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Physicochemical Properties of Polyacrylates Containing Tetraphenylporphinatocobalt(II) and Chloro(tetraphenylporphinato)iron(III) as Side Chains

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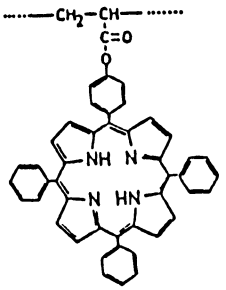
Polyacrylates containing tetraphenylporphinatocobalt(II) (TPP-Co(II)) and chloro(tetraphenylporphinato)iron(III) (TPP-Fe(III)Cl) as side chains were prepared. Their physicochemical properties were investigated by UV-visible spectroscopy, ESR spectroscopy, and magnetic susceptibility (χ_M) measurement. In comparison of the visible spectra of polymers with those of the corresponding monomers, hypochromism of the Soret band and some of Q bands was observed in both polymers. In the measurements of ESR spectra, hyperfine splitting constants and anisotropic *g*-values of TPP-Co(II) or -Fe(III)Cl moieties bound to the polymers were somewhat different from those of TPP-Co(II) and -Fe(III)Cl, respectively. These differences in spectroscopic behavior suggest that there are some interactions between porphinatometal ion moieties in the polymers. The values of χ_M for the polymers containing TPP-Co(II) were found to obey the Curie-Weiss law with θ=190 K, which was explained in terms not only of spin-orbit interaction of the Co(II) ion but also antiferromagnetic interaction among the Co(II) ions. The magnetic moment of the TPP-Co(II) moiety bound to the polymer is smaller than that of TPP-Co(II), indicating occurrence of an antiferromagnetic interaction between Co(II) ions in the polymer. The values of χ_M for polymers containing TPP-Fe(III)Cl were found to obey the Curie-Weiss law with θ=20 K. This can be explained in terms of the presence of antiferromagnetically-interacting sites. From the experimental results, it is concluded that the antiferromagnetic interaction between TPP-metal ions bound to the polymer is larger than that of the corresponding TPP-metal ions. Molecular oxygen is adsorbed to polyAOTPP-Co(II) and 5-(4-propanoyloxyphenyl)-10,15,20-triphenylporphinatocobalt(II) (POTPP-Co(II)) below 180 K. Magnetic susceptibility measurement and ESR study show that molecular oxygen is bound to the Co(II) ion by chemisorption whose binding energy is 24 kJ M^{-1}.

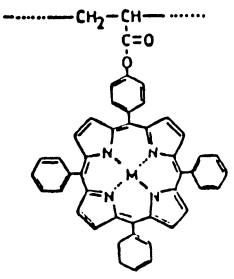
Many studies of physicochemical properties of tetraphenylporphinatometal ions have been reported.[1-5] However, there have been few studies of polymers containing metalloporphins in the side chain, although the polymers seem to have interesting and unusual properties caused by an aggregate of porphin moieties.[6,7] To our knowledge, no homoplymerization of vinyl compounds containing porphin moieties in the side chains has been reported except for our papers.[8] Recently, we succeeded in the preparation of this type of polymer by radical polymerization of 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphine (AOTPP).[8]

In the course of our study of the magnetic properties of polymers containing paramagnetic species in the side chain,[9-12] we found that polyacrylates containing tetraphenylporphinatosilver(II) (TPP-Ag(II)) have strong antiferromagnetic interactions.[9] Since cobalt(II) and iron(III) which are composed of electronic configurations of d^7 and d^5, respectively, have a possibility of multiplet state, and hence have the potential of leading to ferromagnetic substances,[13,14] polyacrylates containing tetraphenylporphinato-Co(II) or -Fe(III)Cl (TPP-Co(II) or -Fe(III)Cl) as side chains were prepared and their magnetic properties were investigated. They showed antiferromagnetic behavior, contrary to expectation.

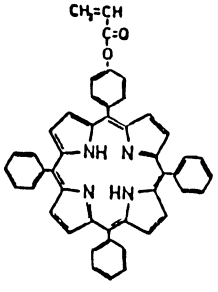
In this paper, we present the results of the preparation and the spectroscopy of the polymers (polyAOTPP-Co(II) and -Fe(III)Cl), as well as their magnetic properties. The antiferromagnetic behavior observed in the polymers is ascribable to the electronic interaction between the TPP-metal moieties bound to the polymers, which was found by UV-visible and ESR spectroscopy. In addition, adsorption of molecular oxygen on polyAOTPP-Co(II) is considered.



PolyAOTPP



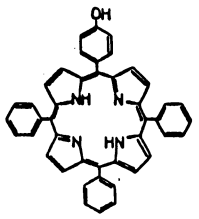
PolyAOTPP-M
M: Co(II) or Fe(III)Cl



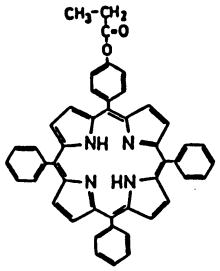
AOTPP

Experimental

Materials. Solvents were purified by distillation under nitrogen atmosphere. 5-(4-Acryloyloxyphenyl)-10,15,20-triphenylporphine (AOTPP) and its polymer (poly(AOTPP)) were prepared as described previously.[8] The molecular weight of the polymer was determined to be 80000—100000 by GPC measurements.[8] 5,10,15,20-Tetraphenylporphine (TPP) was synthesized according to Alder et al.[15] Tetraphenylporphinatocobalt(II) was prepared according to Bucher et al.[16] in 96% yield. Chlorotetraphenylporphinatoiron(III) was prepared according to Maricondi et al.[17] in 64.8%. 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphine (HOTPP) was prepared by the method described previously.[8]



HOTPP



POTPP

5-(4-Propanoyloxyphenyl)-10,15,20-triphenylporphine (POTPP) was prepared by adding propanoyl chloride to a THF solution of HOTPP and triethylamine. The crude product was purified by column chromatography, followed by repeated recrystallization from chloroform-methanol. Yield 90%.

