

# Synthesis and the Magnetic Properties of Novel Metal(II) Complexes of Polyamides

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**ABSTRACT:** Novel polyamides DTPA and DTPyA are prepared from 2,2'-diamino-4,4'-bisthiazole and aromatic polycarbonyl chloride. The complexes of Fe(II) and Cu(II) metal of the polyamides are also prepared. The complexes as well as the polyamides are characterized through IR and EPR, and the magnetic property of each complex are measured through MPMS. It is found the Fe(II) complexes of both DTPA and DTPyA reveal magnetization ability, especially the Fe(II) DTPA complex. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 818–822, 2001

**Key words:** polyamides; polymer complex; synthesis; characterization; magnetic property

## INTRODUCTION

Organic and polymeric ferro-magnetics can be a new kind of soft magnetic material. Compared to common inorganic ferro-magnetics, the organic ferro-magnetics possesses the characteristics of structural diversities, lower density, and readily processing.<sup>1,2</sup> The magnetic feature of organic and polymeric ferro-magnetics can be revealed in the submolecular level, and thus the density as well as the precision for information memory could be improved to a large extent. It may be a new, potential material of magnetic disk of high capacity in the industries of computer and other magnetic recording instruments. Furthermore, such organic and polymeric ferro-magnetics can react with electric conductive polymer to form complexes useful as a microwave absorber, which, because of its broad band and strong ability of

absorption, may have potential application in the field of stealth technique and electromagnetic shield technique.<sup>3</sup>

Unlike the inorganic ferro-magnetics, which have already been widely investigated for a long time, studies in the field of organic and polymeric soft ferro-magnetics are so far very limited. However, the few researches reported to date have already revealed the promising prospects of this field. We have reported the preparation and magnetic properties of Fe(II) complexes of poly-schiff base earlier,<sup>4</sup> and in this article, we would like to report the synthesis of some novel Cu(II) and Fe(II) complexes of polyamides from bisthiazole and aromatic polycarbonyl chloride. Their magnetic properties are also studied and reported.

## EXPERIMENTAL

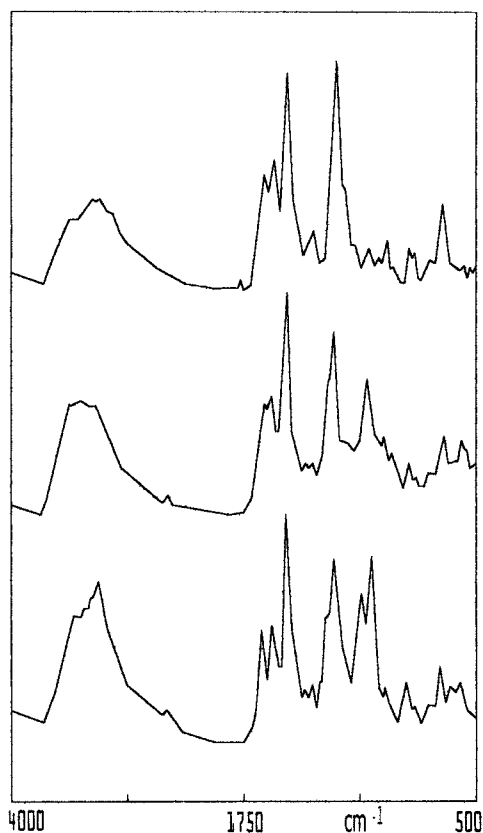
### Polymer Synthesis

#### *Polyamide of 2,2'-Diamino-4,4'-Bisthiazole and p-Phthalyl Chloride (DTPA Formula 1a)*

In a tube reactor, equipped with mechanical stirrer, was added 4.37 g of 2,2'-diamino-4,4'-bisthia-

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**Figure 1** IR spectra of DTPA (a), DTPA-1 (b), and DTPA-2 (c).

zole (99.5%, prepared as described in ref. 5, and recrystallized with 50% aq. alcohol) and 170 g of DMF (A.R., Beijing Reagent Company) as solvent. The mixture was stirred at room temperature for 10 min. After dissolving the monomer, 4.62 g of *p*-phthaloyl chloride (A.R., Shanghai Reagent Company) was added in one pot, and the mixture was stirred at room temperature for 6 h. The mixture gradually turned into a yellow liquid and polymerized to form a polymer solution. The solution can be used to synthesize complexes with ions of Fe(II) or Cu(II) directly. After removing the solvent, a deep yellow powder of DTPA was obtained. The IR spectrum of DTPA is shown in Figure 1(a).

