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Polymer Effects on Reversible Formation of Dioxygen Adduct with Silver(II) Tetraphenylporphyrin Moieties

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ABSTRACT: The anomalous behavior in the temperature dependence of ESR spectra has been discovered for the powder sample and LB film of poly[5-(acrylamidophenyl)-10,15,20-triphenylporphyrinato]silver(II) (denoted by polyAgAATPP) under oxygen atmosphere. The ESR intensity decreased with the decrease of temperature from room temperature to −150 °C. The IR and Raman spectroscopies at liquid nitrogen temperature revealed that the new IR- and Raman-active peaks appeared at 782 and 545 cm^{-1} for the LB film of polyAgAATPP under oxygen atmosphere, respectively. The peaks were assigned to ν(O−O) and ν(Ag−O) in the dioxygen adduct of polyAgAATPP, respectively. The linkage between AgTPP moieties and dioxygen was likely to be of the bridging type. These phenomena were not observed for monomeric AgAATPP.

Introduction

Synthetic metalloporphyrins have been extensively studied as a model system for biomimetic catalysts and oxygen carriers in a blood. Iron and manganese porphyrin derivatives, for example, have been investigated as artificial enzymes to investigate the functions of P-450.[1−6] Cobalt(II) porphyrins have received considerable attention because of their ability to perform reversible redox reactions.[7−11] Relatively little attention has been paid, however, to the silver complexes of porphyrins despite their potentiality as a catalytic center.

In Kamachi's laboratory, various kinds of vinyl polymers with tetraphenylporphyrin and tetraphenylporphyrinatometal ions in their side chains have been prepared for the purpose of synthesizing photoactive and magnetoactive polymers on the basis of molecular design.[12−21] Their features revealed by ESR and UV−visible spectroscopies and magnetic susceptibility measurements have suggested that the metalloporphyrin moieties bonded to a polymer interact with each other magnetically and electronically.[13−21] In addition, unusual oxygen absorption has been found in the measurements of ESR spectra and magnetic susceptibility of polyacrylates containing (tetraphenylporphytinato)-cobalt(II) in their side chains. Very recently, when we measured the temperature dependence of the ESR spectra of silver(II) complexes of the tetraphenylporphyrin (AgTPP) polymers under oxygen atmosphere, it was found that the signal intensity decreased with a decrease in temperature.[22] When we raised the partial pressure of oxygen, this behavior became more remarkable. The results are notable because the intensity of an ESR signal generally increases on lowering temperature owing to a decrease in spin-relaxation rates or the increased difference in population due to the Boltzmann distribution between the ground and excited spin states. In fact, the monomers of AgTPP exhibited a normal behavior; that is, the signal intensity increased monotonically with a decrease in temperature.

We suspected that a decrease in an ESR signal intensity of AgTPP polymer at low temperature was caused by the formation of an ESR-silent species with dioxygen. The unique behavior of the polymer might be related to the microscopic structures of the polymer in a solid state. It was difficult to validate the above

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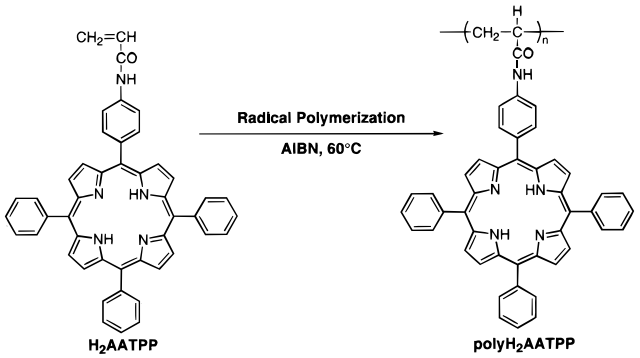
Scheme 1



assumption because of the poor reproducibility of the temperature dependence of the ESR intensity of the solid polymer prepared by reprecipitation from its solution. For understanding the unique behavior of AgTPP polymers, it is necessary to prepare a sample in which the relative distance and orientation of porphyrin moieties were well-defined on a molecular level. One possibility is to prepare the Langmuir−Blodgett (LB) film of AgTPP polymer. We have already reported that it is possible to control the orientation of the porphyrin plane in the LB films of the polymer.[23]

In this report, we present the results on the interaction of dioxygen molecule with the polymer of AgTPP (poly([5-(4-acrylamidophenyl)-10,15,20-triphenylporphyrinato]silver(II) or polyAgAATPP) (Scheme 1). It is intended to clarify the details of the interaction between a Ag(II) ion and O_2 by measuring the ESR, IR, and Raman spectra.

Experimental Section

Synthesis: 5-(4-Acrylamidophenyl)-10,15,20-triphenylporphyrin (H_2AATPP) and its polymer **(polyH_2AATPP)** were prepared according to the literature methods.[24]

[5-(Acrylamidophenyl)-10,15,20-triphenylporphyrinato]silver(II) (AgAATPP). H_2AATPP (0.23 g, 0.34 mmol) and silver(I) acetate (0.17 g, 1.02 mmol) were dissolved in THF. After being refluxed for 11 h, the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was filtered to remove silver(0). The filtrate was washed with water and was dried over anhydrous Na_2SO_4. AgAATPP thus obtained was recrystallized from chloroform−methanol as a reddish purple crystal (64.1 mg, 23.9% yield; mp > 300 °C). The Anal. Calcd for $C_{47}H_{31}N_5$-OAg: C, 71.49; H, 3.96; N, 8.87. Found: C, 71.06; H, 3.94; N, 8.73. FAB-MS: [M] *m/e* 790.3 (calcd (Ag = 107/109) [M] *m/e* 788/790).