Found: C, 82.07; H, 5.04; N, 8.13%

Calcd for $C_{47}H_{35}N_4O_2$: C, 82.07; H, 5.13; N, 8.15%

5-(4-Propyloloxyphenyl)-10,15,20-triphenylporphinatocobalt(II) [POTPP-Co(II)] was prepared as follows: POTPP (0.61g) and cobalt(II) (0.30 g) acetylacetonate were dissolved in 100 ml chloroform. The solution was refluxed for 1 h and chloroform was removed by a rotatory evaporator. The product was purified by repeated precipitation from chloroform-methanol. The content of Co(II) was determined by flame spectrometric analysis.

Found: C, 76.22; H, 4.47; N, 7.64; Co, 7.6%

Calcd for $C_{47}H_{33}N_4O_2Co$: C, 75.80; H, 4.47; N, 7.52; Co; 7.91%.

Poly[5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatocobalt(II): Poly(AOTPP) (0.40 g) and cobalt(II) acetylacetonate (0.40 g) were dissolved in 100 ml THF. The solution was refluxed for 24 h and THF was removed by a rotatory evaporator. During the reflux, the reaction was followed by taking visible spectra of the solution at different times. Chloroform was added to the residue to dissolve the polymer, and the polymer was isolated by precipitation with methanol and purified by repeated precipitations from chloroform-methanol. The precipitated polymer was isolated by centrifugation and dried in vacuo overnight. The content of Co(II) was determined to be 74 mol% of the TPP-moiety by flame spectrometric analysis.

Poly[chloro-5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatoiron(III)Cl]: poly(AOTPP) (0.25 g) and iron(III) chloride (0.14 g) was mixed in 100 ml of toluene containing 5 ml of methanol. The mixture was refluxed for 24 h and filtered to remove unreacted iron(III) chloride. The filtrate was washed with water. The polymer was isolated from the organic layer by evaporation, dried in vacuo, dissolved in benzene, and reprecipitated with ethanol. The polymer was purified by repeated precipitation from benzene-ethanol. The precipitated polymer was isolated by filtration, and dried in vacuo overnight. Yield 0.27 g.

The content of Fe(III) ions was determined to be 92 mol% of the TPP-moiety by flame spectrometric analysis.

Measurements. UV-visible spectra were recorded on a Hitachi 124 spectrophotometer. IR spectra were recorded on a JASC DS-402G spectrophotometer.

ESR spectra were measured with a JEOL Model JES FE 1X ESR spectrometer with 100 kHz modulation. A TE_{011} mode cylindrical cavity with a variable temperature adaptor (ES-UCT-2AX) was used. The temperature was controlled by a variable temperature control unit (ES-VT-3A). ESR measurements at 77 K were carried out using an insertion-type liquid nitrogen Dewar, a tip of which is made of doublefold Suprasil tubes. The *g*-values were estimated using MnO as a standard sample which was provided by JEOL.

Gram magnetic susceptibility (χ_g) was determined by the Gouy method at room temperature. Water was used as a standard sample for χ_g. The value of χ_g for water was found to be -0.727×10^{-6} cgs emu, being in agreement with the established value. The temperature dependence of χ_g was determined by the Faraday method, using a Cahn RH electric balance in a temperature range from 4 K to 300 K. The molar magnetic susceptibilities (χ_M) were corrected by the following equation to remove diamagnetic contributions from the ligand

$$\chi_M=\chi_g\times M-\chi_{dia}$$

where M is molecular weight of TPP-metal or monomer unit of the polymer, and χ_{dia} for TPP-Co(II), TPP-Fe(III)Cl, polyAOTPP-Co(II), and polyAOTPP-Fe(III)Cl were calculated to be -521×10^{-6}, -542×10^{-6}, -498×10^{-6}, and -418×10^{-6} cgs emu, respectively. The effective magnetic moment (μ_{eff}) was calculated from the following equation:

$$\mu_{eff}=2.33\sqrt{\chi_M\cdot T}$$

The amount of molecular oxygen absorped was determined from the difference in the weight of samples before and after O_2 gas was introduced into the system.

Results and Discussion

UV-Visible Spectra. UV-visible spectra of TPP-Co(II) and polyAOTPP-Co(II) are shown in Fig. 1. Both compounds have the Soret band at 411 nm and Q bands in the region from 500 to 700 nm, as shown in the spectra of metalloporphins.[8] The wavelength of the Soret band of polyAOTPP-Co(II) is similar to that of TPP-Co(II), but the molecular extinction coefficient (ε) of polyAOTPP-Co(II) is smaller than that of TPP-Co(II). Q bands of polyAOTPP-Co(II) are broader than those of TPP-Co(II). Close examination of the spectra shows that at 530 nm the value of ε

