Bithiazole-Containing Polymeric Complex and PVA Composite Film: Preparation and Magnetic Properties

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ABSTRACT: Two novel bithiazole-containing polyamides, DClAI and DTTPA, and their complexes were synthesized by condensation and complexation. Novel homogeneous composite films were prepared by *in situ* blending these complexes with polyvinyl alcohol. These polymeric complexes and composite films were characterized by FTIR. The magnetic properties of the complex and its related composite film were measured using a physical property measurement system. It was found that the properties of films are similar to those of their related polymeric complexes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1264–1270, 2004

Key words: polyamides; synthesis; blending; composite films; magnetic polymers

INTRODUCTION

In recent years, there has been considerable interest in organic ferromagnets.[1–4] Organic or polymeric ferromagnetics are a new kind of magnetic materials and frequently appear in the scientific literature.[5–7] Compared with inorganic ferromagnetics, the organic ferromagnetics exhibit characteristics of structural diversities, low density, and ready processing.[8] The magnetic feature of organic or polymeric ferromagnetics operates at the submolecular level, and thus the synthesis of novel organic magnets is significant in the field of magnetic materials.[9,10]

A series of bithiazole-containing polymers as well as the corresponding metal complexes were recently reported.[11–15] The results showed that some of these complexes are ferromagnetic materials. They are probably used as a microwave absorber and have potential applications in the field of stealth technique and electromagnetic shield technique; however, these polymeric complexes showed a very poor solubility and processability. Our interest is in how to make these insoluble ferromagnetic materials solved so that they can be widely applied in various applications.

In this work, we synthesized two novel bithiazole-containing polyamides and their corresponding metal complexes. The magnetic properties of the complexes and the composite films containing these complexes and polyvinyl alcohol (PVA), which were prepared by *in situ* blending method, are also reported.

EXPERIMENTAL

Materials

Dimethyl sulfoxide (DMSO) and dimethyformamide (DMF) were dried and purified by the conventional method. 2,2′-Diamino-4,4′-bithiazole (DABT) was prepared according to the literature.[16]

### Syntheses of polyamides and their metal complexes

Synthesis of DClAI and DClAI–Fe^{2+}

The polymer DClAI was prepared from DABT and 3,4-dianhydride phthalyl chloride, as shown in Scheme 1. An equimolar ratio of DABT and 3,4-dianhydride phthalyl chloride at a concentration of 5% solids content in DMF was magnetically stirred in a round-bottom flask at 60°C for several hours. As the reaction proceeded, the reaction solution became darker and the viscosity of solution increased. The solution was poured into methanol. A yellow precipitate was formed and filtered; washed successively with water, methanol, and ether; and dried under vacuum at 50°C for 24 h. Yield: 70%. The polymer solution prepared above can be used directly in complex preparation with a compound of Fe^{2+}.

The complex was prepared from DClAI and FeSO$_4$·7H$_2$O, which was added to the stirred DMF solution of the polymer in a purified nitrogen atmosphere, and stirring was continued at 60°C. A gray
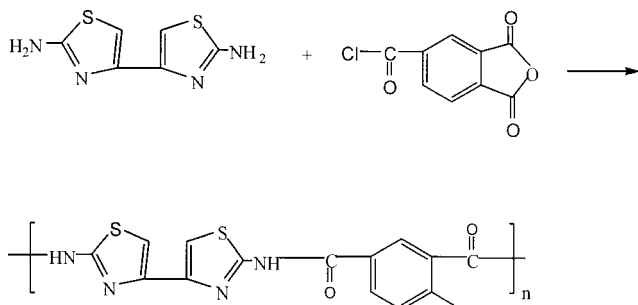
Scheme 1 Synthetic route of DClAI.

precipitate was formed, filtered off, and soaked in methanol for 24 h. The complex was isolated by filtration and dried under vacuum at 60°C for 24 h. Yield: 63%.