Poly[[5-(4-Acrylamidophenyl)-10,15,20-triphenylporphyrinato]silver(II)] (polyAgAATPP) was prepared by introducing a silver(II) ion to the polyH_2AATPP (weight average molecular weight, M_w = 22 500) through the same method as in case of AgAATPP preparation. The reaction time was 45 h. Instead of recrystallization, repeated precipitation was performed from THF−methanol. The weight average molecular weight of the obtained polymer was determined to be M_w = 18 400 with M_w/M_n = 1.9.

Eicosanoic acid ($CH_3(CH_2)_{18}COOH$, Wako Pure Chemical Industries, Ltd.) was recrystallized once from ethanol. $^{18}O_2$ was purchased from Prochem. Chloroform (analytical grade) was used as a spreading solvent for the preparation of LB films. Pure water used as a subphase was purified with a Millipore Milli-Q system.

Preparation of LB Films. LB films were formed at 20 ± 0.5 °C using a USI FSD-110, FSD-23 Langmuir trough (USI, Japan). The trough width was 10 cm. We could not obtain a good LB film of AgAATPP or its polymer because they exhibited a tendency to aggregate each other. Thus we mixed eicosanoic acid with the porphyrin. A chloroform solution containing AgAATPP (or polyAgAATPP) and eicosanoic acid at the molar ratio of [AgAATPP residue]/[eicosanoic acid] = 1/1.5 was spread onto an aqueous subphase. About 20 min after spreading, the trough surface was compressed at the controlled rate of 20 cm^2/min to the pressures where the transfer of the monolayer to a substrate was performed. The surface pressures were 20 and 30 mN/m for the polymer and the monomer, respectively. As reported before the each monolayer was considered to be a solid film at these pressure.[23]

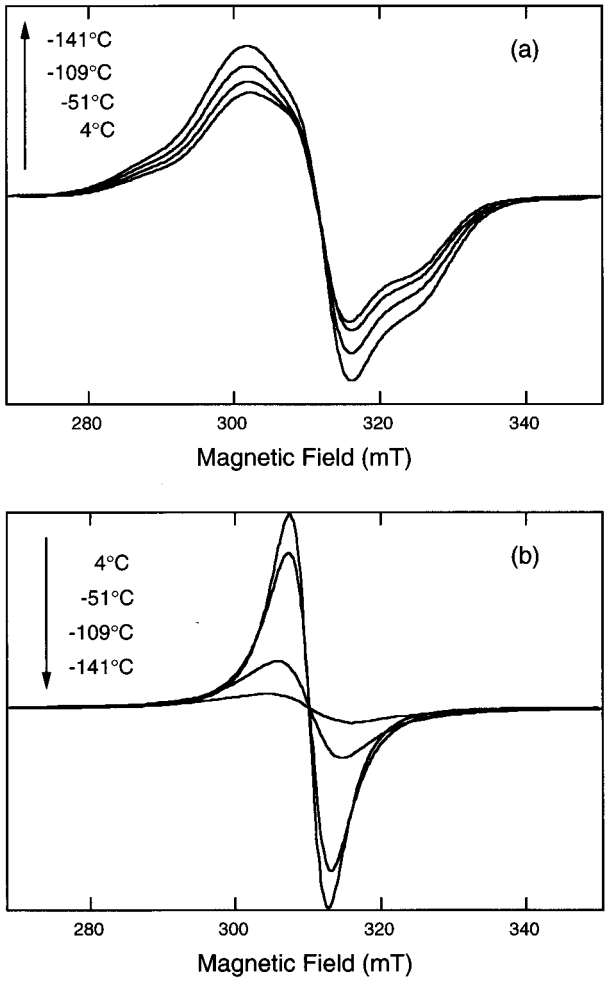


Figure 1. Temperature dependencies of ESR spectra of AgAATPP (a) and polyAgAATPP (b) under air.

As a substrate, we used silicon plates for the measurements of IR spectra, silanized cover glasses for the measurements of ESR spectra, slide glasses for the measurements of Raman spectra, and quartz plates for the measurements of UV−visible absorption spectra and X-ray diffraction measurements, respectively. For silanization, the glasses or quartz plates were first dipped in mixed acid overnight. After being washed with water, the plates were dipped for 3 h in a toluene solution containing 2% of diphenyldichlorosilane purchased from Shinetsu Silicon Chemicals (Japan). Silicon plates were treated first with hot H_2O_2 and then was soaked in an aqueous HF solution. In depositing the LB films, the vertical dipping method was used at a dipping speed of 20 mm/min. The transfer ratio was ~0.7−1 for both the upward and downward strokes, indicating the formation of a Y-type film. Details on the structures of the LB films are described elsewhere.[23]

We were able to remove eicosanoic acid from the LB film of the polymer by treating the film with hot ethanol. The films thus prepared showed no peaks due to the methyl or methylene groups in the FT-IR spectrum, indicating that no eicosanoic acid was left. The method was not applicable to the LB film of AgAATPP/eicosanoic acid. In that case, both components