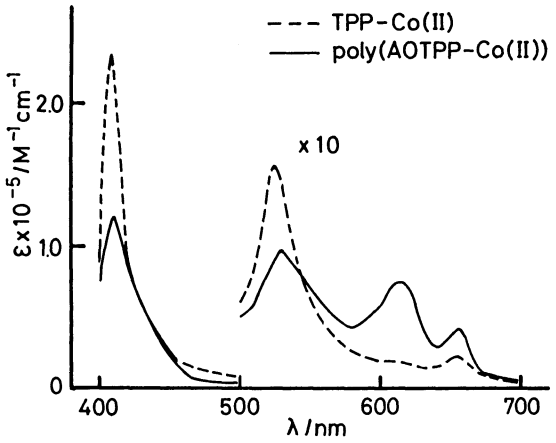


Fig. 1. Visible spectra of TPP-Co(II) and polyAOTPP-Co(II) in chloroform at room temperature. (----) TPP-Co(II), and (——) polyAOTPP-Co(II).

of polyAOTPP-Co(II) is smaller than that of TPP-Co(II), and that at 670 nm the former is larger than the latter. In addition, at 610 nm a stronger and broader absorption band is more clearly observed in spectrum of polyAOTPP-Co(II). The UV-visible spectrum of 5-(4-propanoyloxyphenyl)-10,15,20-triphenylporphinatocobalt(II) (POTPP-Co(II)) was measured to study the influence of the ethoxycarbonyl group bound to the TPP on the spectrum. Since the spectrum of POTPP is almost the same as that of TPP except for the slight change in λ_{max} and ε, the presence of the ethoxycarbonyl group is not considered to be an important factor for the difference in molecular extinction coefficients of the absorption bands between TPP-Co(II) and polyAOTPP-Co(II). The case where all the metal ions incorporated into the polymer are not bound to the TPP moieties might be considered as the origin of this difference. However, IR absorption bands due to TPP-Co(II) moieties of the polymer was almost the same as those of TPP-Co(II). Moreover, the local structure around a Co(II) ion in TPP-Co(II) and polyAOTPP-Co(II) was investigated by the EXAFS method. A Co(II)-N distance was determined to be 2.1 Å in polyAOTPP-Co(II), being consistent with 2.1 Å in TPP-Co(II).[18] This result shows that Co(II) ions incorporated into the polymer are mostly bound to the TPP moieties as TPP-Co(II). Therefore, the difference in the absorption bands between polyAOTPP-Co(II) and AOTPP-Co(II) is reasonably ascribed to the hypochromism and the hyperchromism, which suggests that there are some interactions between TPP-Co(II) moieties in the polymer.[19] It has been usually considered that there is no stacking between TPP rings because of steric repulsion by the phenyl groups.[20] Recently, however, the presence of interaction due to close approach of the two porphin rings has been found in porphin dimers in organic solvents[21] and in aqueous solution of tetrakis(4-sulfophenyl)porphin,[22] and the change in the values of ε has been explained in terms of an exciton coupling model.[7] Bulky TPP moieties bound to a polymer chain are possibly forced into some interactions due to their close approach.

UV-visible spectra of TPP-Fe(III)Cl and polyAOTPPFe(III)Cl are shown in Fig. 2. The values of ε of the Soret band (416 nm) and the absorption band at 515 nm are smaller in polyAOTPP-Fe(III)Cl than in TPP-Fe(III)Cl. The absorption band at 653 nm of polyAOTPP-Fe(III)Cl is stronger and is shifted 3 nm to longer wavelength than the corresponding band of TPP-Fe(III)Cl. In addition, an absorption near 558 nm is observed in polyAOTPPFe(III)Cl. The observed spectroscopic absorption feature of polyAOTPP-Fe(III)Cl is similar to that of polyAOTPP-Co(II), suggesting the presence of exciton coupling between porphin moieties in a polymer chain.

ESR Spectra of Polycrystalline State. Figure 3 shows the ESR spectra of the powdered samples of

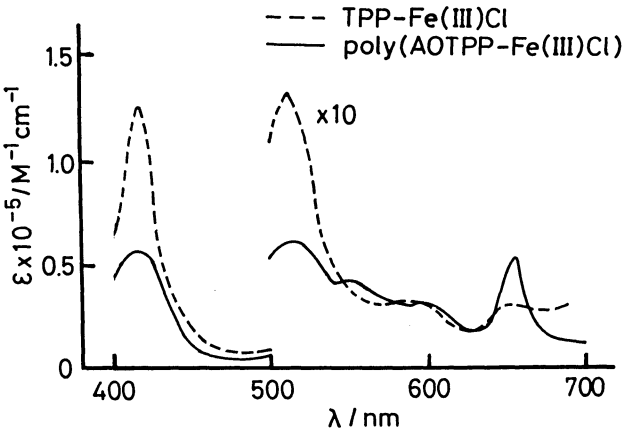


Fig. 2. Visible spectra of TPP-Fe(III)Cl and polyAOTPP-Fe(III)Cl in chloroform at room temperature. (----) TPP-Fe(III)Cl and (——) polyAOTPP-Fe(III)Cl.