**Polyamide of 2,2'-Diamino-4,4'-Bisthiazole and 2,6-Pyridinyl Dicarboxyl Chloride (DTPyA, Formula 1b)**

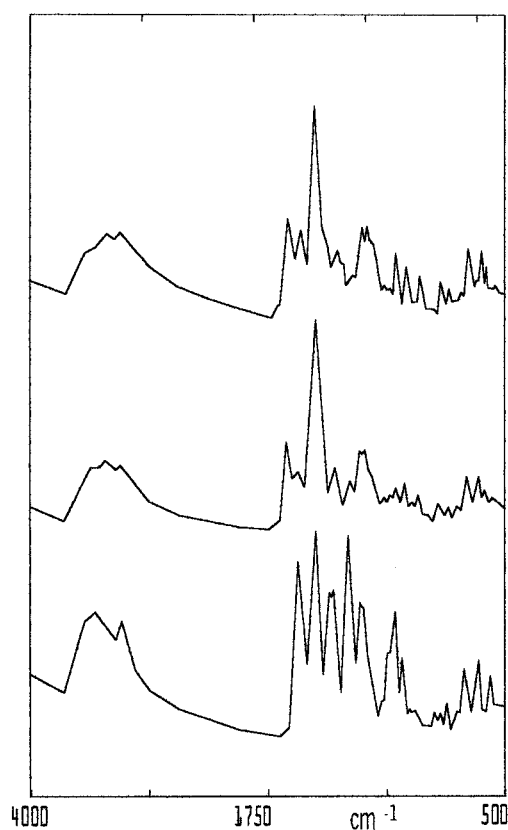
In a tube reactor, equipped with a mechanical stirrer, was added 5.6 g of 2,2'-diamino-4,4'-bisthiazole and 220 g of DMF. The mixture was

stirred at room temperature for 10 min, and then 5.98 g of 2,6-pyridinedicarbonyl chloride (Aldrich) was added in one pot. The mixture thus formed was stirred at room temperature for another 4 h. The yellow polymer solution prepared above can be used directly in the complex preparation with compounds of Fe(II) and Cu(II). After working up of the solution, a yellow powder of DTPyA can be obtained. The IR spectrum of DTPyA is shown in Figure 2(a).

**Complex Synthesis**

**Fe(II) Complexes of DTPA and DTPyA (and DTPyA-1)**

In a three-necked flask equipped with a mechanical stirrer, a gas inlet tube, and a thermometer, was added half of the polymer solution prepared above. After the inner air was removed with nitrogen through the inlet tube, 6.3 g of  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$  (A.R., Shanghai Reagent Company) was added to the polymer solution. While stirred under  $\text{N}_2$  atmosphere, the mixture was heated to



**Figure 2** IR spectra of DTPyA (a), DTPyA-1 (b), and DTPyA-2 (c).

**Table I** The Appearance of Polymers and Their Complexes

Compounds	Appearance	Compounds	Appearance
DTPA	Deep yellow powder	DTPyA	Yellow powder
DTPA-1	Dark green powder	DTPyA-1	Brown powder
DTPA-2	Grayish green powder	DTPyA-2	Dark green powder

80°C and stirred at the same temperature for another 6 h. After cooling down, the reaction mixture was poured into cold ethanol, and the precipitate was collected in a Bush funnel, and washed with ion-free water thoroughly. The crude polymer thus obtained was treated in a solid abstractor with methanol to remove organic impurities and monomers. It was then dried at 60°C in vacuum. The IR spectra of DTPA-1 and DTPyA-1 are shown in Figures 1(b) and 2(b), respectively.

#### ***Cu(II) Complexes of DTPA and DTPyA (DTPA-2 and DTPyA-2)***

Cu(II) complexes of DTPA and DTPyA were prepared in almost the same way as the preparation of the Fe(II) complexes described above unless 6.8 g of  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$  (A.R., Shanghai Reagent Company) was used instead of  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ . The IR spectra of DTPA-2 and DTPyA-2 are shown in Figures 1(c) and 2(c), respectively.

#### **Polymer Characterization**

IR Spectra of the polymer and the complexes were obtained on a Perkin-Elmer 1760 FTIR spectrometer. The EPR spectra of the complexes were obtained on an ESP-300 Model from the Bruker Company, measured using x-band, with 1.61 mW of the microwave power and 9.78 MHz of frequency.

#### ***The Measurement of Magnetic Property***

About 20 mg of the complex sample was sealed in a plastic tube with an inner diameter of 4.5 mm and long about 5 mm. The magnetization of the sample was measured on a Magnetic Property Measurement System (MPMS-7) model at 1.5 K, and the results were plotted vs.  $H$ , the magnetic field intensity.