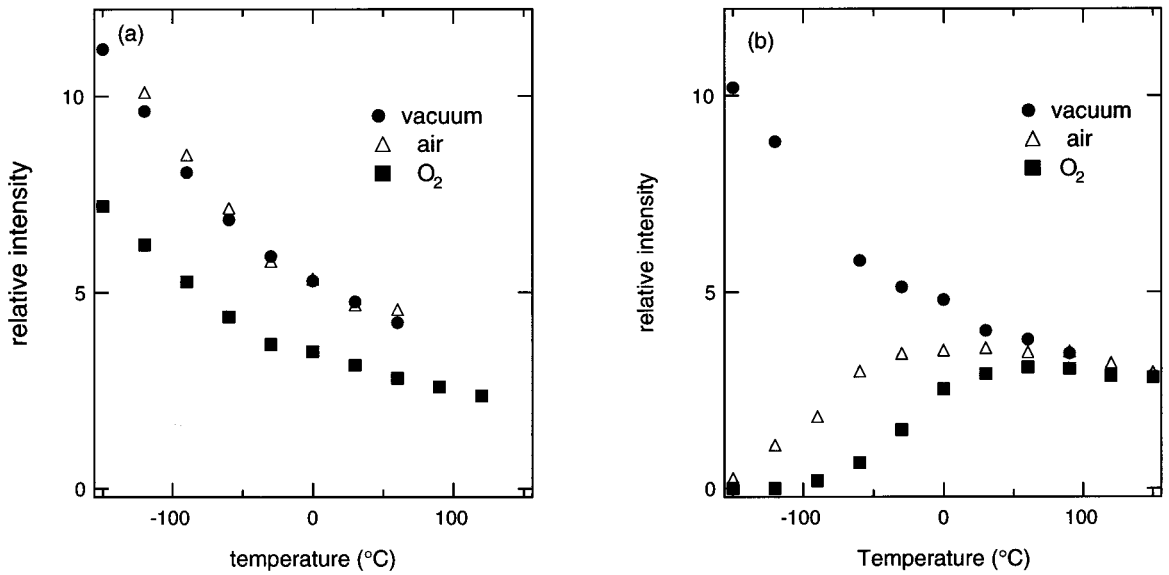


Figure 2. Temperature dependencies of ESR spectra of AgAATPP (a) and polyAgAATPP (b).

flowed away when washed with hot ethanol. Thus we could not remove eicsanoic acid from the LB film of AgTPP.

Measurements. The X-band ESR spectra were obtained with a JEOL JES−RE1X ESR spectrometer. When we measured the temperature dependencies of the AgTPP polymers, we used an Mn marker (Mn^{2+}/MnO) as an external reference, and the signal intensity was calculated from the double integration of the obtained ESR spectra. UV−visible absorption spectra were obtained for a 100-layered LB film and a dichloromethane solution of polyAgAATPP with a Shimadzu UV-160A spectrophotometer. IR absorption spectra were measured for the LB films on a silicon plate with a JEOR JIR-7000 FT-IR spectrometer. KBr was used as a window of an IR cell at low temperature. Raman spectra were obtained with a JASCO NR-1800 spectrometer, using the 514.5 nm line from an argon ion laser (LEXEL MODEL 95) as the excitation source. For polyAgAATPP, the measurement was performed on a 100 layered LB film after being treateed with ethanol to remove eicosanoic acid. For AgTPP, the measurements were performed on a cast film. To obtain the molecular weight of the polymer, GPC analysis was carried out in THF by a TOSOH CO-8011 system using TSK gel. The molecular weight of a polymer was calibrated by using polystyrene standard samples. SEM experiments were carried out with a Hitachi S-510 system. The samples were gold evaporated with a Hitachi E 101 ion sputter.

Results

Temperature Dependency of ESR Signal. The temperature dependence of ESR signal was measured on the powder samples of the monomers and polymers containing the porhyrin moieties under various atmospheres.[22] Figure 1 shows the results for polyAgAATPP and AgAATPP under air. The spectral shapes were different between the monomer and the polymer because of the spin exchange interaction in the polymer side chain as previously reported for other Ag porphyrin polymers.[12−21] As a result, the anisotropy observed in AgAATPP disappeared in its polymer form. In case of the polymer, the signal intensity decreased with a decrease in temperature. The results are notable because the intensity of an ESR signal generally increases on lowering temperature due to the decrease in spin-relaxation rates or the increased difference in the Boltzmann distribution between the ground and excited spin states. In fact, the monomer exhibited normal behavior; that is, the signal intensity increased monotonically with a decrease in temperature. In Figures 2, we show the temperature dependence of the relative intensity of ESR signals for AgTPP monomer and polymers under various conditions. Parts a and b of Figure 2 show the plots of the relative intensity of the ESR signal against temperature for AgAATPP and polyAgAATPP, respectively. In case of the monomer, the signal intensity increased with the decrease of temperature under all conditions studied. In case of the polymer, the signal intensity increased with a decrease in temperature in vacuo, while it more or less decreased under air and oxygen atmospheres. The intensity started to decrease under dioxygen atmosphere at a temperature higher than that under air. On the basis of these facts, we suspected that the AgTPP moieties in the polymer interacted with dioxygen molecules at lower temperature to form an ESR-inactive species. When the temperature was raised again, the signal intensity became stronger, indicating reversible behavior.

