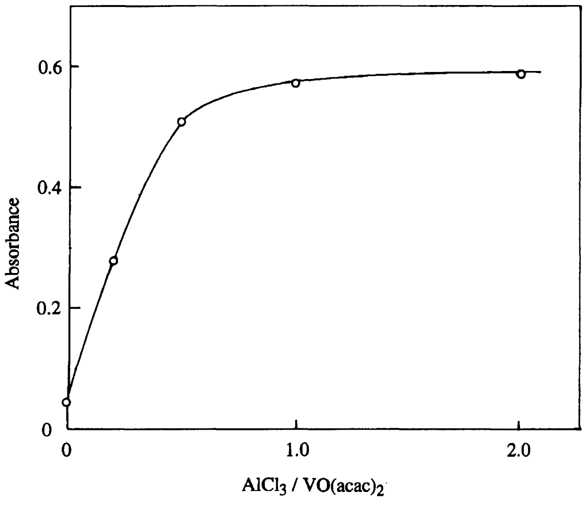


Fig. 2. Change in the absorbance at 840 nm by the addition of $AlCl_3$ into a suspension of $VO(acac)_2$ in acetonitrile. $[VO(acac)_2]=1.67\times10^{-5}$ mol dm^{-3}.

The change in the UV-vis absorption spectra of catalytic systems due to the addition of pyrrole is not so large as that due to the addition of $AlCl_3$, as shown in Figs. 3 and 4. However, $VO(acac)_2$ can be dissolved in acetonitrile by the addition of pyrrole, while $VO(acac)_2$, itself, is only dispersed in acetonitrile. This

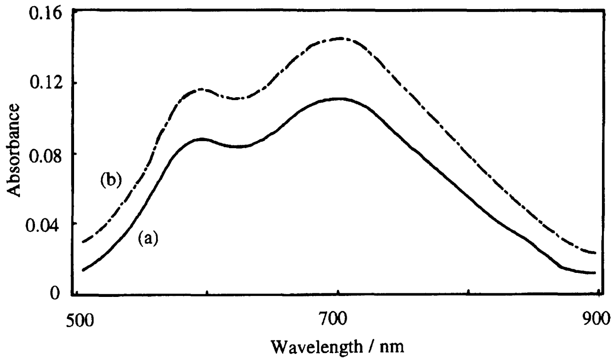


Fig. 3. UV-vis spectra of (a) $VO(acac)_2$, and (b) $VO(acac)_2$–pyrrole in acetonitrile. $[VO(acac)_2]=1.67\times10^{-5}$ mol dm^{-3}, $[\text{pyrrole}]=8.35\times10^{-5}$ mol dm^{-3}.

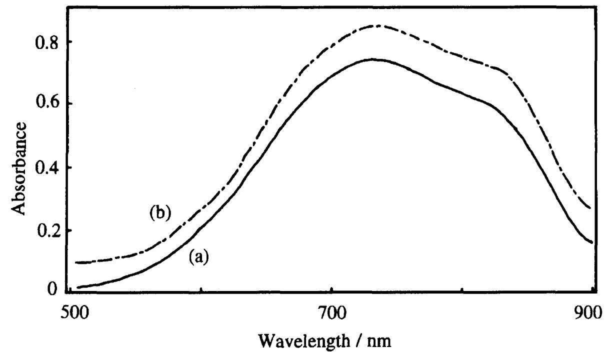


Fig. 4. UV-vis spectra of (a) $VO(acac)_2$–$AlCl_3$ and (b) $VO(acac)_2$–$AlCl_3$–pyrrole in acetonitrile. $[VO(acac)_2]=1.67\times10^{-5}$ mol dm^{-3}, $[AlCl_3]=3.34\times10^{-5}$ mol dm^{-3}, $[\text{pyrrole}]=8.35\times10^{-5}$ mol dm^{-3}.

Table 2. Polymerization of Pyrrole under Various Conditions[a)]

Run	Atmosphere	Temp °C	Additive[b)]	Yield[c)] %	Composition	Conductivity σ/S cm^{-1}
1	O_2	20	None	49.0	$C_{4.25}H_{3.62}NCl_{0.25}O_{0.39}$	1.2×10^{-4}
2	O_2	60	None	128.3	$C_{4.79}H_{3.99}NCl_{0.42}O_{0.61}$	$<10^{-10}$
3	N_2	20	None	60.7	$C_{5.84}H_{7.24}NCl_{0.22}O_{0.80}$	$<10^{-10}$
4	O_2	20	Pyridine	25.1	$C_{4.34}H_{3.70}NCl_{0.30}O_{0.42}$	1.3×10^{-1}

a) Reaction conditions; molar ratio, $VO(acac)_2 : AlCl_3$: pyrrole=1 : 2 : 5, Time, 24 h, Solvent, acetonitrile. b) Molar ratio, $VO(acac)_2 : AlCl_3$: pyridine : pyrrole=1 : 2 : 2 : 5. c) Based on pyrrole charged.