Synthesis of DTTPA and DTTPA–Cu^{2+}

The polymer DTTPA was prepared from DABT, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, and *p*-phthalyl chloride, as shown in Scheme 2. To a round-bottom flask, equipped with a magnetic stirrer, was added 3.98 g (0.02 mol) DABT, 2.04 g (0.01 mol) 2,6-pyridinedicarboxylic acid chloride, and 170 g of DMF. The mixture was stirred at 60°C for 4 h, after which 3.22 g (0.01 mol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride was added to the reaction solution. As the reaction proceeded, the viscosity of the solution increased. The mixture was stirred at the same temperature for another 4 h. A brown-yellow precipitate was formed and filtered; washed successively with water, methanol and ether; and dried under vacuum at 50°C for 24 h. Yield: 65%. The Cu^{2+} complex of DTTPA was prepared in almost the same way as the preparation of the Fe^{2+} complex described above except for use of CuSO$_4$·5H$_2$O instead of FeSO$_4$·7H$_2$O. Yield: 50%.

Preparation of composite films

Composite PVA films of DClAI–Fe^{2+} and DTTPA–Cu^{2+} were prepared in the following way. In a round-bottom flask, PVA was completely solved in DMSO, the polymeric complex powder was added to the so-
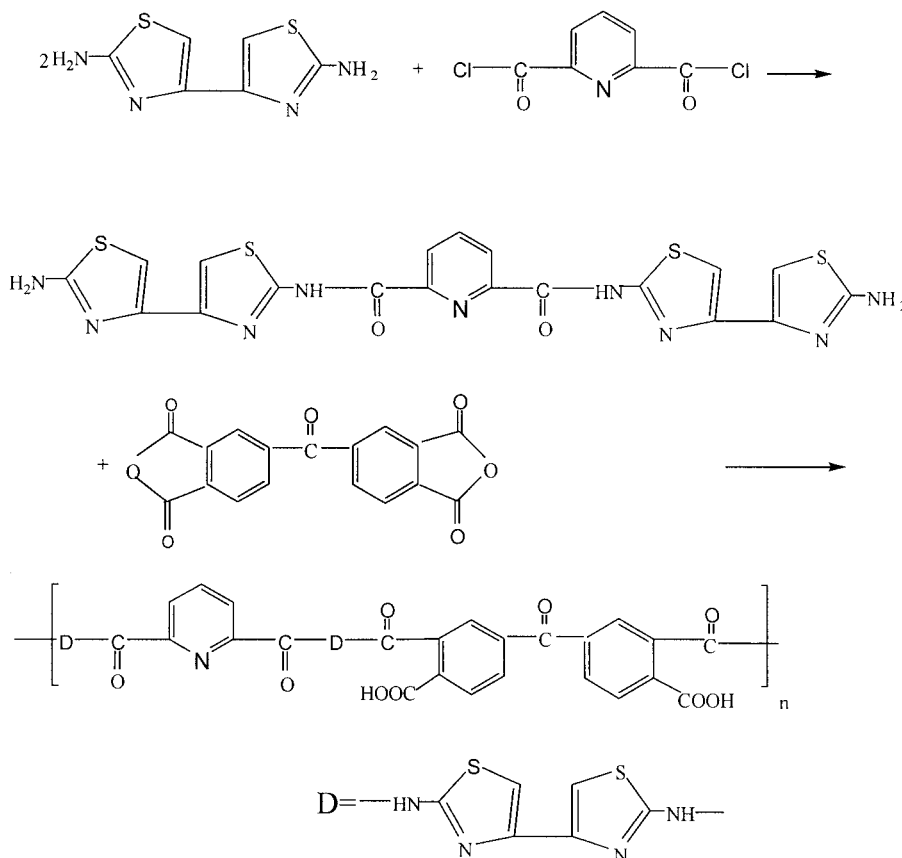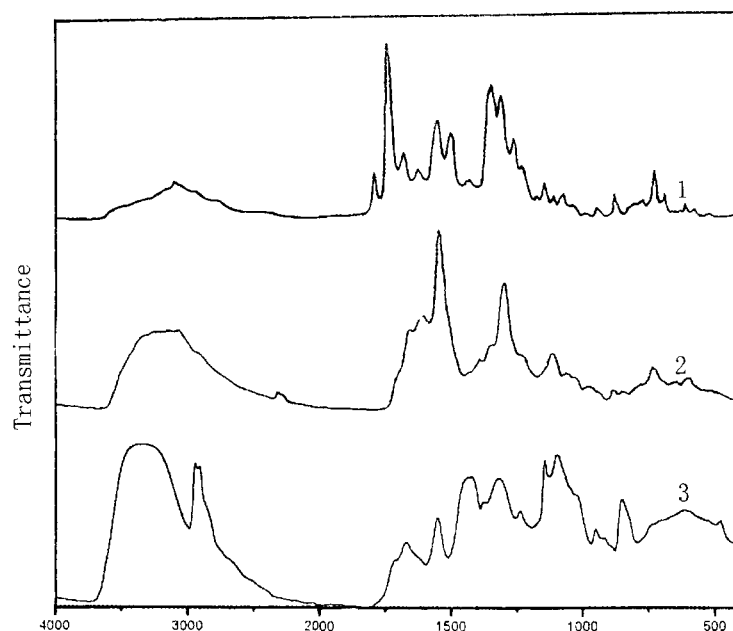