We measured the temperature dependence of ESR spectra on the mixed LB films of eicosanoic acid and AgAATPP (or polyAgAATPP) which were prepared as described in the Experimental Section. For the LB film of eicosanoic acid and AgAATPP, the ESR intensity increased with a decrease in temperature (not shown). The same results were obtained for the LB film of eicosanoic acid and polyAgAATPP under all the conditions studied (Figure 3a). When the film was washed with hot ethanol to remove eicosanoic acid, the ESR intensity decreased with a increase in temperature as already seen for the powder sample of polyAgAATPP (Figure 3b). We noted that the LB film of polyAgAATPP exhibited little sample variation and good reproducibility for repeated measurements. The situations were contrasted with the powder samples of the same polymer. After the ESR spectrum of a polymer sample was measured, the sample was dissolved in an solvent and reprecipitated by a precipitant. It was found that the temperature dependence of the ESR signal intensity varied after the reprecipitation procedure, although the general trend of the temperature dependence was similar.

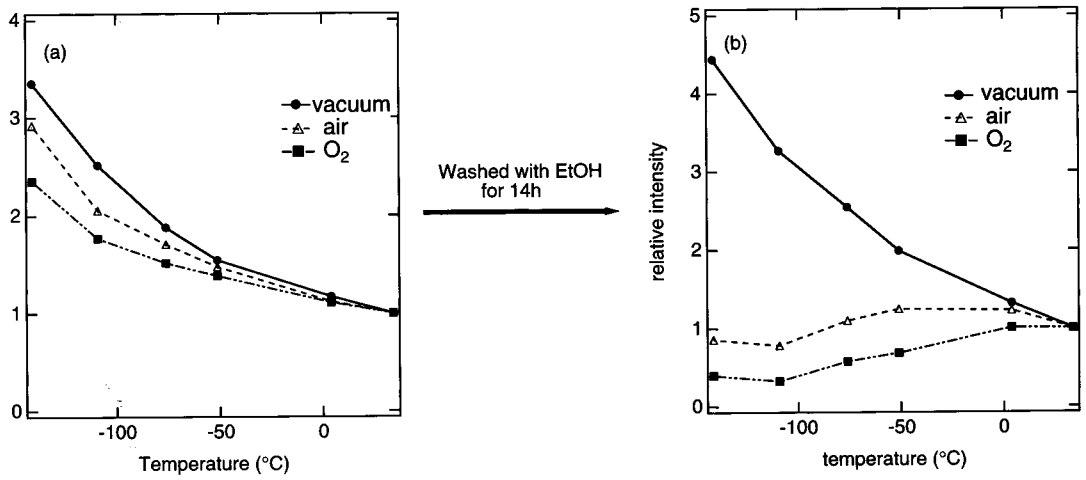


Figure 3. Change of temperature dependencies of ESR spectra of polyAgAATPP/eicosanoic acid LB films (a) before and (b) after ethanol washing.

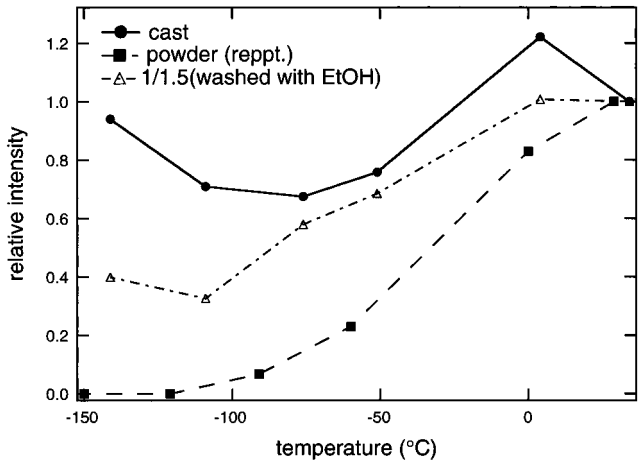


Figure 4. Temperature dependencies of ESR spectra of polyAgAATPP under different conditions.

The temperature dependence of ESR signal for polyAgTPP was measured in toluene under dioxygen. As a result, no new structure appeared in the spectrum, and the intensity increased with a decrease in temperature.

Figure 4 compares the temperature dependence of the ESR signals of polyAgAATPP under dioxygen atmosphere among the precipitated powder, the sample cast on a cover glass, and the eicosanoic acid free LB film. In the figure, the result for the powder sample was chosen so that the largest decrease of the ESR intensity was observed on lowering temperature. The ESR intensity decreased most remarkably for the powder sample with a decrease in temperature. For the LB film, the signal intensity started to decrease at a lower temperature in comparison with the case of powder. The degree of the decrease in the signal intensity at a low temperature was the smallest in the case of the cast sample. On the basis of the assumption that the decrease of the ESR intensity at a low temperature was caused by the formation of a dioxygen adduct, it was concluded that the interaction between the AgTPP moieties with dioxygen decreased in the following order: powder sample > LB film > cast sample.

SEM Measurements. Parts a and b of Figure 5 show the SEM images for the 100 layered LB films of polyAgAATPP before and after removing eicosanoic acid with ethanol, respectivley. It is apparent that the surface of the washed sample (Figure 5b) was rougher than that of the original one (Figure 5a).

