

Syntheses and Magnetic Properties of Novel Bithiazole-Containing Polymeric Complexes

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ABSTRACT: Three novel bithiazole-containing polymers were synthesized from 2,2'-diamino-4, 4'-bithiazole (DABT) condensed with bismaleimide, bis(methyloxycarbonyl ethyl)tin dichloride (BETD), and 4,4'-diphenylmethane diisocyanate (DPDI), respectively. A new series of polymeric complexes were prepared from Fe^{2+} and the three polymers. These polymers and their complexes were characterized through FTIR, $^1\text{H-NMR}$, and related techniques. The chemical compositions of the complexes were determined by XPS. The presence of the exchange interaction between the unpaired electrons was investigated by ESR spectroscopy. The magnetic behavior of these complexes was measured as a function of the magnetic field strength (0–40 kOe) at 5 K and as a function of temperature (5–300 K) at a magnetic field strength of 30 kOe. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1353–1359, 2001

Key words: synthesis; polymer containing bithiazole; polymeric complexes; magnetic properties

INTRODUCTION

In recent years, there has been considerable interest in the magnetic properties of novel organic ferromagnets.^{1–6} The development of organic materials with a magnetic property remains an important challenging goal for chemists. Organic polymers containing paramagnetic species may provide a new kind of magnetic materials owing to the magnetically long-range ordering of unpaired electrons through spin–spin interactions.⁷ The ability to control the sign and magnitude of the magnetic-exchange interaction between adjacent metal ions in a polymeric complex is of fundamental importance for the design and synthesis of new magnetic materials based on polymeric

coordination complexes.⁸ In 1998, Genin and Hoffmann proposed that polymers built from sulfur-, carbon-, and nitrogen-containing five-membered rings would theoretically display magnetic ordering, but none have as yet been synthesized.⁹

We favored a polymer-based route to organic magnetic materials, as magnetic coupling through covalent, intramolecular pathways can be quite strong and predictable. Our interest in bithiazole-based polymers stems from their potential to bind transition-metal ions into conjugated polymeric main chains. The 4,4'-bithiazole moiety is used to provide bidentate *N*-donor sites for binding metal ions. We first reported the syntheses of conjugated bithiazole-containing poly(Schiff base)s (TAPDA and PBDT) by polycondensation of 2,2'-diamino-4, 4'-bithiazole (DABT) with terephthalaldehyde and phthalaldehyde and the conductivity¹⁰ and magnetization of their metal complexes.¹¹ When DABT is condensed with bis(methyloxycarbonyl ethyl)tin dichloride (BETD), 4,4'-diphenylmethane diisocyanate (DPDI), and

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bismaleimide separately, the corresponding resins would be expected to form polymeric metal complexes that could be employed for potential electrical, magnetic, and optical materials.

In this article, we describe the syntheses of several new polymers from DABT condensed with BETD, DPDI, and bismaleimide separately and preparations of their complexes with Fe^{2+} and their preliminary magnetic properties for the first time. The polymers and their complexes were characterized by FTIR, $^1\text{H-NMR}$, XPS, and ESR.

EXPERIMENTAL

Materials

Dimethyl sulfoxide (DMSO) was dried and purified by the usual method. DABT¹² and BETD¹³ were prepared according to the literature, followed by several recrystallizations.

Preparation of Monomer

Bismaleimide (MBT) was prepared from DABT and maleic anhydride and stirred at room temperature for 0.5 h; then, Ac_2O (acetic anhydride), Et_3N (triethylamine), and MgSO_4 were added to the reaction solution at 63°C and stirred for 2 h. A light yellow precipitate was formed, filtered, and dried under a vacuum. Its melting point is over 300°C . Yield: 70%.

IR (KBr, cm^{-1}): 3207(m), 2907(m), 1794(w), 1698(s), 1569(s), 1302(s), 1177(s), 897(m), 873(s), 795(m), 619(m); $^1\text{H-NMR}$ (500 MHz, CF_3COOD): 7.82, 6.59, 6.57 ppm.