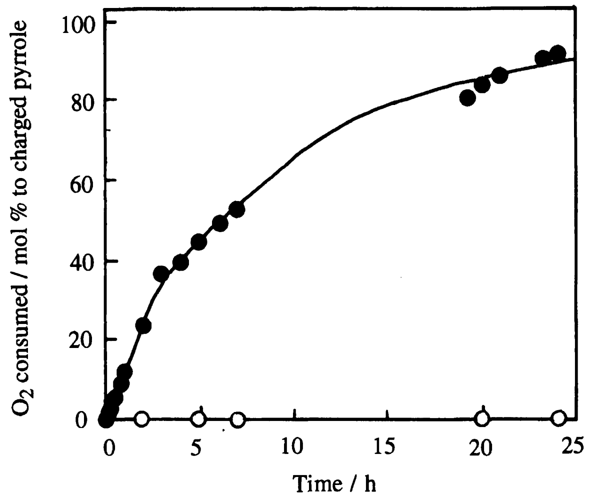


Fig. 5. Plot of oxygen consumption by $VO(acac)_2$–$AlCl_3$ in acetonitrile in the presence (●) and absence (○) of pyrrole. $[VO(acac)_2]=3.85\times10^{-4}$ mol dm^{-3}, $[AlCl_3]=7.70\times10^{-4}$ mol dm^{-3}.

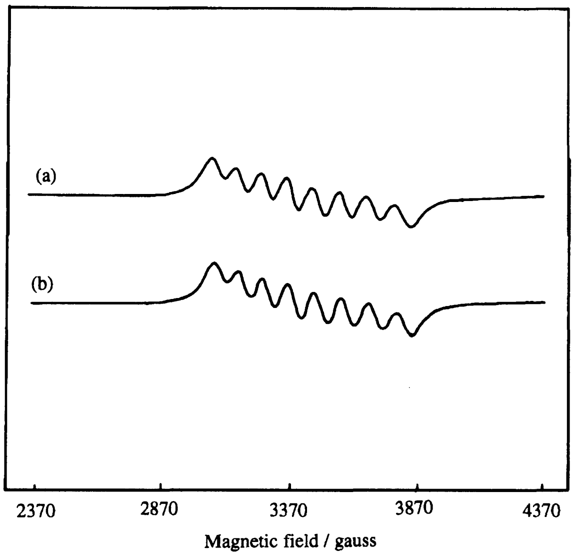


Fig. 6. ESR spectra of $VO(acac)_2$–$AlCl_3$ in acetonitrile under (a) nitrogen, and (b) oxygen. $[VO(acac)_2]=3.85\times10^{-4}$ mol dm^{-3}, $[AlCl_3]=7.70\times10^{-4}$ mol dm^{-3}, P_{N_2} or $P_{O_2}=1$ atm, at room temperature.

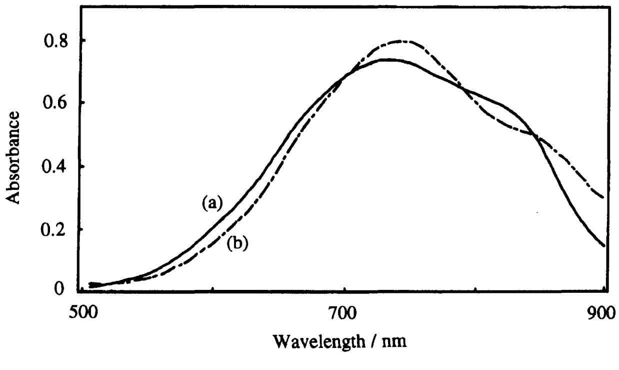


Fig. 7. UV-vis spectra of (a) $VO(acac)_2$–$AlCl_3$, and (b) $VO(acac)_2$–$AlCl_3$–pyridine in acetonitrile. $[VO(acac)_2]=1.67\times10^{-5}$ mol dm^{-3}, $[AlCl_3]=3.34\times10^{-5}$ mol dm^{-3}, [pyridine]$=1.67\times10^{-5}$ mol dm^{-3}.

