

## Magnetic Properties of Poly[5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatocopper(II)] and Poly[5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinosilver(II)]

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**ABSTRACT:** The magnetic properties of polymers containing tetraphenylporphin-Cu(II) (TPP-Cu(II)) or tetraphenylporphin-Ag(II) (TPP-Ag(II)) in the side chains were studied by the magnetic susceptibility ( $\chi_M$ ) measurement (4—300 K) and ESR spectroscopy. The values of  $\chi_M$  for the polymer containing TPP-Cu(II) were found to obey the Curie-Weiss law, and a magnetic moment showed the occurrence of a weak antiferromagnetic interaction between Cu(II) ions. The values of  $\chi_M$  for the polymer containing TPP-Ag(II) did not obey any simple equation such as the Curie-Weiss law or Bleaney-Bowers equation and simulation of temperature dependence of  $\chi_M$  showed the presence of strongly interacting sites. This strong interaction may possibly arise from a hyperexchange interaction through C=O groups situated among the Ag(II) ions. An ESR study also supported the presence of this interaction between the side groups in a polymer chain.

**KEY WORDS** Metalloporphin Polymer / Magnetic Property / Magnetic Susceptibility / Electron Exchange / ESR / Antiferromagnetic Interaction /

Organic polymers containing paramagnetic species may provide a new class of magnetic materials owing to the magnetically long range ordering of unpaired electrons through spin-spin interactions. To our knowledge, only a few studies have been reported on the magnetic properties of polymers.<sup>1,2</sup> We discovered the possibility of the existence of such an interaction from measurements of magnetic susceptibility and ESR spectrum of polymers containing nitroxyl groups in their side chains.<sup>1</sup> Kinoshita *et al.*<sup>2</sup> showed that an iron(II) complex of a polymer obtained from the condensation of 2,6-pyridinedicarbaldehyde and hexamethylenediamine was ferromagnetic.

Recently, we succeeded in the polymerization of an acrylic compound containing

tetraphenylporphin and spectroscopic data suggested the occurrence of an interaction between the porphin groups.<sup>3</sup> Accordingly, polymers having paramagnetic metalloporphin groups may provide a source of new class of magnetic materials.

In this paper, magnetic properties and ESR spectra of polymers containing tetraphenylporphinato-Cu(II) or tetraphenylporphinato-Ag(II) in their side chains are compared with those of the corresponding metalloporphins so as to demonstrate polymer effects on magnetic property.

### EXPERIMENTAL

#### *Materials*

5-(4-Acryloyloxyphenyl)-10,15,20-tri-

phenylporphin (AOTPP) and its polymer (poly(AOTPP)) were prepared as described previously.<sup>3</sup> The molecular weight of poly(AOTPP) was 8000–10000. Tetraphenylporphin (TPP) was synthesized according to Alder *et al.*<sup>4</sup> Tetraphenylporphinatocopper(II) (TPP-Cu(II)) was prepared according to Dorough *et al.*<sup>5</sup> in a 67% yield.

Tetraphenylporphinatosilver(II) (TPP-Ag(II)) was prepared according to Dorough *et al.*<sup>5</sup> in a 79% yield.

*Poly[5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatocopper(II)] [poly(AOTPP-Cu(II))]*. Poly(AOTPP) (0.24 g) and anhydrous copper acetate (0.8 g) were dissolved in 100 ml of chloroform–methanol (9:1). The solution was refluxed for 6 h, concentrated to half its original volume with a rotating evaporator, and then filtered. The filtrate was washed three times with water. The polymer was isolated from the organic layer by evaporation, dried in a vacuum oven, dissolved in benzene, and freeze-dried. Yield, 0.22 g. Found: C, 75.04%; H, 4.66%; N, 6.90%; Cu, 8.26%. Calcd for  $C_{47}H_{30}O_2N_4Cu$ : C, 75.64%; H, 4.05%; N, 7.51%; Cu, 8.51%.