Preparation of Polymer

PMBD

An equimolar ratio of DABT and MBT at a concentration of 5% solids content in DMSO was magnetically stirred in a round-bottom flask at 80°C . The reaction solution became homogeneous as the reaction proceeded. After 3–4 h, the viscosity of the solution increased. The solution was poured into methanol; a red–brown precipitate was formed and filtered, washed successively with water, ethanol, and ether, and dried under a vacuum. Yield: 85%.

IR (KBr, cm^{-1}): 3304(m), 2922(m), 1794(w), 1521(s), 1296(s), 1126(s), 873(s), 669(s); $^1\text{H-NMR}$ (500 MHz, CF_3COOD): 7.76, 4.48, 3.27, 2.93 ppm. $[\eta] = 0.27 \text{ dL/g}$.

PDDP

A mixture of DABT and DPDI in the ratio 1:1 in a DMSO solution was heated at 60°C for 1 h and then at 120°C for 2 h. The solution was poured into methanol and water (1:1), and the gray precipitate was formed and filtered, washed successively with water, methanol, and ether, and dried under a vacuum. Yield: 75%.

IR (KBr, cm^{-1}): 3333(s), 2903(s), 1794(w), 1585(s), 1508(s), 1176(s), 873(s), 810(s); $^1\text{H-NMR}$ (500 MHz, CF_3COOD): 7.59, 7.46, 7.16, 7.06, 7.09, 3.84 ppm. $[\eta] = 0.21 \text{ dL/g}$.

PBD

To a solution of DABT in ethanol and water (1:1) was added a solution of BETD in CHCl_3 . Et_3N was added to the stirred solution; in about a few minutes, a gray precipitate formed. The precipitate was filtered, washed with water, methanol, and ether, and dried under a vacuum. Yield: 50%.

IR (KBr, cm^{-1}): 3447(s), 3128(s), 2899(s), 1794(w), 1598(s), 1525(s), 1460(s), 1350(s), 1298(s), 1035(s), 873(s), 775(m), 669(m); $^1\text{H-NMR}$ (500 MHz, CF_3COOD): 7.12, 4.40, 3.96, 1.31, 1.27 ppm. $[\eta] = 0.39 \text{ dL/g}$.

Preparation of Polymeric Complex

An FeSO_4 solution was added slowly to a stirred DMSO solution of the polymer in a purified nitrogen atmosphere, and stirring was continued at 80°C . A precipitate was formed, filtered, and washed successively with water, methanol, and ether; then, the precipitated complex was soaked in methanol for 24 h. The complex was isolated by filtration and dried under a vacuum at 60°C for 24 h. Polymeric complexes were obtained.

PMBD- Fe^{2+}

The complex was prepared from PMBD with FeSO_4 . Yield: 27%.

IR (KBr, cm^{-1}): 3245(m), 2903(m), 1795(w), 1522(s), 1349(s), 1125(s), 1116(s), 1054(s), 990(s), 952(s), 874(s), 618(s).

Elemental analysis for $[\text{C}_{10}\text{H}_6\text{N}_4\text{O}_2\text{S}_2(\text{FeSO}_4)_{0.01}]_n$: C, 43.11%; H, 2.15%; N, 20.04%. Found: C, 42.89%; H, 2.05%; N, 21.93%.

PDDP- Fe^{2+}

The complex was prepared from PDDP with FeSO_4 . Yield: 45%.

IR (KBr, cm^{-1}): 3275(m), 1794(w), 1508(s), 1410(s), 1307(s), 1115(s), 1054(s), 990(s), 952(s), 873(s), 810(m), 618(s).

Elemental analysis for $[\text{C}_{21}\text{H}_{16}\text{N}_6\text{O}_2\text{S}_2(\text{FeSO}_4)_{0.013}]_n$: C, 56.06%; H, 3.56%; N, 18.69%. Found: C, 55.76%; H, 3.48%; N, 19.02%.

PBD- Fe^{2+}

The complex was prepared from PBD with FeSO_4 . Yield: 60%.

IR (KBr, cm^{-1}): 3211(m), 1896(s), 1794(w), 1456(s), 1113(s), 1053(s), 990(s), 951(s), 873(s), 669(s).