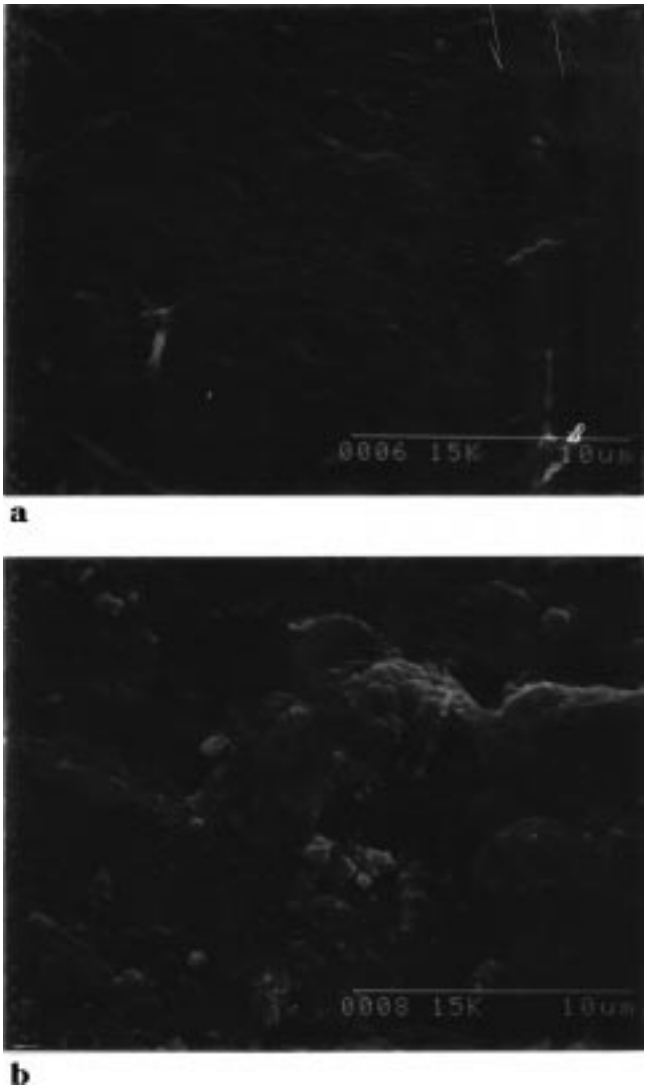


Figure 5. Change of SEM images (a) before and (b) after ethanol washing.

UV−Visible Absorption Spectra. The interaction between dioxygen and AgTPP moieties in the polymer was studied by measuring the UV−visible absorption spectra. The UV−visible spectra were measured on a dichloromethane solution and the eicosanoic acid free

LB film of polyAgAATPP in the temperature range from +20 °C to −80 °C under oxygen atmosphere. As a result, no change of the electronic spectra was observed in both cases (figure not shown). The result for a solution was consistent with the previous observation that no notable change was observed in the ESR measurement on a toluene solution of polyAgAATPP at lower temperature. The result for the LB film, however, was contrasted with the ESR data, which comfirmed the interaction between a dioxygen molecule and the eicosanoic acid free LB film of polyAgAATPP at lower temperature. Therefore it was supposed that the interaction between dioxygen and AgTPP moieties in the polymer occurred only in the solid sate and that such interaction induced no change in the electronic spectrum of a porphyrin moiety.

IR Absorption Spectroscopy. To obtain an evidence for the binding of dioxygen with the silver(II) porphyrin moieties in the polymer at a low temperature, we measured the IR spectra of the eicosanoic acid free LB films of polyAgAATPP under various coonditions. In all cases, the gas pressure was kept at 1 atm. Parts a and b of Figure 6 show the IR spectra of the monomer and polymer films, respectively. In case of the monomer film, no change was observed when the sample was cooled by liquid nitrogen under 1 atm of dioxygen atmosphere. In case of the polymer film, it was noted that a new peak appeared at 728 cm^{-1} when the sample was cooled under the same conditions. The peak was not observed under N_2 atmosphere at 77 K. The results assisted that the peak was assigned to the oxygen adduct of the AgTPP moieties in the polymer. When the same measurements were performed under 1 atom of $^{18}O_2$, the peak at 728 cm^{-1} disappeared. The results indicated that the peak at 728 cm^{-1} shifted toward the lower wavenumber region due to the increase in mass. A simple calculation suggested that the peak should shift from 728 to 686 cm^{-1}. No new peak was detected, however, in the wavenumber range from 650 to 820 cm^{-1}. This was probably because the peak of the $^{18}O_2$ adduct of AgTPP was hidden by the absorption band of CO_2 at 680 cm^{-1}.

Resonance Raman Spectra. Raman spectra of the ethanol-washed polyAgAATPP LB film (100 layers) were measured at −180 °C under O_2 or N_2 atmospheres. To cool the sample, cooled O_2 or N_2 gas was blown against it. The results are shown in Figure 7. Under O_2 atmosphere, there appeared a new peak at 545 cm^{-1}. The peak was very weak under N_2 atmosphere. Therefore the peak at 545 cm^{-1} was assigned to the O_2 adduct of the AgTPP moiety. The slight appearance of the peak under N_2 atmosphere might be caused by the small amount of O_2 which was present in a blowing N_2 gas. When the Raman spectrum was measured on a powder sample of mnonomeric AgTPP at −180 °C under dioxygen, no new peak was observed.