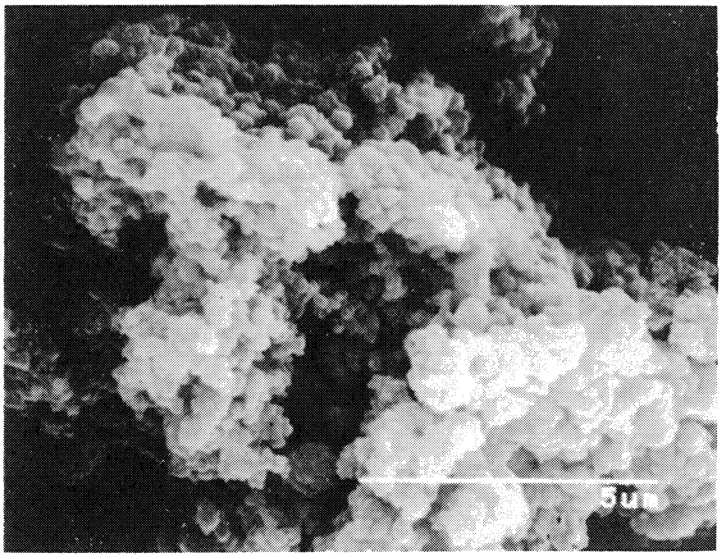
fact suggests the coordination of pyrrole to $VO(acac)_2$, resulting in polymerization of the coordinating pyrrole.

Effect of the Reaction Temperature. The reaction yield of polypyrrole increases with an increase in the reaction temperature from 20 to 60 °C, as shown in Runs 1 and 2 of Table 2. However, the electroconductivity of the polypyrrole produced at 60 °C is much less than that at 20 °C. This is probably due to the shorter π-conjugation of the polypyrrole formed at 60 °C than at 20 °C. Increasing the reaction temperature may promote a side reaction; e.g., substitution at a less-reactive β-position rather than at the reactive α-position of pyrrole, and addition polymerization, rather than oxidative polymerization of pyrrole.

Effect of Oxygen. For preparing polypyrrole from pyrrole in an oxidative reaction, an oxidant is necessary for polymerization. In order to utilize $VO(acac)_2$ as the catalyst for the polymerization of pyrrole, molecular oxygen is necessarily used as the oxidant. If the present reaction was carried out under nitrogen without oxygen, a solid product was obtained. However, the product obtained without oxygen was only that of the addition polymerization of pyrrole, which is obvious from the elemental analysis as well as the electroconductivity, as shown in Run 3 of Table 2. In contrast, the oxidative polymerization of pyrrole took place under oxygen, resulting in hydrogen abstraction from pyrrole and giving polypyrrole with extended π-conjugation.

The consumption of oxygen was followed by volume during the course of time. Without pyrrole, the VO-

(a)



(b)

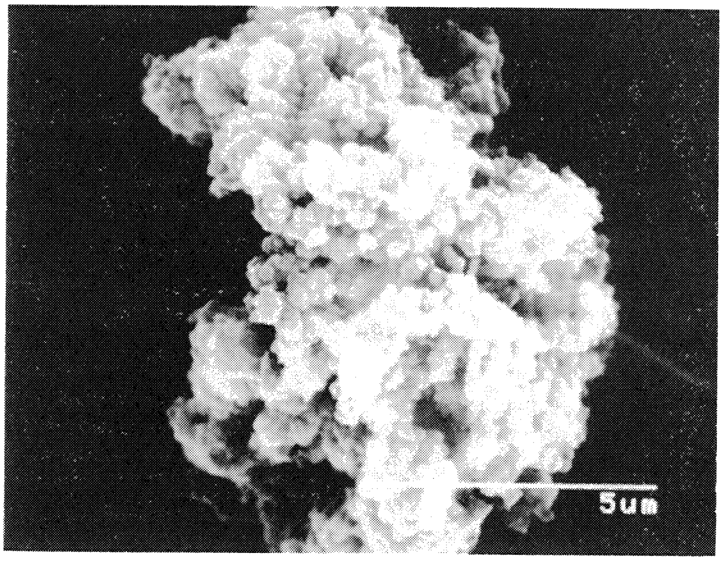


Fig. 8. SEM photographs of polypyrrole produced by (a) VO(acac)$_2$–AlCl$_3$–O$_2$, and (b) VO(acac)$_2$–AlCl$_3$–pyridine–O$_2$ system. [VO(acac)$_2$]=3.85×10^{-4} mol dm^{-3}, [AlCl$_3$]=7.70×10^{-4} mol dm^{-3}, [pyrrole]=1.93×10^{-3} mol dm^{-3}, [pyridine]=3.85×10^{-4} mol dm^{-3}.