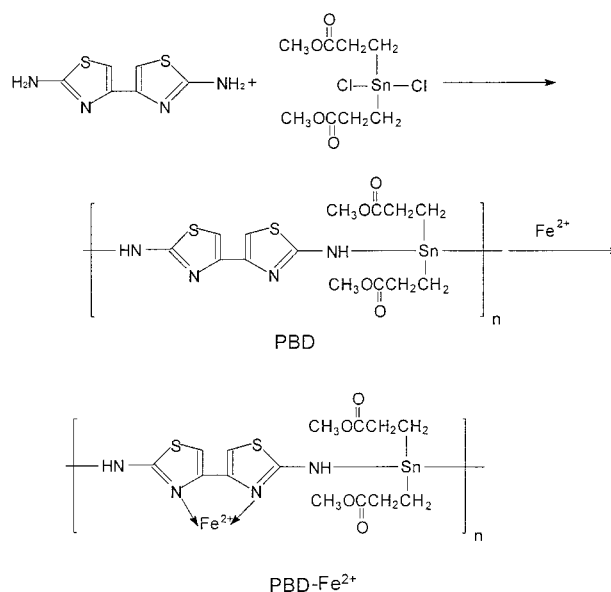
Elemental analysis for $[\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2(\text{FeSO}_4)_{0.01}]_n$: C, 45.02%; H, 4.82%; N, 15.01%. Found: C, 44.87%; H, 4.63%; N, 15.94%.

Fourier transform infrared (FTIR) spectra of the monomer, polymer, and complex were recorded using KBr pellets by a BRUKER VECTOR 22. ESR was measured with a JEOL Model JES-FE1XG ESR spectrometer. The chemical compositions of the complexes were carried out on an ESCACABII X-ray photoelectron spectroscope (XPS). Excitation was produced by monochromatized 1485.6 eV $\text{AlK}\alpha$ radiation. The spectrometer was calibrated with respect to the C_{1s} 284.5 eV line. The intrinsic viscosity of the polymers was measured by an Ubbelohde-type viscometer at 30°C in DMSO. The magnetic measurements were carried out by a magnetometer (MPMS-7). The magnetization of the applied magnetic field (i.e., hysteresis loop) was measured at 200 K, and the temperature dependence of the magnetization was measured at temperature range from 5 to 300 K.

RESULTS AND DISCUSSION

Synthesis of Polymer and Complex

The polymers and complexes were prepared as shown in Schemes 1–3. To prepare the polymers with a high molecular weight, we applied the polycondensation procedure and paid careful attention to drying the solvents used and removing oligomeric fractions. It must be noted that the low temperature was essential to obtain polymers successfully, and the complex reaction between the polymer and Fe^{2+} should be carried out under purified nitrogen and at about 80°C. The intrinsic viscosity of PBD, PMBD, and PDDP was 0.39,



Scheme 1 Preparation of PBD and PBD- Fe^{2+} .