Discussion

The temperature dependence of the ESR signal intensity under oxygen atmosphere demonstrated that only polyAgAATPP in a solid-state behaved in an anomalous way. That is, the ESR intensity decreased with the decrease of temperature. Other samples such as a polyAgAATPP solution, the mixed LB film of polyAgAATPP−eicosanoic acid, solid AgAATPP, and a AgAATPP solution all behaved in a normal way, or the ESR intensity increased on decreasing temperature. The

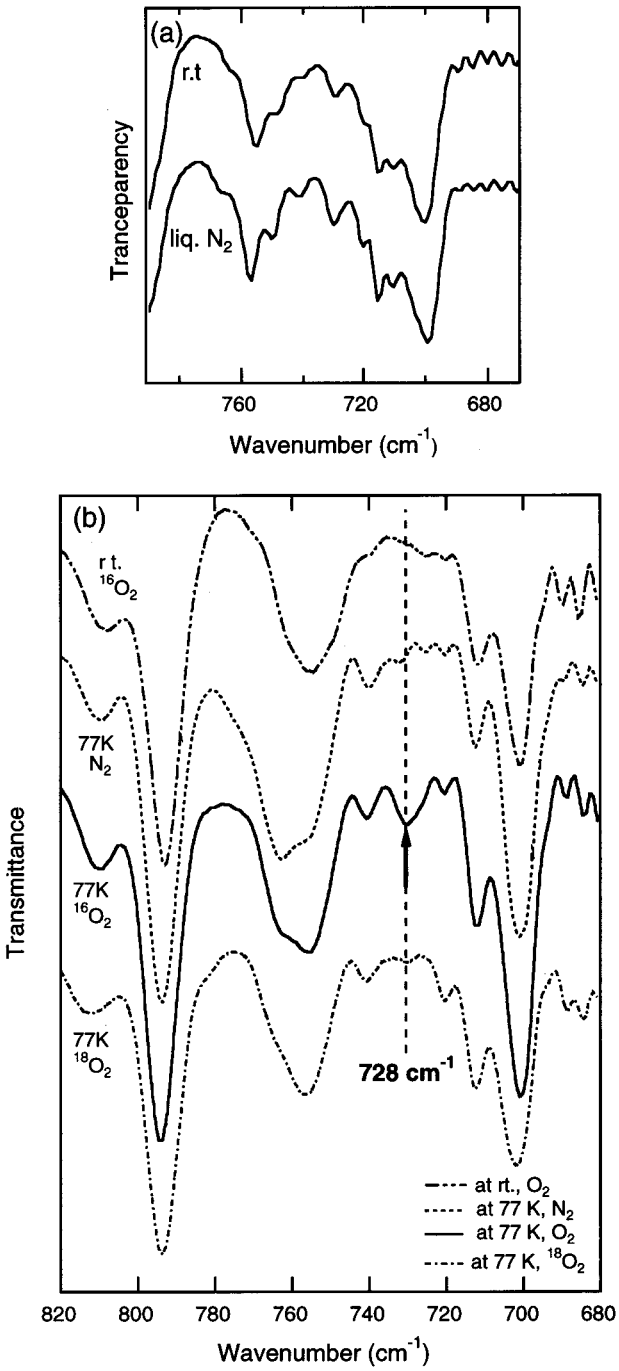


Figure 6. IR spectra of AgAATPP (a) under oxygen at room temperature (upper curve) and liquid N_2 temperature (lower curve) and polyAgAATPP (b) under several conditions.

effects of atmosphere on the ESR, IR, and Raman spectra assisted the view that Ag(II) in polyAgAATPP was bound to dioxygen at lower temperature to form an ESR inert species. The conclusion was further supported by the appearance of the new peaks in the IR and Raman spectra in case of polyAgAATPP under oxygen atmosphere.

The monomer sample was unable to bind dioxygen probably because it had too high a crystallinity. That is, in a crystal, monomeric AgTPP moieties were so closely packed with each other that dioxygen molecules could not permeate to the AgTPP moiety. A similar conclusion was deduced from the X-ray measurements on tetraphenylporphyrin.[25,26]

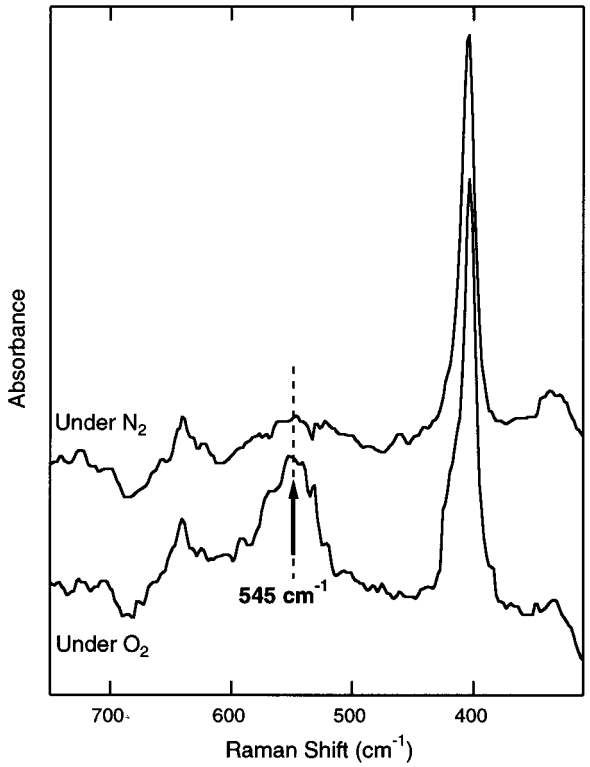


Figure 7. Raman spectra of polyAgAATPP at 88 K, under N_2 (upper curve) and under O_2 (lower curve).