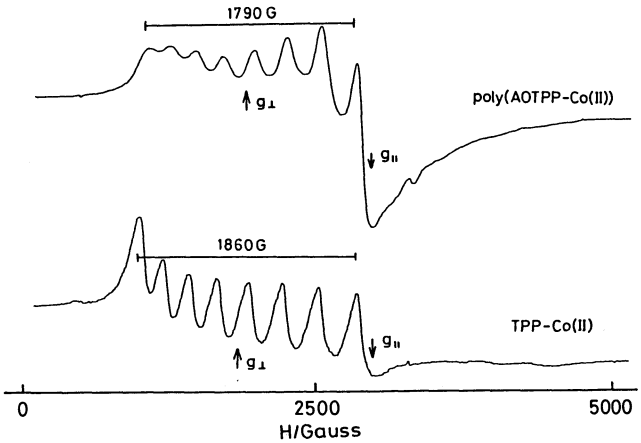


Fig. 3. ESR spectra of TPP-Co(II) and polyAOTPP-Co(II) powders in vacuo at 77 K.

TPP-Co(II) and polyAOTPP-Co(II) in vacuo at 77 K. The spectrum of TPP-Co(II) is similar to those of cobalt(II) phthalocyanine[23] 5,10,15,20-tetrakis(*p*-methylphenyl)porphinatocobalt(II).[24] These spectra are composed of two anisotropic resonance lines ($g_{//}$ and $g_{\perp}$) with an anisotropic magnetic interaction between an unpaired electron and a cobalt nucleus of spin $I=7/2$. The spectrum can be interpreted by the following spin Hamiltonian reflecting the axial symmetry:[23]

$$H=\beta[g_{//}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)]+AS_zI_z+B(S_xI_x+S_yI_y) \quad (1)$$

where A and B are the cobalt nuclear hyperfine interaction constants.

The low-field set of 8 intense lines shows that the resonance lines are not equally spaced and their hyperfine splitting constants increase from 194 to 310 (1G=10^{-4} T) with increasing magnetic field. The progressive hyperfine splitting can be explained in terms of the anisotropic resonance condition with substantial second-order interactions as follow:[23]
For the direction pararell to the magnetic field,

$$H_{//}=(H_0/g_{//})-(AM_I/g_{//})-B^2[I(I+1)-M_I^2](2g_{//}H_0)^{-1}. \quad (2)$$

For the direction perpendicular to the magnetic field,

$$H_{\perp}=(H_0/g_{\perp})-(BM_I/g_{\perp})-(A^2+B^2)[I(I+1)-M_I^2](4g_{\perp}H_0)^{-1}. \quad (3)$$

The high-field set of lines that belong to $g_{//}$ also should be theoretically composed of eight lines. However, the signals of this set were much weaker, being detected as five lines by increasing the amplification of the spectrometer. The remaining three lines are hidden by the strong $g_{\perp}$ resonances. The four hyperfine splitting constants estimated from the five lines are unequal and larger than 300 G. This spectrum is almost the same as that of 5,10,15,20-tetrakis(*p*-methylphenyl)porphinatocobalt(II).[24] The spin Hamiltonian parameters were determined to be $g_{//}=1.80$, $g_{\perp}=3.59$, $A=197\times10^{-4}$ cm^{-1}, and $B=395\times10^{-4}$ cm^{-1} by the same method as Refs. 22 and 23. The deviation from the free electron value of $g=2.0023$ implies that spin-orbit interactions are operative in the Co(II)-TPP molecule.

The ESR spectrum of polyAOTPP-Co(II) shows the superposition of anisotropic resonance lines about $g=2.0$ on the spectrum similar to that of TPP-Co(II). Although accurate g-values of the former are not clear because of the low resolution of the spectrum, the values of $g_{//}$ and $g_{\perp}$ estimated approximately from the maximum and minimum of the spectrum seems to be 2.2 and 2.0, respectively. This anisotropic spectrum is similar to that of reduced vitamin B_{12} which is five-coordinated owing to the attachment of 5,6-dimethylbenzimidazole.[25] The presence of the five-coordinated TPP-Co(II) moieties in polyAOTPP-Co(II) seems to be in accord with the finding of UV-visible spectroscopy that TPP-moieties bound to a polymer chain are forced to make some interaction. The spectrum similar to that of TPP-Co(II) is composed of the low-field set of 8 intense lines whose hyperfine splitting constants increase from 178 to 306 G with increasing magnetic field, and the weaker high-field set which could be observed as 5 peaks, whose hyperfine splitting constants changes from 303 to 430 G, by increasing the amplification. The remaining three lines are hidden by the low field set of $g_{//}$ with stronger intensities. The respective 8 lines in the lower-field set of polyAOTPP-Co(II) are broader than the corresponding lines of TPP-Co(II), and hyperfine splitting constants of the former are smaller than those of the latter. The comparison of these spectra shows that there is an exchange interaction between TPP-Co(II) moieties in polyAOTPP-Co(II),[26] which explains the difference in the temperature dependence of χ_M and μ_{eff} between polyAOTPP-Co(II) and TPP-Co(II) in the section of magnetic properties.

Figure 4 shows the ESR spectra of the powdered samples of TPP-Fe(III)Cl and PolyAOTPP-Fe(III)Cl in vacuo at 77 K. The resonance lines of TPP-Fe(III)Cl were observed at $g=6.4$ and $g=2.0$, being typical of d^5-high spin Fe(III)Cl complexes.[27] The ESR spectrum of polyAOTPP-Fe(III)Cl is similar to that of TPP-Fe(III)Cl except for the broadening of the signal at $g=6.0$ and the increase in the intensity of the resonance line at $g=2.0$. The difference in the line width and the signal intensity between polyAOTPP-Fe(III)Cl and Fe(III)Cl seems to be consistent with the presence of an exchange interaction between TPP-Fe(III)Cl moieties in the polymer, which was observed by measurement of the temperature dependence of χ_M and μ_{eff} in the next section.