## **RESULTS AND DISCUSSION**

#### **Polymer and Complex Characterization**

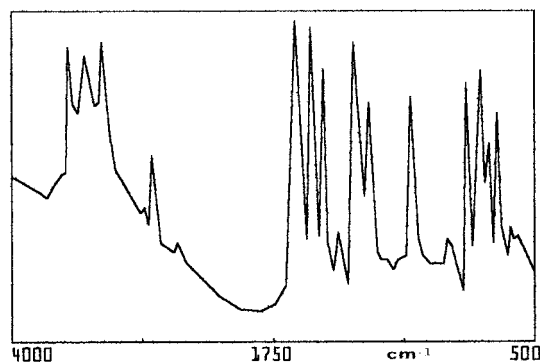
Both of the polymers DTPA and DTPyA isolated from the polymer solution are yellow powders.

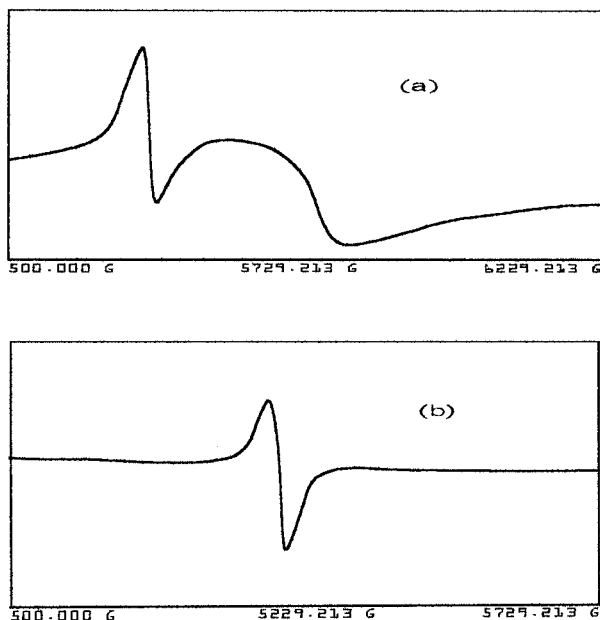
They are different in appearance from 2,2'-diamino-4,4'-dithiazole, which is deep brown crystal, and also different from their complexes (Table 1).

The IR spectra of polymer DTPA and its complexes DTPA-1 and DTPA-2 are shown in Figure 1. For comparison, the IR spectrum of 2,2'-diamino-4,4'-dithiazole is also shown in Figure 3. The absorption peaks in Figure 3 at 3300–3500  $\text{cm}^{-1}$  and at 3100–3300  $\text{cm}^{-1}$  (double) can be attributed to the vibration of two N—H bonds of amino groups of the thiazole ring. It is found that those peaks are dramatically weakened in Figure 1(a) in the case of DTPA, which indicates that the amino groups of 2,2'-diamino-4,4'-dithiazole has reacted with the carbonyl chloride while polymerizing. However, the peaks can still be seen in the spectra of polyamides due to the existence of N—H bonds both in polyamides and amino groups at the end. We can also find that in Figure 1 both the IR spectra of DTPA-1 [Fig. 1(b)] and DTPA-2 [Fig. 1(c)] are almost the same with that of DTPA except for some changes in absorption intensities. These results reveal that DTPA forms complexes with both Fe(II) and Cu(II) ions through the delivering and acceptance of the electron pair, and thus the structure of the polymer remains unchanged.

As shown in Figure 2, the spectra of DTPyA, DTPyA-1, and DTPyA-2 give the same results as in the case of Figure 1.

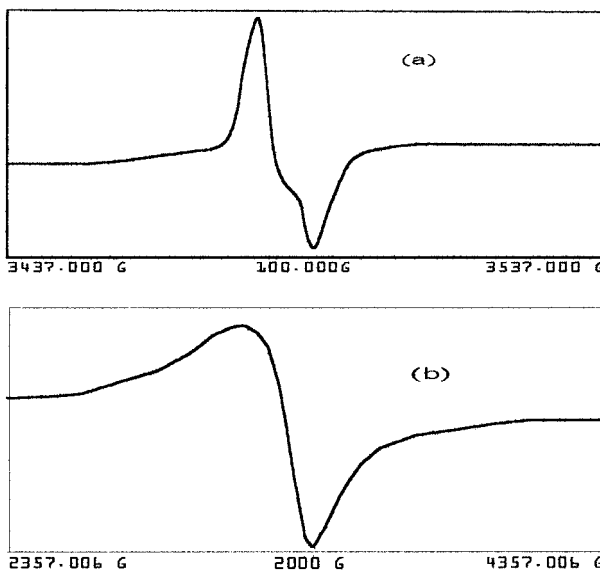
The EPR spectra of Fe(II) and Cu(II) complexes of DTPA and DTPyA are shown in Figures 4 and