*Poly[5(4-acryloyloxyphenyl)-10,15,20-triphenylporphinatosilver(II)] (poly(AOTPP-Ag(II)))*. Poly(AOTPP) (0.21 g) and silver(II) acetate (0.71 g) were dissolved in 200 ml of tetrahydrofuran. The solution was refluxed for 9 h and the solvent was removed by distillation. Chloroform was added to the residue to dissolve the polymer and the mixture was filtered. The filtrate was washed with water and evaporated. The residual polymer was dried in vacuum, dissolved in benzene, and freeze-dried. Yield, 0.22 g. Found: C, 71.66%; H, 4.67%; N, 6.14%; Ag, 10.50%. Calcd for  $C_{47}H_{30}N_4Ag$ : C, 71.40%; H, 3.82%; N, 7.09%; Ag, 13.64%.

#### Measurements

ESR was measured with a JEOL Model JES FE 1X ESR spectrometer with a 100 kHz modulator. The *g*-values were estimated using

MnO as a standard sample.

Gram magnetic susceptibility ( $\chi_g$ ) was determined by the Gouy method at room temperature. The temperature dependence of the  $\chi_g$  was determined by the Faraday method, using a Cahn electric balance in a temperature range from 4 K to 300 K. The molar magnetic susceptibilities ( $\chi_M = \chi_g \times M$ , *M*, molecular weight of TPP-metal or monomer unit of the polymer) were corrected for diamagnetic contributions from the ligands; the  $\chi_{dia}$  values for TPP and poly(AOPTT) were  $-435 \times 10^{-6}$  and  $-486 \times 10^{-6}$  cgsemu, respectively.

The effective magnetic moment ( $\mu_{eff}$ ) was calculated from the following equation:

$$\mu_{eff} = 2.83 \sqrt{\chi_M \cdot T}$$

The diffusion reflection spectra of the complexes were measured in a region from 400 to 1000 nm on a Hitachi 323 Recording Spectrometer equipped with a reflection attachment.

## RESULTS AND DISCUSSION

### *TPP-Cu(II) and poly(AOTPP-Cu(II))*

The values of  $\chi_g$  and  $\mu_{eff}$  of TPP-Cu(II) at room temperature were  $1.13 \times 10^{-6}$  cgsemu

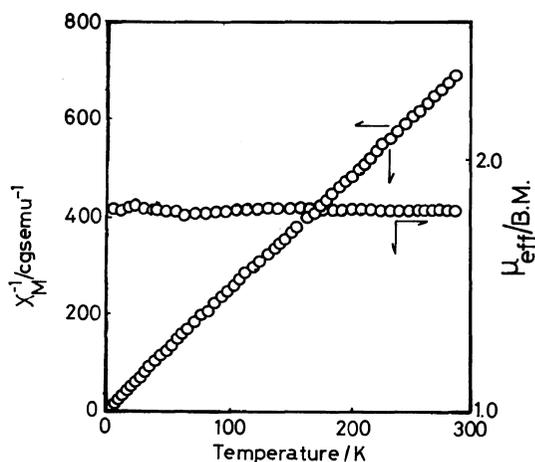


Figure 1. Temperature dependence of magnetic susceptibility and magnetic moment of TPP-Cu(II).

and 1.83 B.M., respectively. The temperature dependences of  $\chi_M^{-1}$  and  $\mu_{\text{eff}}$  are shown in Figure 1. Since the straight line for the  $\chi_M^{-1}$ -temperature relationship passes through the origin and  $\mu_{\text{eff}}$  is constant independent of temperature,  $\chi_M$  obeys the Curie law ( $\chi_M = C/T$ ,  $C = \text{constant}$ ), indicating that no interaction occurs between the unpaired electrons of Cu(II).<sup>6</sup> The values of  $\chi_M^{-1}$  of the AOTPP-Cu(II) obey the Curie law and no influence of the methacryloyl group on  $\chi_M^{-1}$  was found.