Magnetic Properties. The temperature dependence of χ_M^{-1} and μ_{eff} is shown in Fig. 5. The straight line for the χ_M^{-1}-temperature relationship intersects

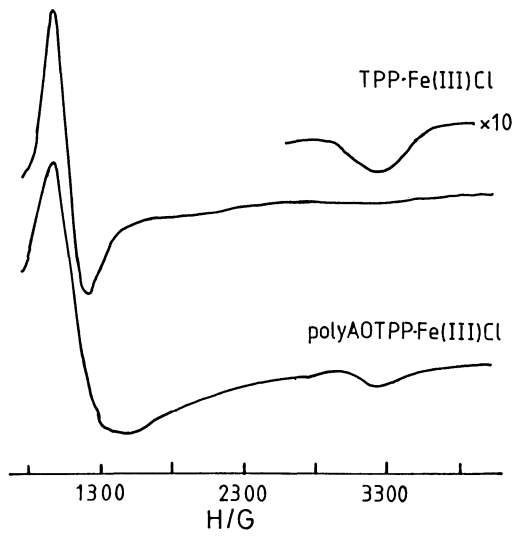


Fig. 4. ESR spectra of TPP-Fe(III)Cl and polyAOTPP-Fe(III)Cl powders in vacuo at 77 K.

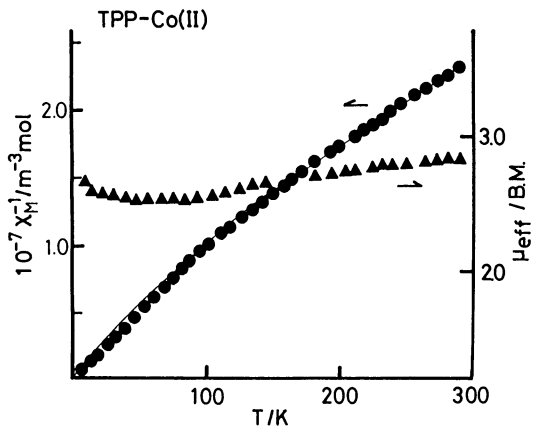


Fig. 5. Temperature dependence of χ_M^{-1} and of TPP-CO(II). (——) Calculated line.

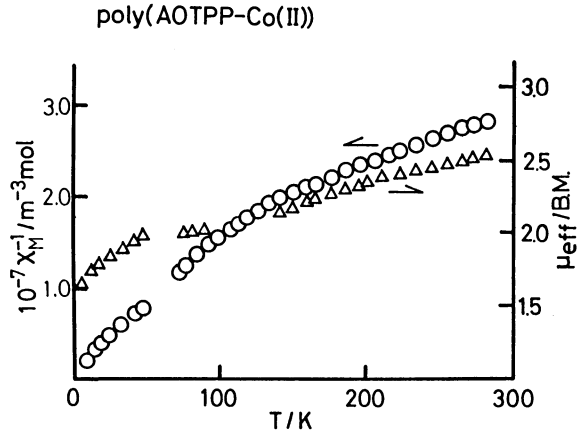


Fig. 6. Temperature dependence of χ_M^{-1} and of polyAOTPP-Co(II).

the ordinate above the origin, indicating that χ_M obeys the Curie-Weise law ($\chi_M=C/(T-\theta)$) with $\theta=-45$ K. This result suggests an antiferromagnetic interaction between TPP-Co(II) molecules each of which has an unpaired electron because of low spin d^7 configuration.[28] If the deviation from the Curie law ($\chi_M=C/T$) is due to the antiferromagnetic interaction the magnetic moment estimated from χ_M should be lower than the spin-only value of 1.73 B.M.[29] The magnetic moment observed at room temperature is 2.83 B.M., being larger than the spin-only value. This rather large value of the magnetic moment leads to the supposition that incomplete quenching of the orbital moment takes place in TPP-Co(II) because of low spin d^7 configuration and results in an anisotropic magnetic susceptibility ($g_{//}$ and $g_\perp$) due to the spin-orbit interaction.[30] Accordingly, the deviation of the temperature dependence of χ_M^{-1} from the Curie law is probably caused by the anisotropic magnetic susceptibility. Anisotropic susceptibilities are estimated by Eqs. 4 and 5:[30,31]

$$\chi_{//} = \frac{N\beta^2}{kT} \tag{4}$$

$$\chi_\perp = \frac{N\beta^2}{4kT}\left(2+\frac{6\lambda}{\Delta E}\right)^2 + \frac{3N\beta^2}{\Delta E+\lambda/2} + \frac{3N\beta^2}{\Delta E+\lambda/2} \tag{5}$$

where λ is a spin-orbit coupling constant, ΔE transition energy, N Avogadro's number, B Bohr magneton, k Boltzmann constant, and T temperature.

The value of ΔE is determined by Eq. 6 on the assumption[32] that λ is 400 cm^{-1}, which is 75% of that for the free Co(II) ion.

$$\Delta E = \frac{6\lambda}{g_\perp - g_e} \tag{6}$$

where the $g_\perp$ value was determined to be 3.32 from ESR spectra. From Eq. 6, ΔE was estimated to be 1800 cm^{-1}. Anisotropic magnetic susceptibilities at various temperatures were calculated from Eqs. 5 and 6 by using these ΔE and λ various.[31] Average magnetic susceptibilities χ at various temperature were calculated from Eq. 7 using $\chi_{//}$ and $\chi_\perp$.

$$\chi = \frac{1}{3}\chi_{//} + \frac{2}{3}\chi_\perp \tag{7}$$

The temperature dependence of the average magnetic susceptibility is in agreement with the experimental data shown Fig. 5. Therefore, the temperature dependence of χ_M is mainly ascribed to the spin-orbit coupling of Co(II) itself rather than the antiferromagnetic interaction between TPP-Co(II) molecules.