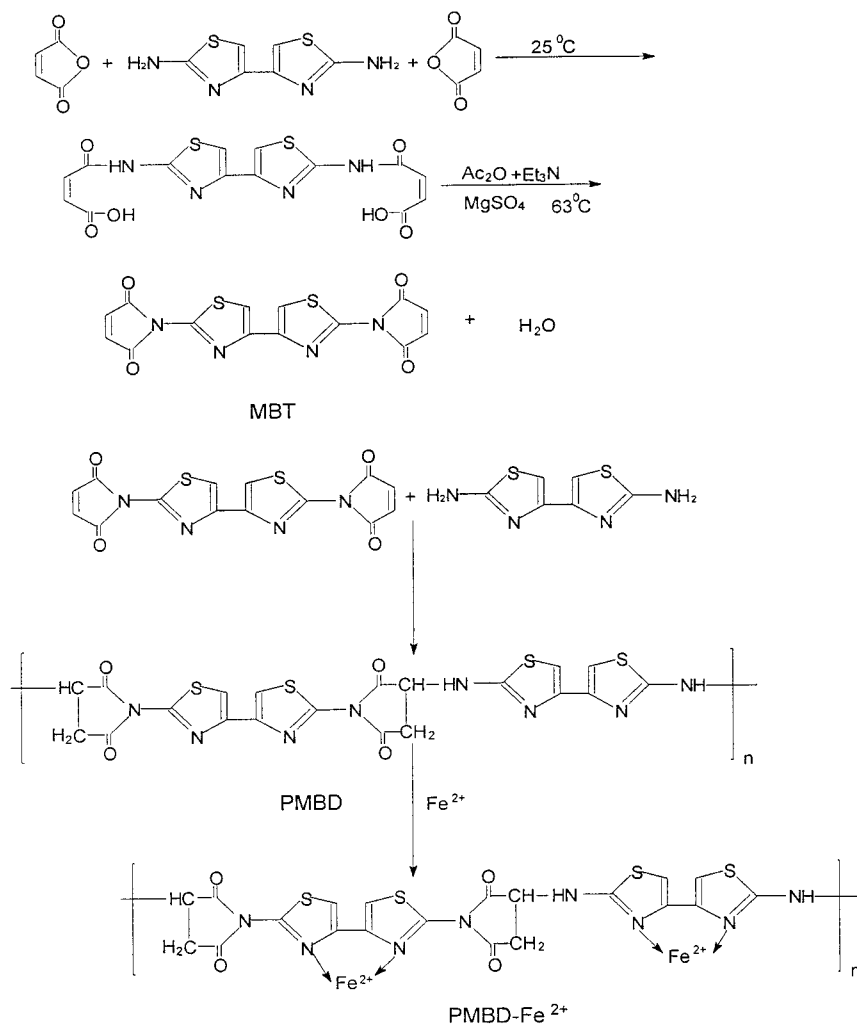
0.21, and 0.27dL/g, respectively. The obtained polymers are soluble in DMSO, dichloroacetic acid, trifluoroacetic acid, and other strong protonic acids. The good film-forming ability of all the polymers indicates that their molecular weights are reasonably high.

Characterization of Molecular Structure

The proposed MBT and polymer structures were derived from $^1\text{H-NMR}$ and FTIR. The $^1\text{H-NMR}$ spectra of MBT and the polymers were obtained in deuterated CF_3COOH . The chemical shifts of the bithiazole proton resonance are generally in the range of 7.12–7.82 ppm, depending on the monomer and polymer structures.

In the $^1\text{H-NMR}$ spectrum of MBT, as expected, two main peaks are present: The resonance of the bithiazole protons occurs at 7.82 ppm. The double peaks at 6.59 and 6.57 ppm are due to the $\text{HC}=\text{CH}$ protons. In the $^1\text{H-NMR}$ spectrum of PMBD, the resonance of thiazole protons occurs at 7.76 ppm. The peak at 4.48 ppm is due to the NH proton resonance. The resonance of CH protons occurs at 2.93 ppm. The peak at 3.27 ppm is due to CH_2 proton resonance.

In the $^1\text{H-NMR}$ spectrum of PBD, the resonance of the bithiazole protons occurs at 7.12 ppm. The peaks at 4.40, 3.96, 1.31, and 1.27 ppm are assigned to the CH_3 , SnCH_2 , CH_2COO , and HN proton resonance, respectively. In the $^1\text{H-NMR}$ spectrum of PDDP, the resonance of the



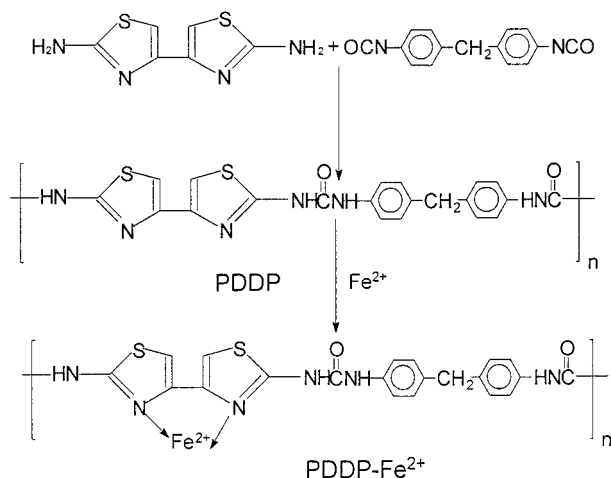
Scheme 2 Preparation of PMBD and PMBD-Fe²⁺.

bithiazole protons occurs at 7.59 ppm. The double peaks at 7.06 and 7.09 ppm are ascribed to the phenylenic proton resonance. The peaks at 7.46 and 7.16 ppm are due to the thiazole-NHCO and OCNH-benzene protons resonance, respectively. Thus, overall, the solution ¹H-NMR spectra are in excellent agreement with the proposed structures.

