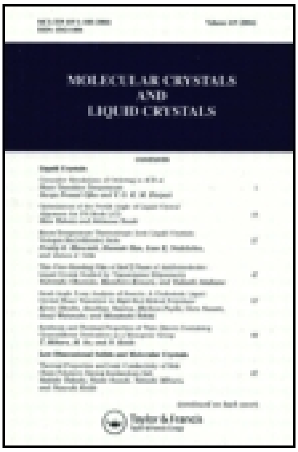

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MAGNETIC BEHAVIOR OF POLYMERS CONTAINING PARAMAGNETIC METALLOPORPHYRINS

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Abstracts Polymers containing tetraphenylporphyrin moieties in their side chains were prepared by radical polymerizations of 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphine(AOTPP), 5-(4-methacryloyloxyphenyl)-10,15,20-triphenylporphine(MAOTPP), 5-(4-acrylamidephenyl)-10,15,20-triphenylporphyrin (AATPP), 5-(4-methacrylamidephenyl)-10,15,20-triphenylporphyrin(MAATPP), 5-(4-vinylphenyl)-10, 15, 20-triphenylporphyrin(VTPP), and by polymerizations of 5-(4-ethynylphenyl)-10,15,20-triphenyl porphyrin (ETPP) with rhodium catalyst ((bicyclo[2,2,1]hepta-2,5-diene)rhodium (I) dimer). The magnetic behavior of their silver (II) complexes was investigated by measuring their magnetic susceptibilities and ESR spectroscopy. Comparison of their magnetic susceptibilities shows that stronger antiferromagnetic interaction was observed in polymers with carbonyl group, and that the origin of the antiferromagnetic interaction is likely due to superexchange interaction through oxygen atoms of carbonyl group.

INTRODUCTION

Porphyrin and its derivatives play an important role in photochemical system and living system.[1-7] Accordingly, many studies on physicochemical properties of porphyrins, metalloporphyrins, and their derivatives have been reported so far.[1-7] Especially, an aggregate of porphyrin moieties has been paid attention from the points of molecular design of artificial photochemical system. Polymers containing metalloporphyrins in the side chains have been of interest as a precursor for the preparation of the artificial photochemical system. No homopolymers of vinyl monomers containing porphyrin moieties in their side chains had been reported but we fortunately obtained polymers of acrylate and methacrylate containing porphyrin moieties in the side chains by radical

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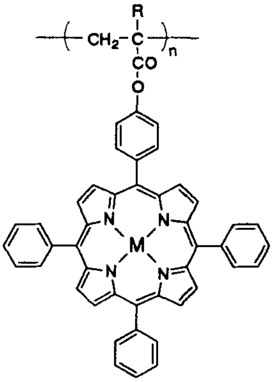
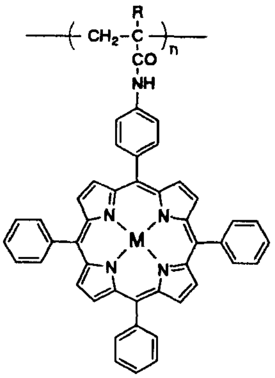
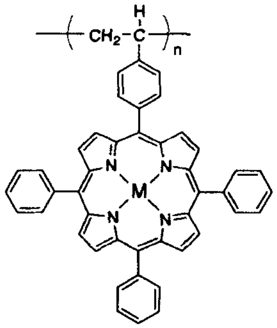
polymerizations of 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphine(AOTPP) and 5-(4-methacryloyloxyphenyl)-10,15,20-triphenylporphine(MAOTPP).[8,9] Hypochromism in the Soret band of porphyrin moieties of these polymers was clearly observed in the measurements of UV and visible spectra, indicating that there is an electronic interaction between porphyrin moieties in the polymers. Thus, we studied the magnetic properties of polymers containing paramagnetic metalloporphyrins in the side chains (**1** and **2**) such as Ag(II), Cu(II) and VO(II). In the course of the study of the magnetic properties of polymers containing paramagnetic species in the side chains,[9-12] we came across the fact that antiferromagnetic interaction takes place in polyAOTPP-Ag^{II}. Accordingly, we considered that polymers having paramagnetic species in their side chains might be new magnetic materials, because an ordering of the spins of paramagnetic species through an exchange interaction of unpaired electrons is



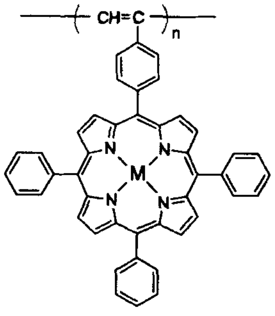
R=H AOTPP (1)
$=CH_3$ MAOTPP (2)



R=H AATPP (4)
$=CH_3$ MAATPP (5)



VTPP (3)



ETPP (6)

possible in the polymers.[1-3] In the extension of this work, we prepared other types of polymers containing tetraphenylporphynatometal ions (**3**-**6**)[13-15], where M(X) are Ag(II),Cu(II) and VO(II) and compared their magnetic properties to get information on the occurrence of magnetic interaction.

