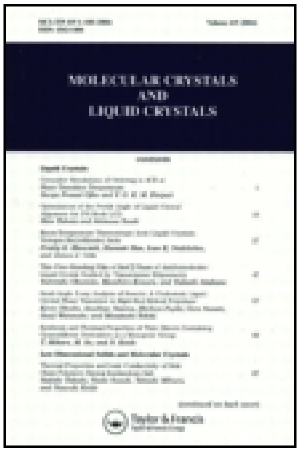

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MAGNETIC PROPERTIES OF POLYMERS CONTAINING PARAMAGNETIC METALLOPORPHYRINS IN THEIR MAIN CHAIN

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Abstract
Polymers containing paramagnetic metalloporphyrins in their main chains were prepared by condensation copolymerization of 5,10-bis(ethoxyphenyl)-15,20-bis(hydroxyphenyl)porphyrin (HETPP) with dibromomethane. Paramagnetic metal ions were introduced to porphyrin moieties. This type of polymer is expected to show novel magnetic behavior through both intra- and inter-molecular interactions. PolyHETPP-M (M = Ag^{II}, Cu^{II}, Co^{II}, or $V^{IV}O$) contains 5-10 HETPP units and is soluble in many organic solvents. Magnetic properties of polymer and monomer were investigated by measurements of magnetic susceptibilities. In the course of this research, solvent effects on magnetic properties of obtained polymers in reprecipitation of polymer containing vanadyl ion was observed. Magnetic interactions of vanadyl complex of polymer were varied from antiferromagnetic to ferromagnetic by precipitation in methanol. ESR measurements indicated that the origin of the difference was caused from ligation of methanol, which was used as precipitation solvent, to vanadyl ion to prevent stacking of porphyrin moieties. From this result, it is possible that magnetic property of polyHETPP-$V^{IV}O$ can be controlled by the selection of solvents for purification of polymers.

INTRODUCTION

Magnetic properties of polymers containing nitroxide radicals or paramagnetic metalloporphyrins in their side chains (Scheme 1 (1), (2)) have been investigated in our laboratory.[1-8] Recently, we have studied magnetic properties of polymers containing paramagnetic metalloporphyrins in their main chains. This type of polymer is expected to show novel magnetic behavior through both intra- and inter-molecular interaction.

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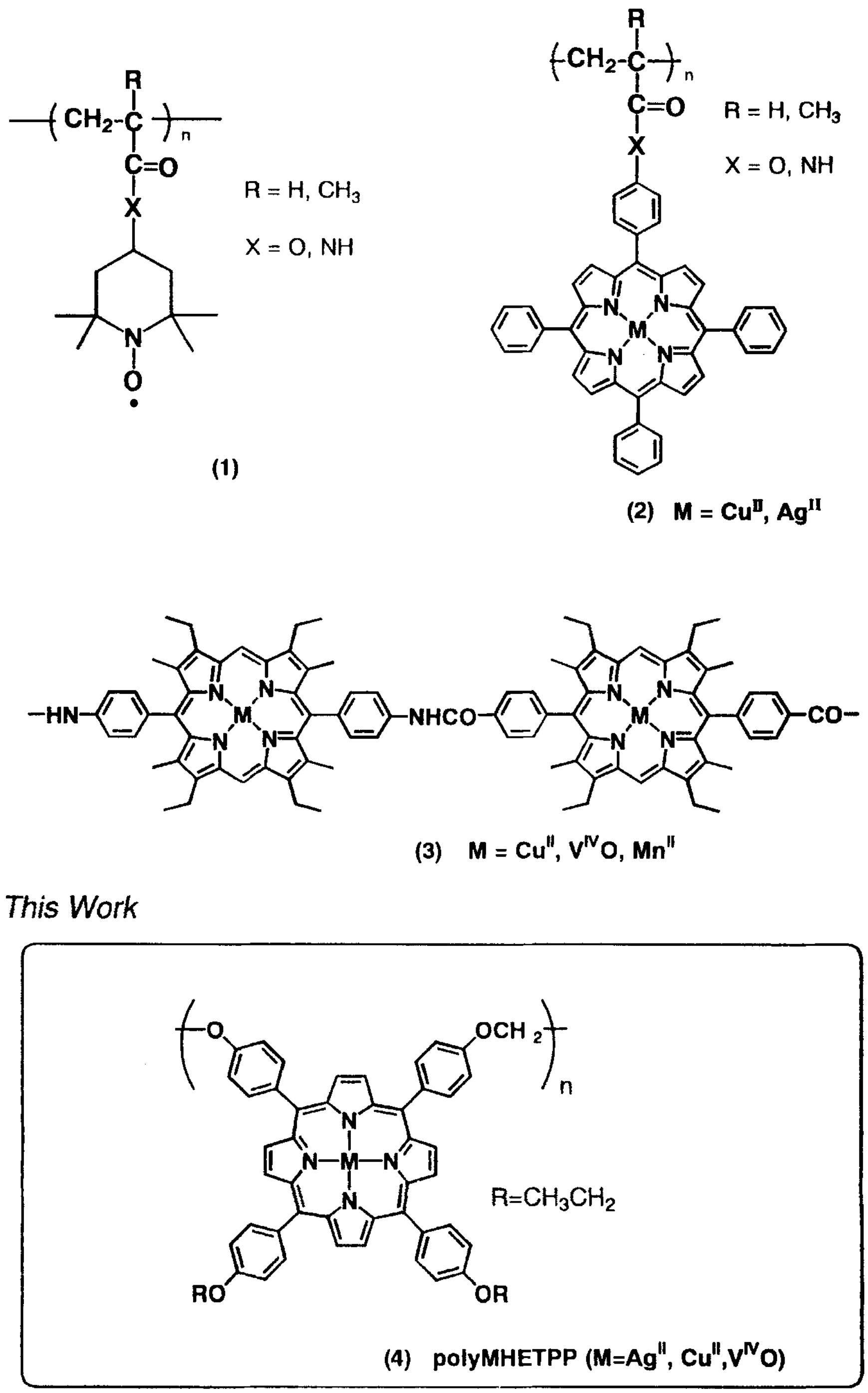