FTIR spectra of the monomer and polymers were obtained to confirm the features of the proposed structures. The most obvious absorption peak in the FTIR spectra of MBT and the polymers is near 1794 cm⁻¹ and it is assigned to the C=O stretching vibration. A second major structural feature of MBT and the polymers revealed by the FTIR spectra is the bithiazole ring and skeletal stretching vibration peaks in the 1035–1528 cm⁻¹ region.

In the FTIR spectra of the polymeric complex, the significant change observed was that the peak at 1298 cm⁻¹ in the spectra of the polymers disappeared. The peak at 1298 cm⁻¹ in the polymers might be due to the skeletal vibration, which was caused by the imino-interchange isomer of 2-aminothiazole.¹⁴ Due to coordination, the imino-interchange isomer no longer existed, and the skeletal vibration of bithiazole appeared at 1349 cm⁻¹. This suggests that the coordination took place through the ring nitrogen atom of thiazole. The peaks at 1116, 1054, 990, and 952 cm⁻¹ in the spectra of the polymers, which were assigned to ν_{3a} , ν_{3b} , ν_{3c} , and ν_1 of SO₄²⁻, suggested that the SO₄²⁻ is a bidentate ligand via oxygen atoms.¹⁵

As an example, IR spectra of PBD and PBD-Fe²⁺ are shown in Figure 1. Compared to the IR spectra of the polymer and the complex, it can be



Scheme 3 Preparation of PDDP and PDDP-Fe²⁺.

found that the IR absorption changes very obviously at the 1250–1600, 1000–1200, and 450–750 cm⁻¹ regions, which indicates the forming of a polymeric complex.

Determining the chemical composition of the complexes, an XPS survey in the range of binding energy from 0 to 1400 eV was conducted. It was found that the complexes consist of Fe, N, C, O, and S elements, and the atomic concentration of these elements was determined based on the individual XPS spectrum of each element. Table I summarizes the concentration of these elements in polymers. The results are consistent with the elemental analysis. Figure 2 shows the Fe (2*p*) XPS spectrum of PBD-Fe²⁺. It is considered that the two peaks near 709 and 721 eV may be, respectively, related to the binding energies of Fe (2*p*_{3/2}) and Fe (2*p*_{1/2}). These two values do not exactly conform to those for typical FeO, Fe₃O₄, or

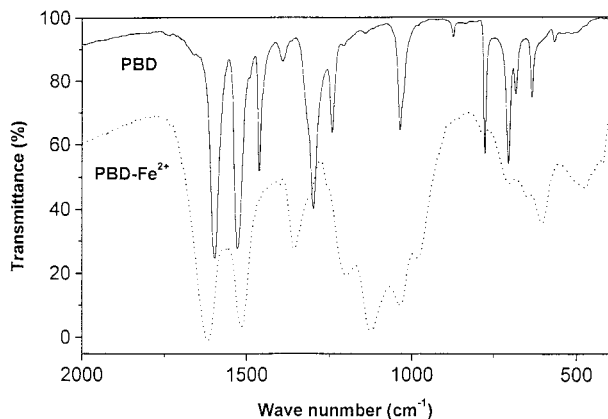


Figure 1 FTIR spectra of PBD and PBD-Fe²⁺.

Table I Composition of the Complexes Determined by XPS

Complex	Composition (%)				
	C	S	N	O	Fe
PMBD-Fe ²⁺	41.2	22.9	21.3	12.5	2.1
PBD-Fe ²⁺	44.2	17.4	16.1	18.5	4.2
PDDP-Fe ²⁺	54.9	14.4	19.6	8.7	2.6

Fe₂O₃ reported in the past.¹⁶ The X-ray powder diffraction patterns of the polymeric complexes revealed a poor order degree. Except for the amorphous phase, the peak of FeO, Fe₃O₄, or Fe₂O₃ is not observed.