In this paper, preparations of the polymers and the magnetic behavior of their silver(II) complexes will be reported.

EXPERIMENTAL

PolyVTPP, polyAATPP, and polyMAATPP were obtained by radical polymerizations of the corresponding monomer, respectively, with AIBN at 60 °C for 60 h in benzonitrile. The polymers were isolated as purple solids by addition of methanol or hexane as precipitants. $\overline{M_w}$ and $\overline{M_n}$ were determined by GPC calibrated by standard polystyrene. A homopolymerization of ETPP was carried out in $CHCl_3$ or THF using commercially available (bicyclo[2,2,1]hepta-2,5-diene)rhodium(I) dimer (norbornadiene rhodium(I) dimer, $[Rh(NBD)Cl]_2$) as catalyst.[16] Polymer was isolated by addition of acetone and separated into THF-soluble and THF-insoluble polymers by extraction with THF. The crude THF-soluble polymer was purified by reprecipitation from THF-acetone for several times. The THF-insoluble polymer was washed with THF several times and dried *in vacuo*. Molecular weights of THF-soluble polymers were determined by GPC on the basis of standard polystyrene.

Measurements

UV-visible spectra were recorded on a Shimadzu UV-2100 spectrometer. IR spectra were recorded on a JASCO DS-402G spectrometer. 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 adapter (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 double fold Suprasil tubes. Gram magnetic susceptibility(χ_g) was determined by the Gouy method at room temperature. The temperature dependence of χ_g was determined by the Faraday method, using a Cahn RH electric balance in a temperature range from 4K to 300K.

RESULTS AND DISCUSSION

Characterization of the Polymers

Polymer **3**, in which tetraphenyl porphyrin (TPP) moieties directly joined to a main chain, was prepared by the radical polymerizations of the corresponding monomers with AIBN at 60 °C. High-molecular weight polymers (M_W >100000) were obtained. Polymers **4** and **5** in which porphyrin moieties are joined to a main chain through amide linkage were prepared by the radical polymerization of 5-(4-acrylamidephenyl)-10,15,20-triphenylporphyrin (AATPP) and 5-(4-methacrylamidephenyl)-10,15,20-triphenylporphyrin (MAATPP). In these radical polymerizations, the fact that addition polymerization of C=C bonds took place is clearly confirmed by the disappearance of absorption bands due to C=C bond in IR spectra of polymers and by agreement of elementary analysis between polymers and the corresponding monomers.

Typical example is shown in Figure 1.

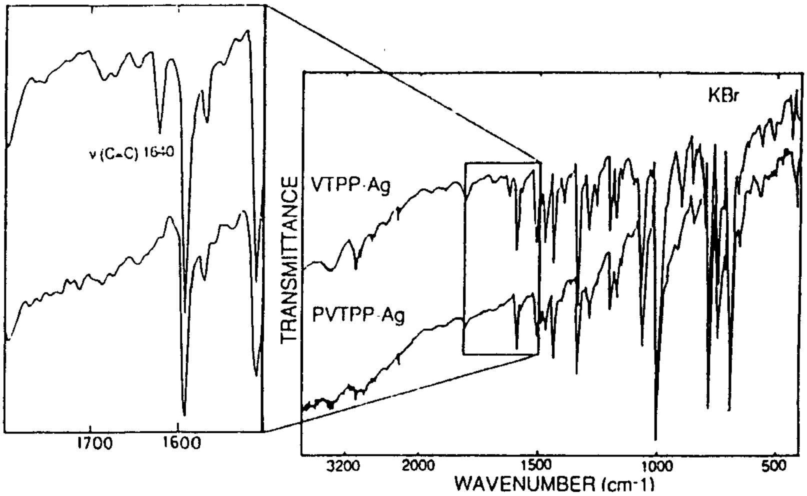


Figure 1 IR spectra of VTPP-Ag^{II} and polyVTPP-Ag^{II}

Polymer **6**, in which tetraphenylporphyrin moieties are directly joined to a polyene, was prepared by polymerizations of 5-(4-ethynylphenyl)-10,15,20-triphenyl porphyrin (ETPP) with rhodium catalyst ((bicyclo[2,2,1]hepta-2,5-diene)rhodium (I) dimer). The IR band of the monomer at 2110 cm^{-1} assignable to the stretching vibration mode of C≡C triple bond disappeared after polymerization. This finding indicates that the polymerization occurred though C≡C triple bond of ethynyl group. IR spectra of THF-insoluble polymer is the same as that of THF-soluble polymer.