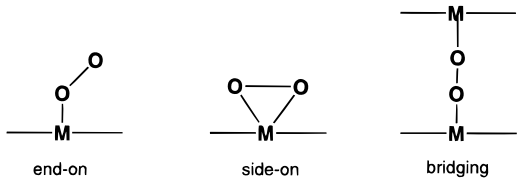
In the case of the mixed LB film of polyAgAATPP and eicosanoic acid, AgTPP moieties were not in such a position as to interact with dioxygen because of the surrounding eicosanoic acid molecules. The SEM images of the polyAgAATPP LB films with or without eicosanoic acid demonstrated that porous structures were observed in the latter film while such a structure did not exist in the former film. Therefore, the observed order of the binding strength toward dioxygen molecules as deduced from Figure 6 (or powder sample > LB film > cast sample) may represent the order of the abundance of porosity. The LB film of polyAgAATPP and eicosanoic acid did not have a porous structure, either. It was suggested that cavities were generated by removing eicosanic acid from a LB film with ethanol.

From the results of IR and Raman spectra, we assigned the peak at 728 cm^{-1} (IR) to ν(O−O) and the peak at 545 cm^{-1} (Raman) to ν(Ag−O) in the dioxygen adduct of polyAgAATPP. The present value of ν(O−O) is compared with those of other oxygen adducts of metalloporphyrin: $Co(TPP)O_2$,[27] 1276 cm^{-1}; $Fe(TPP)O_2$,[28] 1195, 1106 cm^{-1}; $Mn(TPP)O_2$,[29] 983 cm^{-1}. When our work is included, the order of wavenumber is obtained as follows:

$$Co(TPP)O_2 > Fe(TPP)O_2 > Mn(TPP)O_2 > Ag(TPP\ polymer)O_2$$

The binding structures of dioxygen adducts are classified into three types of the end-on, side-on and bridging configurations (Scheme 2).[30] Among the above adducts, $Co(TPP)O_2$ takes the end-on structure, and $Mn(TPP)O_2$ the side-on structure. In case of $Fe(TPP)O_2$, the peaks at 1195 and 1106 cm^{-1} are assigned to the end-on and the side-on structure, respectively. The lower the wavenumber of ν(O−O), the higher the tendency for the side-on structure. Because the present

Scheme 2



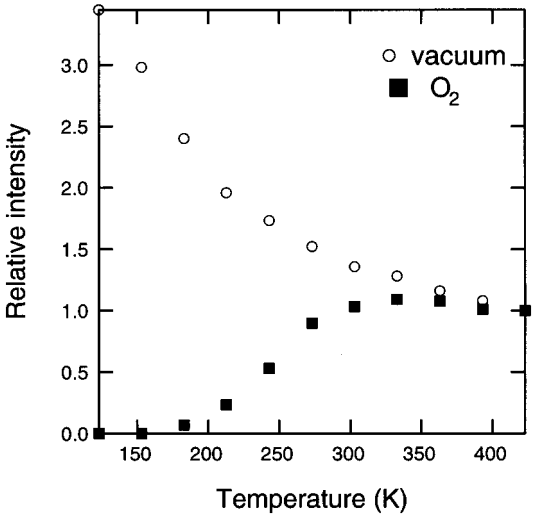
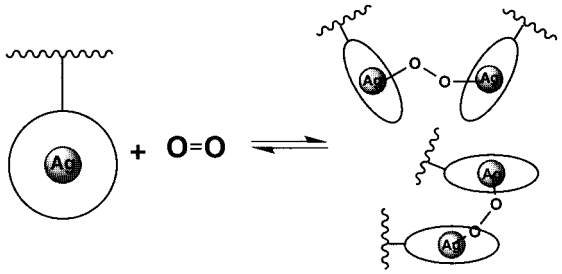


Figure 8. Temperature dependence of the relative intensity of ESR signals for polyAgAATPP.

Scheme 3



adduct has the lowest ν(O−O), the structure seems to be side-on type. However, if (AgTPP polymer)O_2 is assumed to take the side-on structure, the same adduct will be possible in AgTPP itself, which is not the case in the present study. Moreover the ν(O−O) was active in IR spectroscopy but inactive in Raman spectroscopy. This means that the vibration of ν(O−O) in the present adduct is asymmetric. If the bond type is side-on, the vibration of ν(O−O) is symmetric so that the transition will be Raman-active and not IR-active (Scheme 2). On the basis of these facts, we finally assume that the dioxygen attached to AgTPP takes a bridging form. Dioxygen is considered to bridge between two AgTPP moieties which randomly orient in a solid state as illustrated in Scheme 3.

Dioxygen adducts are also classified into two types in terms of the bond order of a dioxygen molecule.[30] One is called "superoxo" which exhibits ν(O−O) in the 1200−1100 cm^{-1} region and the other "peroxo" whose ν(O−O) is in the 920−750 cm^{-1} region. Since ν(O−O) in the AgTPP polymer is observed at 728 cm^{-1}, the present dioxygen adduct can be classified into "peroxo". The wavenumber of ν(O−O) is appreciably lower than those for the dioxygen adducts of CoTPP, FeTPP, and MnTPP. The fact suggests that the bond length of O−O in the present adduct is longer than those in these porphyrin

compounds.