PolyAOTPP-Co(II): The temperature dependences of χ_M^{-1} and μ_{eff} of polyAOTPP-Co(II) are shown in Fig. 6. The straight line covering the high temperature range of the χ_M^{-1}-temperature relation intersects above the origin, indicating that χ_M obeys the Curie-Weiss law with $\theta=-190$ K. The magnetic moment of polyAOTPP-Co(II) was 2.58 BM, being smaller than that of TPP-Co(II)(2.83 BM). Moreover, the former decreased more markedly with lowering the temperature than the latter. This result shows that the antiferromagnetic interaction as well as anisotropic susceptibilities caused by the spin-orbital coupling should be involved in the magnetic behavior of polyAOTPP-Co(II). Accordingly, the temperature-dependence of magnetic susceptibility involving both factors was estimated. The theoretical temperature dependence χ_M^{-1} was found to be in better agreement with the experimental data by using the spin-spin interaction between three Co(II) ions rather than two Co(II) ions. Equations 4 and 5 were corrected by taking into account an antiferromagnetic interaction between three Co(II) ions as in Eqs. 8 and 9:[33]

$$\chi_{//} = \frac{N\beta^2}{3kT}\frac{\exp(3x)+5}{\exp(3x)+1} \tag{8}$$

$$\chi_\perp = \frac{1}{3}\frac{N\beta^2}{3kT}\left(2+\frac{6\lambda}{\Delta E}\right)\frac{\exp(3x)+5}{\exp(3x)+1} + \frac{3N\beta^2}{\Delta E+\lambda/2} + \frac{3N\beta^2}{\Delta E-\lambda/2} \tag{9}$$

where $x=-J/kT$.

In this calculation, λ and ΔE were assumed to be the same as those used in Eqs. 4 and 5, because the remarkable wavelength changes in these values between TPP and poly AOTPP was not found in UV-visible absorption and g values in ESR, respectively. The temperature dependence of the average $\bar{\chi}$ was estimated by using various coupling constants for antiferromagnetic interaction. Results are shown in Fig. 7. The best fit between theoretical and experimental curves was obtained with $J=-45$ cm^{-1}. Since polyAOTPP-Co(II) is considered to have various sites of different J values, this $J=-45$ cm^{-1} is an average of various J values.

TPP-Fe(III)Cl and PolyAOTPP-Fe(III)Cl: The temperature dependences of χ_M^{-1} and μ_{eff} of TPP-Fe(III)Cl are shown in Fig. 8. The straight line for the χ_m^{-1}-temperature relationship intersects the ordinate above the origin, indicating that χ_M obeys the Curie-Weiss law with $\theta=-11$ K. Since the ESR spectrum of TPP-Fe(III)Cl shows the high-spin d^5 config-

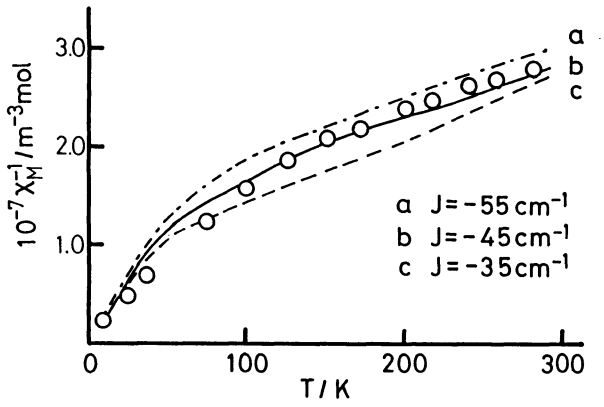


Fig. 7. Theoretical curves for the temperature dependence of the magnetic susceptibility of polyAOTPP-Co(II) with various antiferromagnetic interaction. $J=-55$ cm^{-1}, (b) $J=-45$ cm^{-1}, (c) $J=-35$ cm^{-1}.

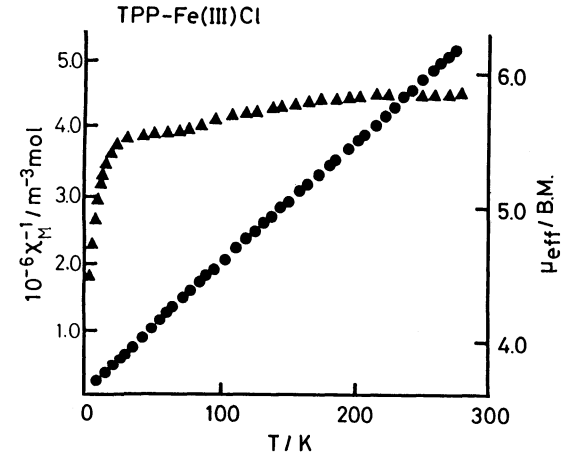


Fig. 8. Temperature dependence of χ_M^{-1} and μ_{eff} of TPP-Fe(III)Cl.