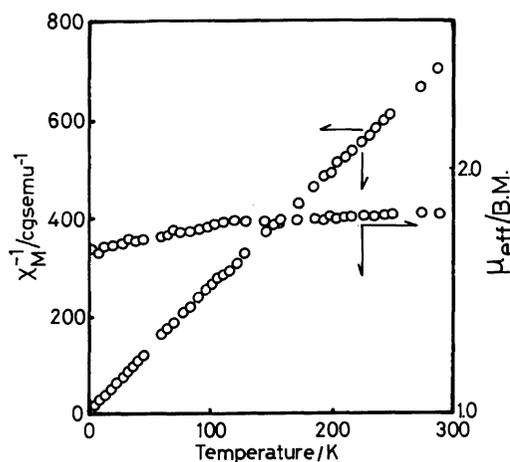


Figure 2. Temperature dependence of magnetic susceptibility and magnetic moment of poly(AOTPP-Cu(II)).

The values of  $\chi_g$  and  $\mu_{\text{eff}}$  of poly(AOTPP-Cu(II)) at room temperature were  $1.16 \times 10^{-6}$  cgsemu and 1.18 B.M., respectively. The temperature dependence of  $\chi_M^{-1}$  and  $\mu_{\text{eff}}$  are shown in Figure 2. The straight line for the  $\chi_M^{-1}$ -temperature relationship intersects the ordinate slightly above the origin, indicating that  $\chi_M$  obeys the Curie-Weiss law ( $\chi_M = C/(T-\theta)$ )<sup>6</sup> with  $\theta = -9.8$  K. This suggests a weak antiferromagnetic interaction between the TPP-Cu(II) groups in the polymer. The  $\mu_{\text{eff}}$  of poly(AOTPP-Cu(II)) was somewhat smaller than that of TPP-Cu(II) and decreased at lower temperatures, indicating the occurrence of an antiferromagnetic interaction between the TPP-Cu(II) groups in a polymer chain.

The ESR spectrum of poly(AOTPP-Cu(II)) was compared with that of TPP-Cu(II) and anisotropic  $g$  factors ( $g_{\parallel}$  and  $g_{\perp}$ ) were observed in the TPP-Cu(II), while a symmetrical line of an isotropic  $g$  factor was observed in poly(AOTPP-Cu(II)) (Figure 3). These results indicate that a rapid exchange of electron spin through the side chain in the polymer creates an average dipolar field on any electron zero. The presence of the exchange interaction in poly(AOTPP-Cu(II)) was supported by the ESR spectrum, indicating the distance between the Cu(II) ions in the polymer to be shorter than that in TPP-Cu(II).

To clarify the origin of the interaction, the

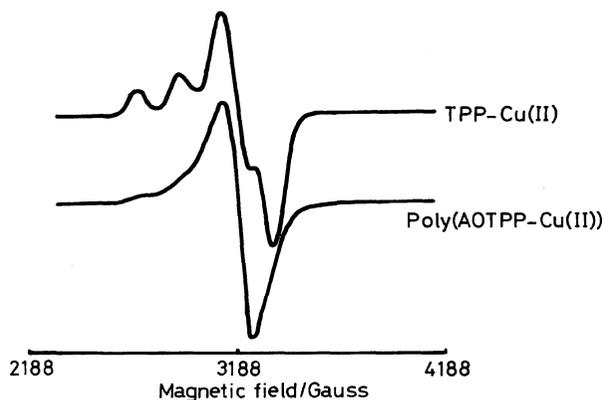
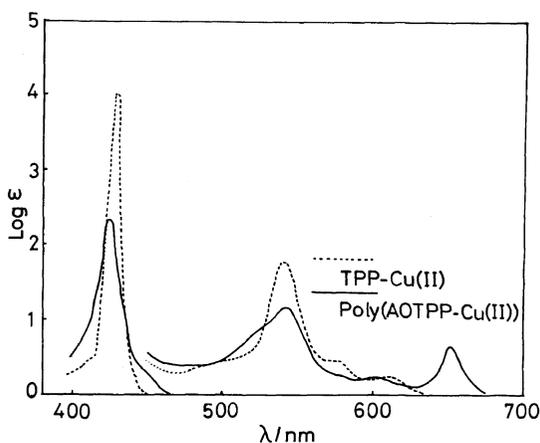


Figure 3. ESR spectra of TPP-Cu(II) and poly(AOTPP-Cu(II)) powders at room temperature.