Results of the polymerizations are shown in Table 1.

Table 1 Polymerization of Metalloporphyrin Monomers

Monomer	[Monomer]	Yield, %	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
VTPPAg^{II}	0.66	95.9^a	3.90×10^4	2.00
AATPPAg^{II}	0.60	12.3^a	4.20×10^3	1.03
MAATPPAg^{II}	0.43	20.8^a	5.80×10^3	1.54
ETPPAg^{II}	0.054	94.0^b	2.28×10^5 ^{c}	2.57

a) Polymerized in benzonitrile at 60 °C for 60 h.

b) Polymerized in THF at 30 °C for 1 h..

c) THF soluble part.

UV-visible spectra

All polymers have the Soret band at 411 nm and Q bands in the region from 500 to 700 nm. The Soret band of polymers is similar in the wave length to that of the corresponding monomers, but is smaller in the molecular extinction coefficient (ε) than that of corresponding monomers, respectively. A typical example is shown in Figure 2.

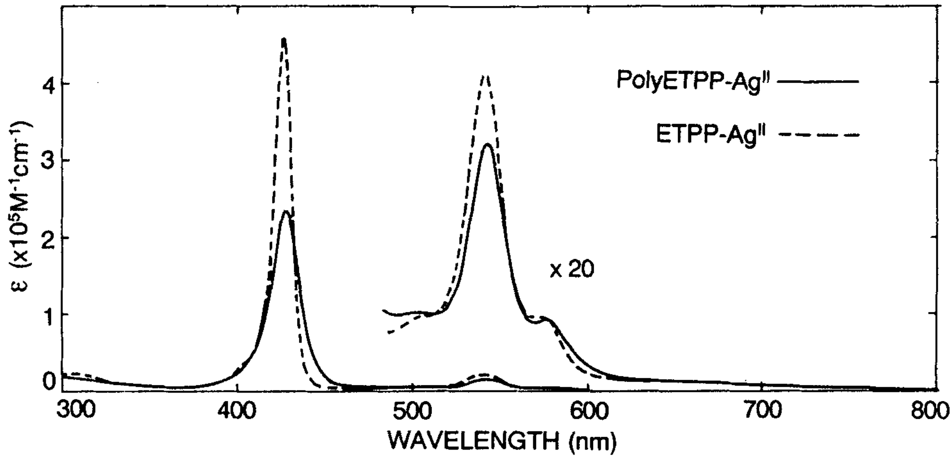


Figure 2 UV-visible absorption spectra of ETPP-Ag^{II} and polyETPP-Ag^{II}

The difference in the Soret bands between polymers and the corresponding monomers is reasonably ascribed to the hypochromism, which suggests that there are some electronic interaction between TPP moieties in the polymer.[19] The interaction is supported by observation of electron spin exchange interaction among Ag^{II}-complexes in the polymer. Bulky TPP moieties bound to a polymer chain are possibly forced to make some interactions due to their close approach.

ESR spectra of polycrystalline state

ESR spectra of polymers showed a symmetrical single line of an isotropic g-factor even in the measurement of powder sample, while anisotropic g-factors was clearly observed in the spectra of the corresponding monomers. Typical example is shown in Figure 3, indicating that a rapid exchange of electron spins takes place in the polymer.