Concluding the above discussions, a dioxygen molecule is attached to Ag(II) in polyAgAATPP to form a peroxide-type dioxygen with an asymmetric bridging structure. This dioxygen complex was inert for ESR. It is well-known that, in the case of a cobalt(II) porphyrin, the oxygen adduct gives an ESR-active species whose spectrum is different from that of a free cobalt porphyrin.[18,31−33] This is because Co(II) in the porphyrin is d^7 so that other unpaired electrons remain to be detected in ESR when the cobalt ion is linked with a dioxygen molecule. In case of AgTPP, Ag(II) is d^9 so that, if the d-electron forms a linkage with a peroxide-type oxygen, the unpaired electron disappears and the species is diamagnetic. In other words, the silver ion in the porphyrin moiety become an ESR-inactive d^8 species when it binds to dioxygen.

On the basis of the above scheme, we estimated the heat of dioxygen adsorption to the Ag(II) ion in polyAgAATPP. The binding equilibrium of dioxygen with AgTPP is expressed as

$$[(\mathrm{AgTPP})_2] + \mathrm{O_2} \overset{K}{\rightleftharpoons} [\mathrm{AgTPP{-}O_2{-}AgTPP}] \quad (1)$$

in which $(AgTPP)_2$ represents a pair of the nearest neighboring AgTPP moieties. The dioxygen adduct of AgTPP moiety, [AgTPP−O_2−AgTPP], is assumed to be ESR inactive. Since no AgTPP in the polymer binds to dioxygen at 150 °C, the intensity of the signal is normalized by being divided with the one at 150 °C (423 K). Figure 8 shows the plots of the relative ESR intensity thus obtained, (○) and (□), as a function of temperature for the measurements performed under vacuum (I_{vac}) and 1 atm of dioxygen (I_{ox}), respectively.

When we divide I_{ox} by I_{vac} at the corresponding temperature, we obtain the fraction of free $(AgTPP)_2$ out of the whole $(AgTPP)_2$, $[(AgTPP)_2]_0$:

$$[\mathrm{AgTPP}]/[(\mathrm{AgTPP})_2]_0 = I_{ox}/I_{vac} \quad (2)$$

The equilibrium constant K at the partial pressure of dioxygen, P_{O_2}, is expressed by

$$K = [\mathrm{AgTPP{-}O_2{-}AgTPP}]/(P_{\mathrm{O_2}}[(\mathrm{AgTPP})_2]) \quad (3)$$

In the preset case, the measurement was performed under 1 atm dioxygen, leading to $P_{O_2} = 1$. The fraction of the dioxygen adduct of AgTPP moiety in the polymer is obtained from the following equation:

$$[\mathrm{AgTPP{-}O_2{-}AgTPP}]/[(\mathrm{AgTPP})_2]_0 = 1 - I_{ox}/I_{vac} \quad (4)$$

From these equations, the equilibrium constant K is estimated to be 4.17×10^{-4} $mmHg^{-1}$ at 30 °C (303 K). The heat of adsorption (E_a) is estimated according to the following equation:

$$\ln K = -E_a/RT + A \quad (5)$$

In Figure 9, ln K is plotted as a function of the reciprocal of temperature. From the slope of the straight line between 213 and 333 K, E_a is obtained to be −4.5 kcal/mol.

In Table 1, we summarize the results obtained as well as the ones of modified CoTPP fixed in a polymer membrane which were reported by Nishide *et al.*[34] Comparing the results of these porphyrin complexes, the heat of dioxygen adsorption of polyAgAATPP is one-third that for CoTPP membrane and the equilibrium constant of polyAgAATPP is almost a tenth of that. This implies that adsorption energy of AgTPP polymer is much weaker than that of modified CoTPP. The observed low binding energy explains why the dioxygen adduct of AgTPP is not observed in a solution.

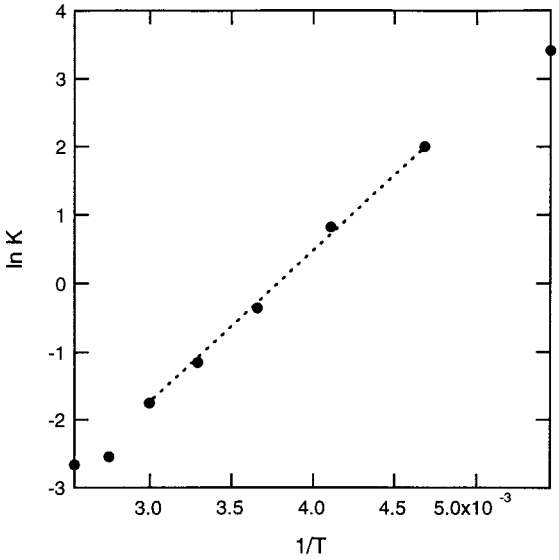


Figure 9. Plot of ln K vs $1/T$ for dioxygen adsorption to AgTPP moieties in polyAgAATPP.

Table 1. Equilibrium Constants and Heat of Adsorption for Dioxygen Binding of Metal Porphyrins

	10^3 K,[a] $mmHg^{-1}$	E_a, kcal/mol	ref
AgTPP	0.42	−4.5	this work
CoTPP[b]	3.8	−14	35

[a] Data at 30 °C. [b] [α,α′,α″,α‴-*meso*-tetrakis(o-pivalamidophenyl)porphyrinato]cobalt(II)−1-methylimidazole mixed with poly(butyl methacrylate) (M_w = 32 000). The dioxygen binding measurement was performed on the membrane of the polymer mixture which contained 2.5−4.5 wt % of the cobalt complex.

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