Scheme 1 Polymers containing paramagnetic spices

More than 5 years ago, we tried to prepare such main chain type polymer by condensation of 5,10-bis(4-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin with 2,8,12,18-tetraethyl-5,10-bis(4-methoxycarbonylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (Scheme 1 (3)).[9] Although the condensation occurred, the resulting polymer was not soluble in any solvents. In 1992, Scamporrino et al.[10] reported a synthesis of polymer containing tetraphenylporphyrin moiety in the main chain through condensation of bis(ethoxyphenyl)-15,20-bis(hydroxyphenyl)porphyrin (HETPP) with dibromomethane (Scheme 1 (4)). The polymer is reported to be soluble in some organic solvents. We synthesized some paramagnetic metal complexes of this type of polymer, investigated their magnetic properties and compared them with those of side chain type polymers.

In this paper, the characteristic magnetic behavior of vanadyl complex of the polymer will be reported. Magnetic properties of Ag^{II}, Cu^{II}, and Co^{II} complexes of polymers were also investigated.

EXPERIMENTAL SECTION

Polymers were synthesized by condensation of HETPP and dibromomethane according to the method described by Scamporrino et al.[10]

PolyHETPP-$V^{IV}O$

Bis(ethoxyphenyl)-15,20-bis(hydroxyphenyl)porphyrin vanadium(IV) oxide (300 mg, 0.375 mmol) and powdered potassium hydroxide (60 mg, 1.1 mmol) were dissolved in N-methyl-2-pyrrolidone (6 ml). The mixture was heated at 70 °C under stirring in nitrogen atmosphere to obtain homogeneous solution; then 1.7 ml (25 mmol, large excess) of dibromomethane was added. After 24 h, the mixture was cooled and poured into 300 ml of chloroform. After washing with water several times, chloroform layer was concentrated and poured into large excess of methanol to precipitate the resulting polymer. The polymer was purified by reprecipitation from chloroform into a large excess of methanol three times. The purple powder was obtained in 71 % yield (240 mg). mp. > 300 °C. Anal. Calcd for $C_{49}H_{36}N_4O_5V$: C, 72.50; H, 4.47; N, 6.90. Found: C, 71.17; H, 4.47; N, 6.83.

PolyHETPP-Cu^{II}

This polymer was prepared by the same method described for vanadyl complex to give purple powder in 34 % yield. mp. > 300 °C. Anal. Calcd for $C_{49}H_{36}N_4O_4Cu$: C, 72.80; H, 4.49; N, 6.93. Found: C, 71.49; H, 4.79; N, 6.54.