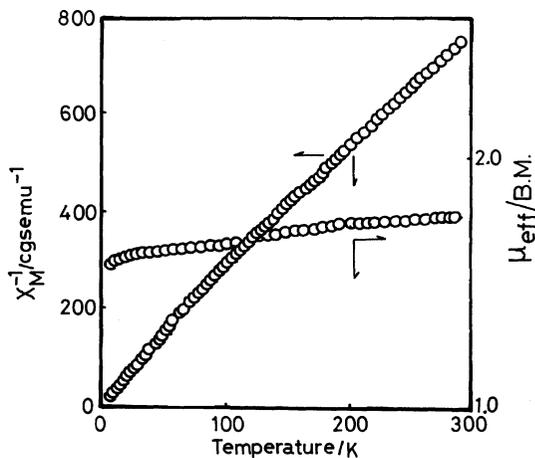


**Figure 4.** Visible spectra of TPP-Cu(II) (-----) and poly(AOTPP-Cu(II)) (—) in chloroform at room temperature.

visible spectrum of a chloroform solution of poly(AOTPP-Cu(II)) was compared with that of TPP-Cu(II), as shown in Figure 4. In poly(AOTPP-Cu(II)), hypochromism was observed at 420 and 550 nm, and hyperchromism and a bathochromic shift were observed at 620 nm. The same at 620 nm was also observed in the reflection spectra in the solid state. The visible spectra and ESR measurements showed a stacking between the porphin rings in the polymer, which is considered unfavorable in TPP. The antiferromagnetic interaction between the Cu(II) ions may possibly arise as a result of the approaching Cu(II) ions because of the stacking of porphin rings in the polymer.

#### *TPP-Ag(II) and Poly(AOTPP-Ag(II))*

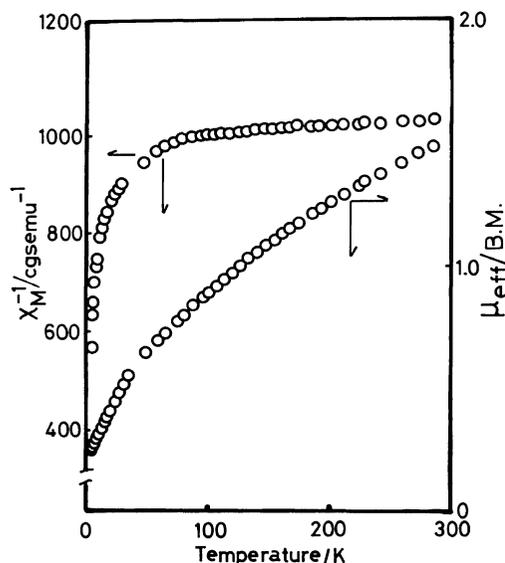
The values of  $\chi_g$  and  $\mu_{\text{eff}}$  of TPP-Ag(II) were  $1.14 \times 10^{-6}$  cgsemu and 1.79 B.M., respectively. The temperature dependences of  $\chi_M^{-1}$  and  $\mu_{\text{eff}}$  are shown in Figure 5. The straight line for the  $\chi_M^{-1}$ -temperature relationship intercepts the ordinate in the positive part, indicating that  $\chi_M$  obeys the Curie-Weiss law with  $\theta = -22.4\text{K}$  and there is a weak antiferromagnetic interaction between Ag(II) ions. The  $\mu_{\text{eff}}$  gradually decreased as the temperature was lowered, indicating an intermolecular



**Figure 5.** Temperature dependence of magnetic susceptibility and magnetic moment of TPP-Ag(II).

antiferromagnetic interaction.