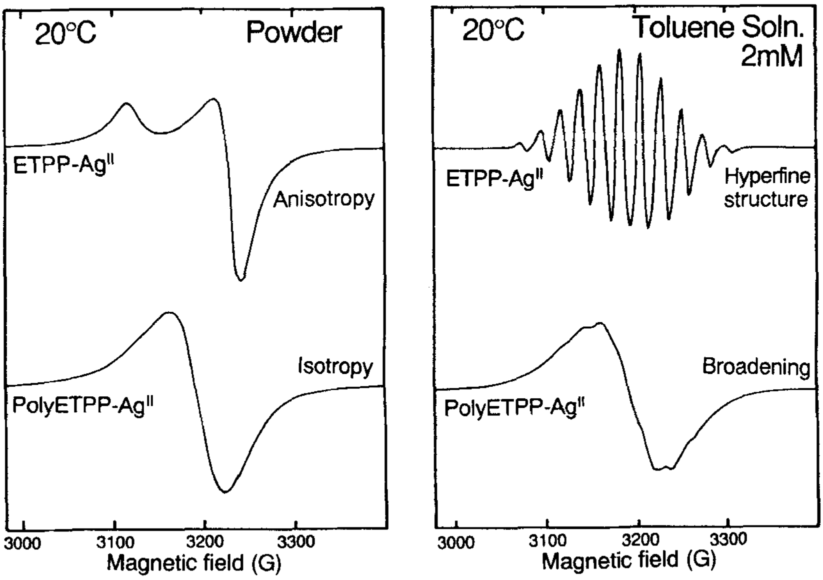


Figure 3 ESR spectra of ETPP-Ag^{II} and polyETPP-Ag^{II}

Magnetic properties

Antiferromagnetic behavior was observed in temperature dependence of magnetic susceptibility of polyAOTPP-Ag^{II} (Fig. 4), while the magnetic interaction was much weaker in AOTPP-Ag^{II}.[2] We previously suggested that the stronger antiferromagnetic interaction of polyAOTPP-Ag^{II} is likely due to a superexchange interaction through oxygen atoms of carbonyl group.[8] In order to confirm this suggestion, we have synthesized other polymers possessing paramagnetic metal complexes of tetraphenylporphyrin in their side chains. In polyVTPP-Ag^{II}, in which TPP moieties are directly joined to a polymer chain and no carbonyl group has in the polymer chain, the temperature dependence of magnetic susceptibility followed the Curie law (Fig. 4). This result suggests no interaction between TPP-Ag(II) molecules even in polymer. In polyAATPP-Ag^{II} and polyMAATPP-Ag^{II}, in which TPP moieties were joined to a polymer chain through amide linkage, antiferromagnetic interaction was clearly

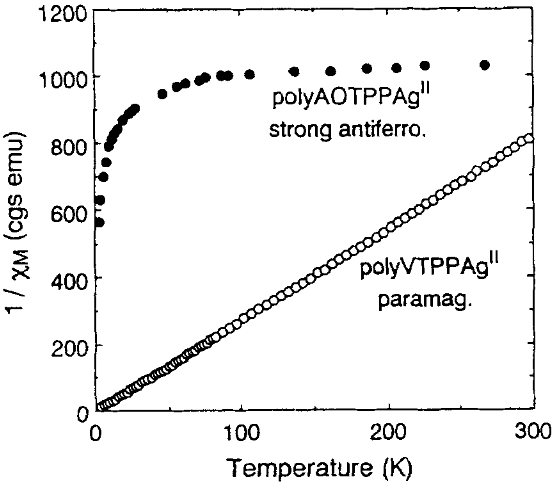


Figure 4 Temperature dependence of χ_m^{-1} of polyAOTPP-Ag^{II} (●) and polyVTPP-Ag^{II} (○).

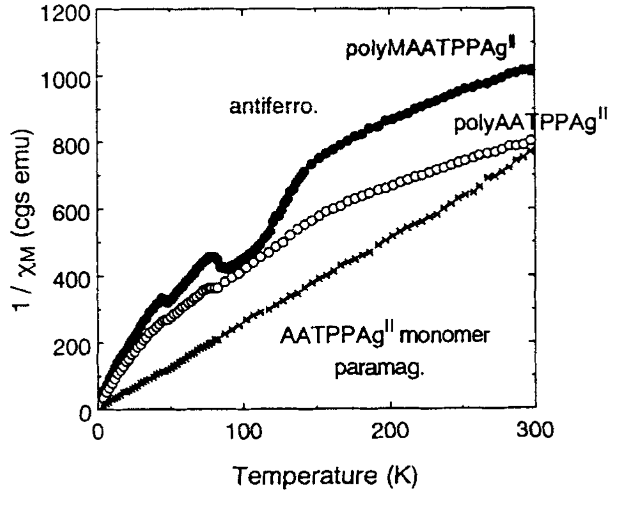


Figure 5 Temperature dependence of χ_m^{-1} of polyAATPP-Ag^{II} (○), polyMAATPP-Ag^{II}(●), and AATPP-Ag^{II} (monomer) (×).

observed in the temperature dependence of magnetic susceptibility (Fig. 5). Much weaker antiferromagnetic interaction (θ = ca. -70 K) was observed in the measurement of the temperature dependence of magnetic susceptibility of polyETPP-Ag^{II} in which main chain is composed of π-system and no carbonyl group is joined to main chain.

Comparison of the temperature dependence of magnetic susceptibility of different types of polymers support suggestion that the stronger antiferromagnetic interaction of polyAOTPP-Ag^{II} is likely due to a superexchange interaction through oxygen atoms of carbonyl group.[2]

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