PolyHETPP-Ag^{II}

The silver(II) ion in this polymer was introduced by polymer reaction of metal-free polymer with silver(I) acetate. Purple powder was obtained in 65 % yield. mp. > 300 °C. Anal. Calcd for $C_{49}H_{36}N_4O_4Ag$: C, 69.02; H, 4.26; N, 6.57. Found: C, 68.71; H, 4.63; N, 6.39.

PolyHETPP-Co^{II}

The cobalt(II) ion in this polymer was introduced by polymer reaction of metal-free polymer with cobalt(II) acetylacetonate under argon atmosphere. Purple powder was obtained in 65 % yield. mp. > 300 °C. Anal. Calcd for $C_{49}H_{36}N_4O_4Co(H_2O)_{1.5}$: C, 70.84; H, 4.73; N, 6.74. Found: C, 70.50; H, 4.86; N, 6.52.

Measurements

UV-visible spectra were recorded on a Shimadzu UV-2100 spectrometer. IR spectra were measured on a JASCO DS-402G spectrometer. ESR spectra were obtained with a JEOL JES RE-2X ESR spectrometer operating in the X-band, utilizing a 100 kHz field modulation, and a microwave power of 1 mW. TE_{011} mode cavity was used. Temperature was controlled by JEOL DVT2 variable-temperature accessory. 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 4 K to 300 K.

RESULTS AND DISCUSSION

Characterization of the Polymers

PolyHETPP-M's (M = Ag^{II}, Cu^{II}, Co^{II}, or $V^{IV}O$) were purified by repeated reprecipitation from chloroform to methanol or by freeze-drying from benzene solution. The molecular weights of polyHETPP-M were in the range of 4000-9000 which correspond to polymers containing 5-10 HETPP units. They are soluble in many organic solvents as reported in the case of metal-free polymers.[10]

Absorption spectra of HETPP-$V^{IV}O$ and polyHETPP-$V^{IV}O$ are shown in Figure 1. From both the spectra and the results of elemental analysis, introductions of metal ion are almost 100 %.

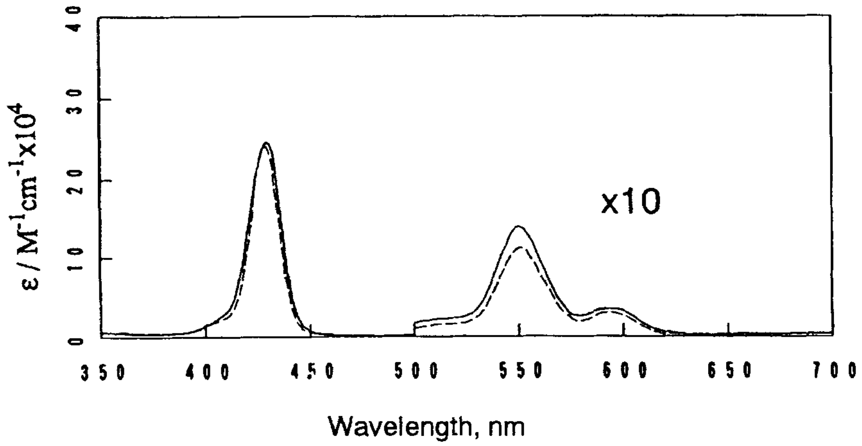


Figure 1 Absorption spectra of polyHETPP-$V^{IV}O$ (——) and HETPP-$V^{IV}O$ (-----) in tetrahydrofuran (THF).

Magnetic Properties

In the case of silver(II) complexes, both monomer and polymer of HETPP showed typical paramagnetic behavior in temperature dependence of magnetic susceptibility. In our previous research,[3] on the contrary, strong antiferromagnetic interaction was observed in poly(5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphyrin) (polyAOTPP-Ag^{II} (Scheme 1 (2) R = H, X = O)) which have paramagnetic metalloporphyrin moieties in its side chain. Although monomeric HETPP-Cu^{II} and HETPP-V^{IV}O showed paramagnetic interaction, respectively, polyHETPP-Cu^{II} and polyHETPP-V^{IV}O exhibited antiferromagnetic interaction with Weiss temperature = -37 K and -161 K, respectively. Antiferromagnetic interaction was observed in both polyHETPP-Co^{II} and HETPP-Co^{II}, and interaction in monomer was stronger than polymer. The reason of this phenomenon may be ascribed to difference in coordination environment between monomer and polymer indicated by ESR measurements.[11]

Magnetic properties of Ag^{II}, Cu^{II}, and Co^{II} complexes of polyHETPP showed good reproducibility. However, V^{IV}O complex of polyHETPP showed various magnetic interactions by precipitation in methanol (Fig. 2).