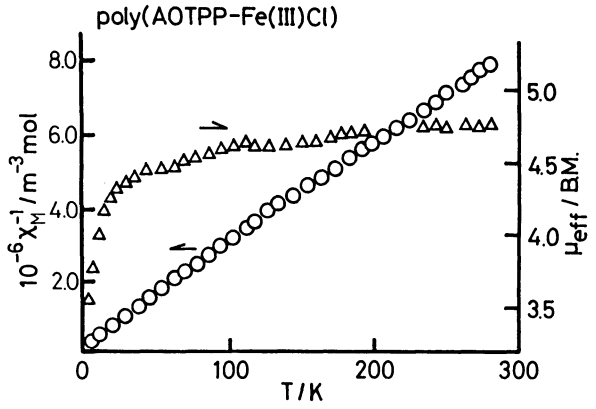


Fig. 9. Temperature dependence of χ_M^{-1} and μ_{eff} of polyAOTPP-Fe(III)Cl.

uration, anisotropic magnetic susceptibility due to the spin-orbit coupling interaction might be reasonably removed from the origin of deviation of the temperature dependence of χ_M^{-1} from the Curie law. Accordingly, the deviation is ascribed to the antiferromagnetic interaction. The magnetic moment of 5.82 B.M. is smaller than 5.92 B.M. of the spin-only value of d^5-high spin configuratic,[33] supporting that there are weak antiferromagnetic interaction.

The temperature dependences of χ_M^{-1} and μ_{eff} of polyAOTPP-Fe(III)Cl are shown in Fig. 9. The straight line for χ_M^{-1}-temperature relation intersects above the origin, indicating that χ_M^{-1} obeys the Curie-Weiss law with $\theta=-20$ K. The magnetic moment of polyAOTPP-Fe(III)Cl was 4.90 B.M. at room temperature, being smaller than that of TPP-Fe(III)Cl. Since TPP-Fe(III)Cl moieties bound to a polymer chain are considered to have various antiferromagnetically interacting sites, the temperature dependence of χ_M was apparently simulated by Eq. 10 derived for paramagnetic compound with exchange interaction of J on the assumption of the two paramagnetic sites with J_1 and J_2 as primary approximation.[34]

$$\chi_M=\sum_i\left(\frac{P_iNg^2\beta^2}{kT}\right)\frac{55+30x^{10}+14x^{18}+5x^{14}+x^{18}}{11+9x^{10}+7x^{18}+5x^{14}+3x^{18}+x^{30}} \quad (10)$$

where $x=\exp(-J_i/kT)$ and P_i indicates molar fraction of site occupancy with J_i.

The temperature dependence of χ_M^{-1} for polyAOTPP-FeCl(III)Cl was best simulated using the ratio of $P_1:P_2=42:58$ for the sites with $J_1=-50$ cm^{-1} and $J_2=0$ cm^{-1}, respectively. The reason why polyAOTPP-Fe(III)Cl has larger antiferromagnetic interaction than TPP-Fe(III)Cl might be ascribed to the fact that the porphin moieties are forced to collect near the chain.

Oxygen Adsorption of PolyAOTPPCo(II). The temperature dependences of χ_M^{-1} and μ_{eff} of TPP-Co(II) and polyAOTPP-Co(II) under 20 mmHg (1 mmHg≈133.322 Pa) of O_2 are shown in Figs. 10

and 11, respectively. These temperature dependences of χ_M^{-1} and μ_{eff} of TPP-Co(II) were not different from those in the absence of O_2, indicating that there is no special interaction between O_2 and the Co(II) ion.

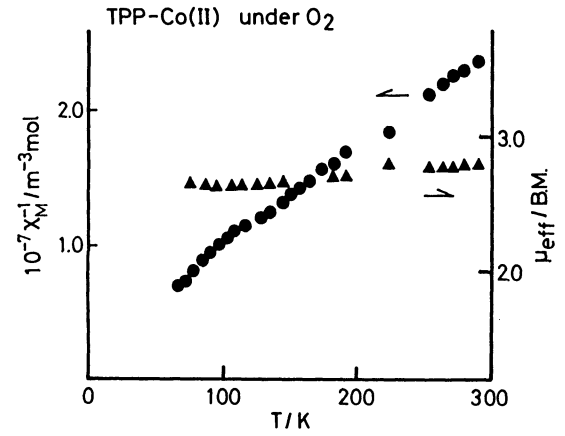


Fig. 10. Temperature dependence of χ_M^{-1} and μ_{eff} of TPP-Co(II) in the presence of molecular oxygen.

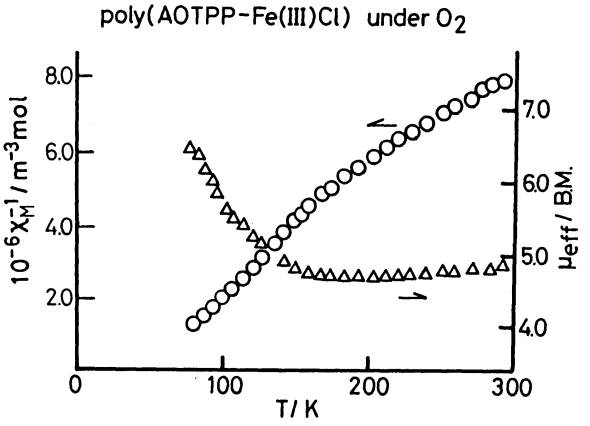


Fig. 11. Temperature dependence of χ_M^{-1} and μ_{eff} of polyAOTPP-Co(II) in the presence of molecular oxygen.