The values of  $\chi_g$  and  $\mu_{\text{eff}}$  of poly(AOTPP-Ag(II)) at room temperature were  $0.304 \times 10^{-6}$  cgsemu and 1.49 B.M., respectively, and much smaller than those of TPP-Ag(II). The temperature dependence of  $\chi_M^{-1}$  and  $\mu_{\text{eff}}$  are shown in Figure 6. The  $\mu_{\text{eff}}$  decreased at lower temperatures, thus indicating the occurrence of an antiferromagnetic interaction possibly as a result of the exchange between the electron spins of Ag(II) ions attached to the polymer. However, since the temperature dependence of



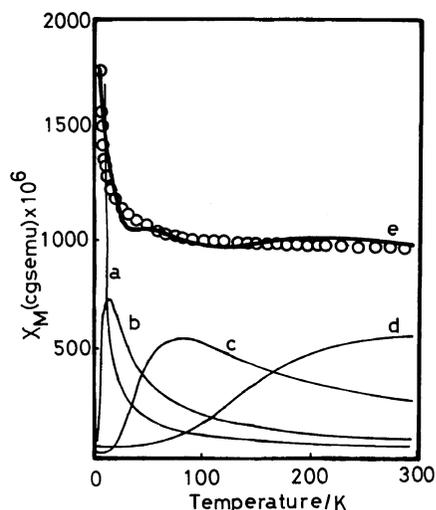
**Figure 6.** Temperature dependence of magnetic susceptibility and magnetic moment of poly(AOTPP-Ag(II)).

$\chi_M^{-1}$  obeyed no simple equation such as the Curie-Weiss law or Bleaney-Bowers equation, poly(AOTPP-Ag(II)) apparently contained various sites of different antiferromagnetic interactions as in heteropolycyber compounds.<sup>7</sup> The remarkable increase in  $\chi_M$  below 10 K also suggests non-interacting paramagnetic sites ( $J=0$ ). Temperature variation in  $\chi_M$  of poly(AOTPP-Ag(II)) was thus simulated by the following equation, assuming four paramagnetic sites of different antiferromagnetic interactions ( $J_1, J_2, J_3,$  and  $J_4$ ) as a primary approximation, although the polymer should have various antiferromagnetic sites.

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \sum_{i=1}^4 \left( \frac{K_i \times 1/100}{1 + \frac{1}{3} e^{J_i/T}} \right)$$

where  $K_i$  indicates % of site occupancy.<sup>8</sup>

The simulation qualitatively explains the complicated nonlinear temperature dependence of  $\chi_M$  on the basis of  $J_1 = -20$  K,  $J_2 = -120$  K,  $J_3 = -480$  K, and  $J_4 = 0$  K. The best ratio for the simulation with four sites was  $K_1 :$



**Figure 7.** Temperature dependence of magnetic susceptibility of poly(AOTPP-Ag(II)) and its simulation.  $\circ\circ$ , observed data; e, simulated data. a, b, c, and d are theoretical curves for  $J = -20$  K,  $-120$  K,  $-480$  K, and 0 K, respectively.

$K_2 : K_3 : K_4 = 4.5 : 19.5 : 74.0 : 2.0$  (Figure 7). From the results, poly(AOTPP-Ag(II)) is considered to be a new type of material since the organic polymer showed strong antiferromagnetism.

The strong interaction in poly(AOTPP-Ag(II)) was also supported by a comparison of the ESR spectrum with that of TPP-Ag(II) (Figure 8). Anisotropic  $g$  factors ( $g_{\perp}$  and  $g_{\parallel}$ ) were observed in TPP-Ag(II), while a symmetrical line of an isotropic  $g$  factor was observed even with the powdered polymer, indicating that a rapid exchange of electron spins through the side chains in the polymer creates an average dipolar field on any electron zero.

The visible spectrum of poly(AOTPP-Ag(II)) was compared with that of TPP-Ag(II) so as to determine the origin of this strong interaction (Figure 9). In the polymer, hypochromism at 420 and 540 nm and a bathochromic shift from 580 and 610 nm to 605 and 660 nm, respectively, were observed. The differences in the visible spectra of poly(AOTPP-