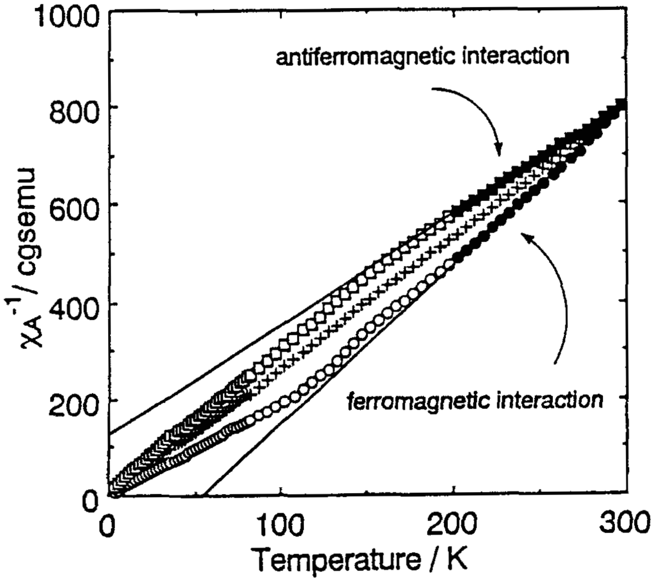


Figure 2 Various temperature dependent magnetic behavior of polyHETPP-V^{IV}O treated with methanol reprecipitation.

In the course of this research, solvent effects on reprecipitation of the polymer was observed. Magnetic interactions were varied from antiferromagnetic to ferromagnetic by the addition of methanol. Vanadyl complexes have been known to form V=O---V=O---V=O linear interacting chain through ligation of oxygen of V=O bond to another vanadium ion.[12] Methanol can ligate to vanadyl ion to break V=O---V=O interacting chain.[13] Molecule of vanadyl complexes may form various kinds of three-dimensional alignments through such ligation and they might show various magnetic interaction owing to their mutual orientation. Since the information about the environment of vanadyl ion could be obtained from ESR spectroscopy, ESR spectra were measured.

ESR spectroscopy

In order to investigate the environment of ligation of vanadyl ion, ESR spectra of polymers containing vanadyl ion were measured in both toluene and toluene/methanol (2.5 vol%) mixed solvents in frozen state (-120 °C). The results are shown in Figure 3. Both spectra showed similar typical anisotropic pattern with A_{para} = 169 G, A_{perpen} = 58 G, and A_{iso} = 95 G. However, two kinds of signals were observed at highest field in the case of toluene/methanol mixed solvent. This suggests that there are two kinds of species in the system. One is the same in toluene solution and another is considered to be a methanol ligated species which have 92 G of A_{iso}. Decrease of A_{iso} is ascribable to decrease of spin density of vanadyl ion by ligation of methanol. Schematic diagrams of the effect of methanol are shown in Figure 4.