The temperature dependences of χ_M^{-1} and μ_{eff} of polyAOTPP-Co(II) under 20 mmHg O_2 was not different from those in the absence of O_2 at temperatures higher than 250 K, but they were markedly different from that in the absence of O_2 below 200 K (Fig. 6). Magnetic moment μ_{eff} increased from 2.5 BM to 3.3 BM with lowering the temperature from 180 K to 70 K. In order to make clear the origin of the abnormal behavior of the magnetic susceptibility under O_2 at low temperature, the O_2 pressure dependence of weight at 77 K was measured at various pressures of O_2 using a magnetic balance. The weight increased on increasing the pressure of O_2, and became a limiting value at pressures higher than 70 mmHg, in which the ratio of O_2 to Co(II) ion is almost 1.0. The pressure dependence of the adsorbed O_2 shows a Langmuir type isotherm curve. This result shows that there is special interaction between Co(II) and O_2. The ESR spectrum of polyAOTPP-Co(II) was measured in the presence of O_2 and compared with that in vacuum, as shown in Fig. 12. The ESR spectrum of polyAOTPP-Co(II) under O_2 shows the appearence of a new absorption band at 3350 G (g=2.01) in addition to that in the absence of O_2. The intensity of the new resonance line increased on lowering the temperature. Similar ESR spectra have been observed in oxygen-containing samples of tetrakis(*p*-methylphenyl)-porphine and tetrakis(*p*-methoxyphenyl)porphine in toluene-glass with *N*-substituted imidazole and amine,[24] and have been ascribed to the O_2 adduct prepared by chemical adsorption of O_2 on five-coordinated amine-Co(II) complex.[24,35] Since the ESR spectrum of polyAOTPP-Co(II) in vacuo showed the presence of the five-coordinated TPP-Co(II) moieties, the new resonance line at 3350 gauss in the presence of O_2 can reasonably be ascribed to the O_2 adduct of the TPP-Co(II) moiety. For an understanding of the strength of the adsorption of O_2,

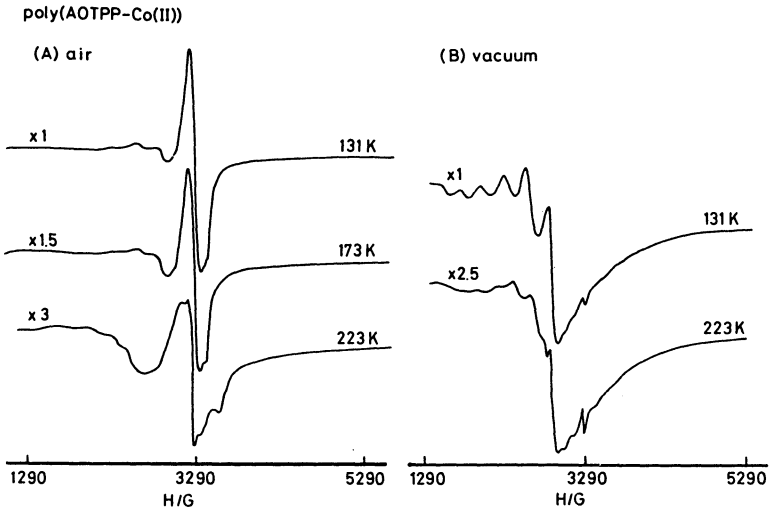


Fig. 12. ESR spectrum of polyAOTPP-Co(II) under molecular oxygen at 77 K.

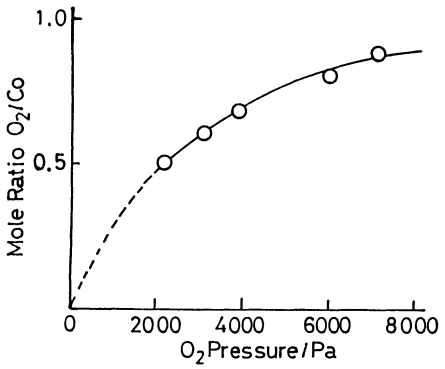


Fig. 13 Oxygen adsorption of polyAOTPP-Co(II) as a function of oxgen pressure at 77 K. (——) Eye-guided line.

the oxygen-pressure dependence of weight of polyAOTPP-Co(II) was measured at various temperatures under 20 mmHg of O_2. The weight of O_2 adsorbed depended on the temperature and reversibly changed on varying the temperature. Therefore, the following relation is considered on the adsorption.

$$\mathrm{Co(II)\cdots O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Co(II)} + \mathrm{O_2} \tag{11}$$

$$k = \frac{k_1}{k_{-1}} = \frac{[\mathrm{Co(II)}][\mathrm{O_2}]}{[\mathrm{Co(II)}\cdots\mathrm{O_2}]} = \frac{[\mathrm{Co(II)}]\,P_{\mathrm{O_2}}}{[\mathrm{Co(II)}\cdots\mathrm{O_2}]} \tag{12}$$

Since the amount of oxygen adsorbed is estimated to be less than 3% of total O_2 of the measuring system even if the TPP-Co(II) moieties adsorb completely O_2, P_{O_2} can resonably be regarded as constant in all experiments. The temperature dependence of K/P_{O_2} is regarded as that of K. Thus, the binding energy for O_2-adsorption was estimated to be 24 kJ mol^{-1} from the temperature dependence of K/P_{O_2}, which corresponds to the chemical adsorption.

Similarly, POTPP-Co(II) adsorbs O_2. Since TPP-Co(II) does not adsorb O_2, it is assumed that the ester group plays an important role for the chemical adsorption of O_2.

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