**Figure 3** IR spectrum of 2,2'-diamino-4,4'-dithiazole.



**Figure 4** EPR spectrum of DTPA-1 (a) and DTPA-2 (b).

5, respectively, and their EPR parameters are shown in Table II. No EPR signals were detected for either of the DTPA and DTPyA polymers. We can see from Figures 4 and 5 that each of the Cu(II) complexes DTPA-2 and DTPyA-2 has a single signal, which appears at the central field



**Figure 5** EPR spectrum of DTPyA-1 (a) and DTPyA-2 (b).

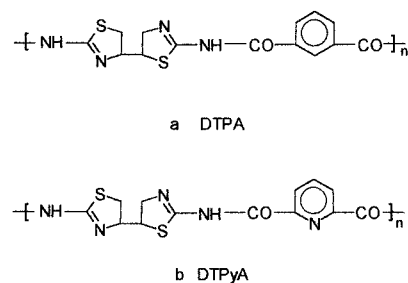
**Table II** The EPR Parameters of the Compounds

Compounds	Resonance Field (H/Gauss)	Line Width (H/Gauss)	<i>g</i> Value
DTPA-1	1668.234	197.561	4.1897
	3400.118	1080.002	2.0557
DTPA-2	3226.10	287.73	2.1665
DTPyA-1	3487.962	9.7261	2.0040
DTPyA-2	3328.056	235.047	2.1000

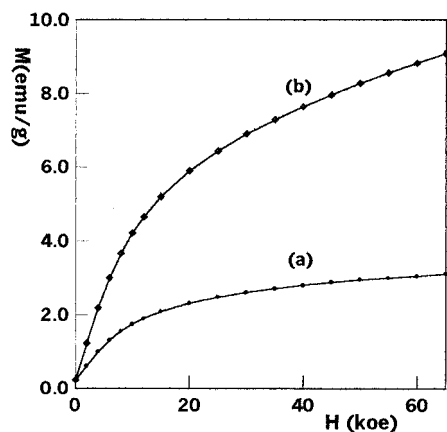
$H_0 = 3226$  Gauss ( $g = 2.1067$ ) and  $3328$  Gauss ( $g = 2.1030$ ), respectively. It indicates that Cu(II) complexes of both DTPA and DTPyA are normal paramagnetic compounds. However, it is different in the case of Fe(II) complexes. DTPyA-1 also has a single signal with a  $g$  value of 2.004 at  $H_0 = 3487$  Gauss, while DTPA-1 has another signal at a much lower field. Besides the difference in signal number, the signal width of each Fe(II) complexes differs greatly from that of the Cu(II) complexes. The  $L$  value of DTPA-2 is almost equal to that of DTPyA-2, but in the Fe(II) complexes, the  $L$  value of DTPA-1 becomes 1080 Gauss (for the signal of  $g = 2.0557$ ) and 197.56 Gauss (for the signal of  $g = 4.1897$ ) from 9.73 Gauss for DTPyA-1. This dramatic change may be due to the existence of some kind of super strong magnetic moment in the complex of DTPA-1.

### The Magnetization of the Fe(II) Complexes

The magnetization of the Fe(II) and Cu(II) complexes of both DTPA and DTPyA are measured at 1.5 K, and the results are shown in Figure 6. It is found that under the magnetic field of 65 koe, the magnetization of the Cu(II) complexes of both DTPA and DTPyA are almost equal to zero. Unlike them, each of the Fe(II) complexes of DTPA



**Scheme 1**



**Figure 6** The magnetization of Fe complexes of DTPA-1 (b) and DTPyA-1.

and DTPyA can be magnetized. However, it can be seen from Figure 6 that the magnetization of DTPA-1 [Fig. 6(b)] is much larger than that of DTPyA-1 [Fig. 6(a)]. It is very interesting that the magnetization measurement shows a coincidence with the EPR results.

## CONCLUSIONS

Two polymers DTPA and DTPyA and their Fe and Cu complexes are prepared and characterized.

The Fe–DTPA complex reveals abnormal EPR spectrum, and it is considered the result of some superstrong magnetic moments interaction.

The magnetization of the four complexes are measured, and it is found that only Fe complexes have ferromagnetic property, especially the Fe–DTPA complex.

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