The ESR spectra of the polymeric complexes were measured at 77 K; an unsymmetrical line of an anisotropy *g* factor was observed. The *g* factors of three polymeric complexes were 4.1912 for PBD-Fe²⁺, 4.1907 for PMBD-Fe²⁺, and 4.2210 for PDDP-Fe²⁺. All the ESR spectra showed broad spectra, implying that the large exchange region is more efficient for the present polymeric complexes. These results indicate that the distance between the metal ions in the polymers is so large that the antiferromagnetic interaction between the metal ions may not arise, and two spin centers may also be well separated from each other. For a bulk ferromagnet, it is necessary that parallel coupling dominates on the scale of the lattice, but the orthogonality conditions are difficult to impose on all the neighbors of a given spin. In other terms, avoiding some bonding interaction between the unpaired electrons represents a big problem. If the spins are different from each other, then the nonorthogonality ions of the mag-

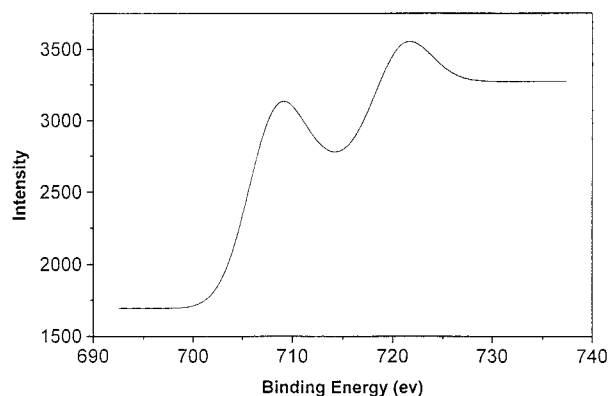


Figure 2 Fe (2*p*) XPS spectrum of PBD-Fe²⁺.

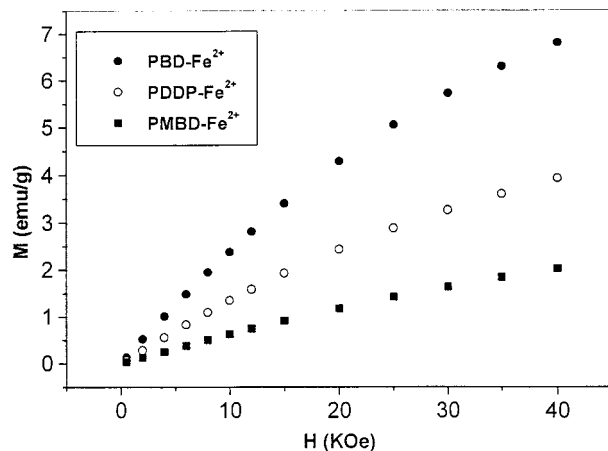


Figure 3 Magnetization curve M versus H at $T = 5$ K for polymeric complexes.

netic orbitals are not too severe a problem, because an antiparallel alignment of the spins will lead to uncompensated moments and to a weak ferromagnet.¹⁷

A typical relationship between the magnetization and the applied field for polymeric complexes at 5 K is shown in Figure 3. As one can see, the values of the relative saturation magnetization are 6.7 emu/g for PBD-Fe²⁺, 3.9 emu/g for PDDP-Fe²⁺, and 1.8 emu/g for PMBD-Fe²⁺. The M increases sharply until about 35 kOe and an increasing trend is slowly above 40 kOe. This is a typical characteristic of a ferromagnet. PBD-Fe²⁺ has a higher relative saturation magnetization than that of the others, which may be due to two kinds of metal ions in the main and side chains, forming a superexchange interaction.

The temperature dependence of the magnetization of the polymeric complexes at an applied magnetic field of 30 kOe from 5 to 300 K was measured as shown in Figure 4. The magnetization of the polymeric complexes decreases with increase of the temperature. The temperature dependence of the χT products of PDDP-Fe²⁺ is shown in Figure 5. The value of χT monotonically increases with a decreasing T above 100 K; below 100 K, an abrupt increase in the slope of χT is observed and also a decrease of χT with decreasing temperature. This suggests that the system approaches a magnetic phase transition at 100 K. The result indicates that the polymeric complex may be ordered three dimensionally at 100 K.