(acac)$_2$–AlCl$_3$ system in acetonitrile did not adsorb oxygen at all, which means that VO(acac)$_2$ was not further oxidized. In contrast, the reaction system with pyrrole did adsorb oxygen to produce polypyrrole. The oxygen consumption curve is shown in Fig. 5, where the amount of oxygen consumed was calculated in mole % on the basis of the amount of pyrrole charged. The consumption of oxygen observed, however, was higher than that expected. For example, in the case of AlCl$_3$/VO(acac)$_2$ (2/1), the oxygen consumed in 24 h was about 80% based on the pyrrole monomer charged (Fig. 5), while the isolated yield was 49% (Table 1). The difference is too large, even when considering that some soluble oxidized products could not be isolated. This is probably because some oxygen could be consumed for the further oxidation of polypyrrole. In fact, the IR spectrum of the polypyrrole produced contained a weak peak at 1690 cm^{-1}, thus showing the presence of a carbonyl group. In addition, the polypyrrole produced in the present experiments contains chlorine in addition to the oxygen in the elemental analyses, as shown in Tables 1 and 2. Contaminated chlorine may exist both as chlorine covalently bound to carbon and as the chloride ion as a dopant, which has been the case in polypyrrole prepared by the catalytic oxidative polymerization of pyrrole over the $AlCl_3/CuCl$ catalyst.[3)]

The ESR spectra of vanadium were measrued with and without oxygen, as shown in Fig. 6. Under nitrogen, the reference spectrum (Fig. 6(a)) indicates the presence of the V(IV) species, which does not change upon an exchange of the atmosphere with oxygen (Fig. 6(b)). This again reveals that the vanadium species are not oxidized by oxygen. Thus, oxygen is not used for oxidation of vanadium(IV) species, but for the oxidation of pyrrole.

On the basis of the above-mentioned results, it could be concluded that the oxygen, which is activated by a weak coordination to the vanadium(IV) species, can oxidize the monomeric pyrrole directly to produce polypyrrole, or indirectly oxidize the polymeric addition product of pyrrole to produce ideal polypyrrole with extended conjugation by hydrogen abstraction.

Effect of Pyridine Additive. In the oxidative polymerization of pyrrole by the $CuCl–AlCl_3–O_2$ system, the addition of pyridine has been reported to increase the electroconductivity of the produced polypyrrole by two orders of magnitude.[3)] Therefore, the effect of the addition of pyridine was examined based on the property of the polypyrrole produced in the presence of a $VO(acac)_2–AlCl_3–O_2$ system. Then, the addition of pyridine again increased the electroconductivity of the produced polypyrrole by three orders of magnitude, though decreasing the yield of the polymer. The results are shown in Run 4 of Table 2.

The role of the pyridine additive was investigated by UV-vis absorption spectroscopy in acetonitrile. As shown in Fig. 7, the absorption spectrum of $VO(acac)_2–AlCl_3$ with pyridine is different from that without pyridine, although the difference is not very large. Thus, the pyridine is believed to coordinate to the $VO(acac)_2$. The electroconductivity of polymers is affected not only by the chemical structure of the polymer, but also by the physical structure, such as morphology. In fact, the higher conductivity of the polypyrrole prepared by using a $CuCl–AlCl_3–O_2$ system with the addition of pyridine than that prepared without pyridine has been attributed to the fibrillar morphology. In the present $VO(acac)_2–AlCl_3–O_2$ system, in contrast, a clear difference in the morphology is not observed by SEM photographs between the polymers prepared with and without pyridine, as shown in Fig. 8. However, there is some difference in the compressing processability. Thus, a polymer prepared with pyridine was more easily compressed to form disks for measuring the electroconductivity than that prepared without pyridine.

It could be concluded on the basis of the above observation that the addition of pyridine can delay the reaction rate by decreasing the yield of the polypyrrole, but can produce polypyrrole with extended conjugation and good compressing processability.

Conclusion

The polymerization of pyrrole to produce polypyrrole by using the $VO(acac)_2–AlCl_3–O_2$ system can take place via a complex of $VO(acac)_2$ and $AlCl_3$. In the reaction, pyrrole, which weakly coordinates to the $VO(acac)_2–AlCl_3$ complex, is oxidized by the oxygen to produce polypyrrole directly, or is polymerized to form an oligomeric adduct as an intermediate, which is then oxidzed by the oxygen to produce polypyrrole with extended conjugateion. The addition of pyridine to the present system can increase the electroconductivity of the produced polypyrrole by three orders of magnitude, although no clear effect on the morphology of the polymer can be observed. Thus, the present catalytic system can produce a large amount of polypyrrole by using a small amount of metal salt as a catalyst and a sufficient amount of oxygen as an oxidant, which provides one of the effective methods for the mass-production of electroconductive polypyrrole.

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