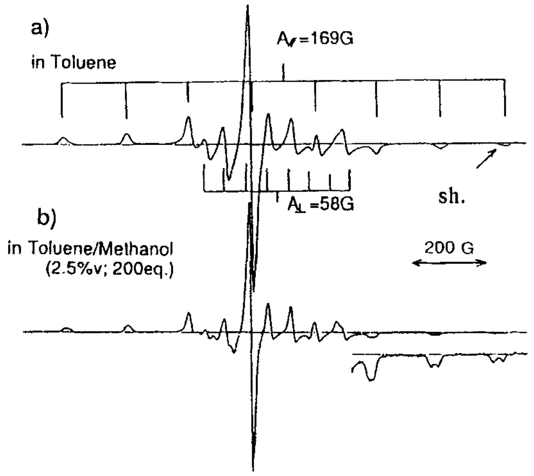
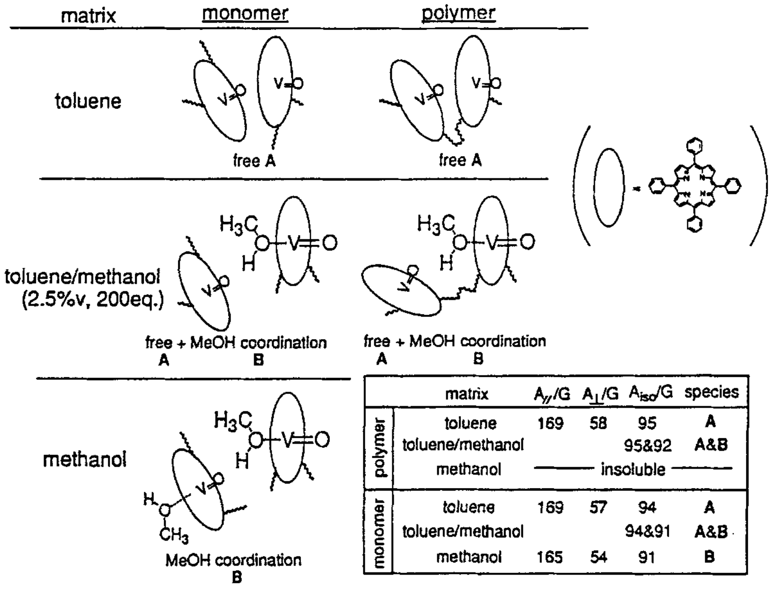


Figure 3 ESR spectra of polyHETPP-$V^{IV}O$ (a) in toluene and (b) in toluene/methanol (2.5 v/v%) at -120 °C (2 mM for porphyrin moiety).



	matrix	$A_{//}$/G	$A_{\perp}$/G	A_{iso}/G	species
polymer	toluene	169	58	95	A
	toluene/methanol			95&92	A&B
	methanol	———	insoluble	———	
monomer	toluene	169	57	94	A
	toluene/methanol			94&91	A&B
	methanol	165	54	91	B

Figure 4 Schematic drawing of paramagnetic species of HETPP-$V^{IV}O$ and polyHETPP-$V^{IV}O$ in toluene, toluene/methanol, and methanol solution.

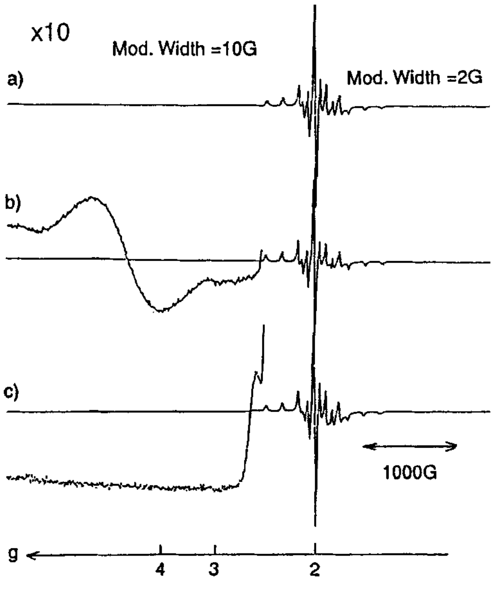


Figure 5 ESR spectra at -120 °C; (a) HETPP-$V^{IV}O$ in toluene (b) polyHETPP-$V^{IV}O$ in toluene (c) methanol (2.5 v/v%) was added to (b). 2 mM for porphyrin moiety.

The spectra observed in wider field (± 2500 G) gave another important information (Fig. 5). Although HETPP-$V^{IV}O$ (monomer) in toluene (a) showed no signal in the region of 0-2000 G, polyHETPP-$V^{IV}O$ exhibited broad and intense signal in the field of 200-2000 G. Upon addition of methanol, the broad signal disappeared completely. The low field broad signal is considered to be due to spin-spin interaction of vanadyl ion which cause a self induced field by an alignment of spins. Without methanol, vanadyl ion may stack and V=O bond ligate to vanadyl ion to make interacted chain. Added methanol may ligate to vanadyl ion from the reverse side of vanadyl oxygen and disturb spin-spin interaction among vanadyl ion.

This is the first evidence of relationship between higher structure of polymer and its magnetic interaction investigated by spectroscopic methods. The possibility of control of magnetic interaction of paramagnetic metal ion in magnetic polymer was shown in this research.

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