Field-dependent hysteresis loops were generated from 5 to 300 K. As an example, the trend exhibited by PMBD-Fe²⁺ is described through

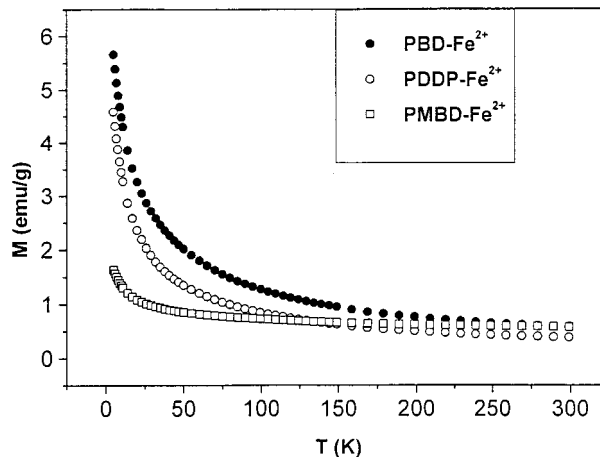


Figure 4 Magnetization versus temperature at $H = 30$ kOe for polymeric complexes.

the hysteresis loop recorded at 200 K in Figure 6. The values of the remanence magnetization and the coercivity are 0.014 emu/g and 360 Oe, respectively. These data show that the polymeric complexes are organic soft ferromagnetic polymers. Further investigations are in progress in our group.

CONCLUSIONS

Several new containing bithiazole polymers were synthesized, and their complexes were also prepared. PBD-Fe²⁺ has a higher relative saturation magnetization. The hysteresis loop of PMBD-Fe²⁺ can be observed at 200 K, and the coercivity

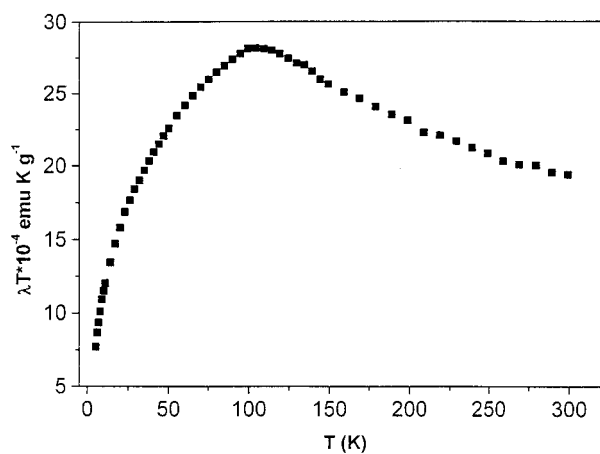


Figure 5 Magnetic susceptibility data for PDDP-Fe²⁺.

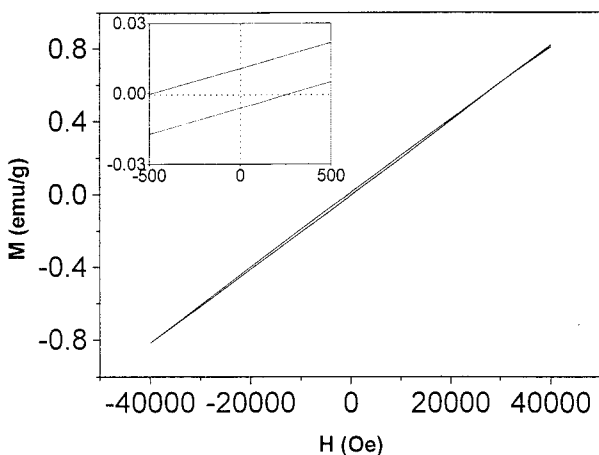


Figure 6 Magnetic hysteresis loop of PMBD-Fe²⁺ at 200 K. Insert: Expanded view of the minimum region.

was low. Thus, a few new organic soft ferromagnets were obtained.

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