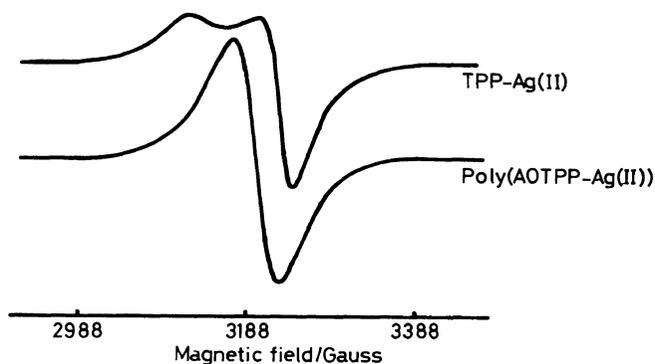


Figure 8. ESR spectra of TPP-Ag(II) and poly(AOTPP-Ag(II)) powders at room temperature.

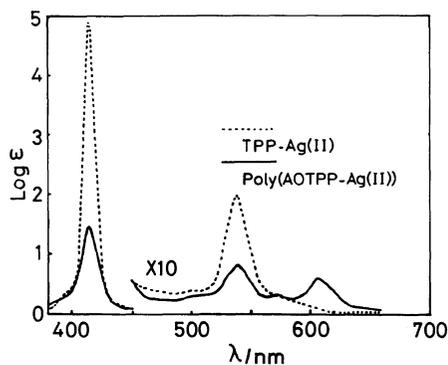


Figure 9. Visible spectra of TPP-Ag(II) (-----) and poly(AOTPP-Ag(II)) (—) in chloroform at room temperature.

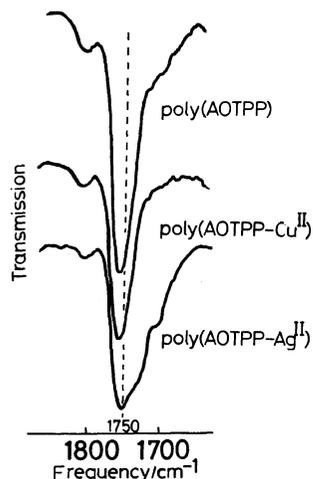


Figure 10. IR spectra of poly(AOTPP), poly(AOTPP-Cu(II)), and poly(AOTPP-Ag(II)) (KBr disc).

Ag(II)) and AOTPP-Ag(II) were similar to those of poly(AOTPP) and AOTPP as well as those of poly(AOTPP-Cu(II)) and AOTPP-Cu(II). Accordingly, the interaction between porphyrin rings might be a factor leading to the exchange interaction. However, it is difficult to explain why the interaction is so much larger in poly(AOTPP-Ag(II)) than poly(AOTPP-Cu(II)). Even though the electronic configuration of Ag(II) is similar to that of Cu(II). Consequently, a comparison was made of IR spectra of poly(AOTPP), poly(AOTPP-Cu(II)), and poly(AOTPP-Ag(II)) (Figure 10). The absorption of the C=O group at about  $1720\text{ cm}^{-1}$  in poly(AOTPP-Ag(II)) was broader than those in other polymers, indicating the presence of a complex between the C=O

group and Ag(II) ion. The exchange interaction between the Ag(II) ions may be possible through their formation of a complex with the carbonyl group. The antiferromagnetic exchange interaction may possibly arise from a hyperexchange interaction through the C=O group between Ag(II) ions.

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REFERENCES

1. M. Kamachi, M. Tamaki, Y. Morishima, S. Nozakura, W. Mori, and M. Kishita, *Polym. J.*, **14**, 363 (1982).
2. T. Kanno and M. Kinoshita, The 47th Spring Meeting of Chemical Society of Japan, 1983, 2B44, p. 38.
3. M. Kamachi, H. Akimoto, and S. Nozakura, *J. Polym. Sci., Polym. Phys. Ed.*, in press.
4. A. D. Alder, F. Longs, J. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
5. G. D. Dorough, J. R. Miller, and F. M. Heunneken, *J. Am. Chem. Soc.*, **73**, 4315 (1951).
6. A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, London, 1968, p 213.
7. C. J. O'Connor, "Progress in Inorganic Chemistry," Vol. 28, C. J. O'Connor, Ed., John-Wiley, New York, 1980, p 257.
8. Reference 6, p 75.