Scheme 2 Synthetic route of DTTPA.

Figure 1   IR spectra of (1) DClAI, (2) DClAI–Fe^{2+}, and (3) DClAI–Fe^{2+} composite film.

lution, and stirring was continued at room temperature for several days until the polymeric powder disappeared and the mixture became homogeneous and transparent. The film was prepared by casting the polymer solution onto a clean and dried polytetrafluoroethylene mold and heated to evaporate the solvent. A transparent polymeric composite film remained after cooling. A series of composite films were prepared by changing the molar ratios of the polymeric complexes and PVA.

RESULTS AND DISCUSSION

Characterization of polyamide, complex, and its related composite film

The complexes DClAI–Fe^{2+} and DTTPA–Cu^{2+} are not soluble in the usual solvents; even in strong polar solvents, such as DMF and DMSO, the solubility is very poor. By *in situ* blending with PVA these complexes are soluble in DMSO solution and can form a transparent solution. PVA plays an important role in determining the solubility of complexes. PVA contains an abundance of hydroxyl groups and the structure of the complexes includes carboxylate groups and metal ions. Interactions such as hydrogen bonding, van der Waals forces, and coulombic interactions between the complexes and PVA enable the complexes to become soluble. The method provides a unique way to synthesize soluble magnetic materials. By compounding, composite PVA films, which are transparent and homogeneous, were obtained, thus offering the prospect

of broadening the application of these magnetic materials.

The DClAI, DClAI–Fe^{2+} complex, and polymer composite film obtained were examined by FTIR spectra (Fig. 1). It must be noted that there is a significant difference in IR spectra between DClAI and its complex. The peak at 1298 cm^{-1} in DClAI might be attributable to the skeletal vibration of imino-interchange isomer of 2-amino-thiazole.[17] However, in the spectrum of the complex, imino-interchange isomer no longer existed, and a skeletal vibration of bithiazole appeared at 1349 cm^{-1}, which suggests that the coordination took place through the ring nitrogen atom of thiazole. The bithiazole ring and skeletal stretching vibration absorption are also observed at 1528, 1460, 1390, 1298, 1241, and 1034 cm^{-1}. The IR spectra of composite films include the characteristic peaks of PVA and peaks of metal complexes. As shown in Figure 2, the spectra of DTTPA, DTTPA–Cu^{2+}, and polymer composite film give the same results as in the case of Figure 1.

Studies on the magnetization of the complexes and their composite films

Magnetization of DClAI–Fe^{2+} and its PVA composite film

A typical relationship between the magnetization (*M*) and the applied field (*H*) for DClAI–Fe^{2+} is shown in Figure 3. It can be seen that as the field decreases, the values of the relative saturation mag-
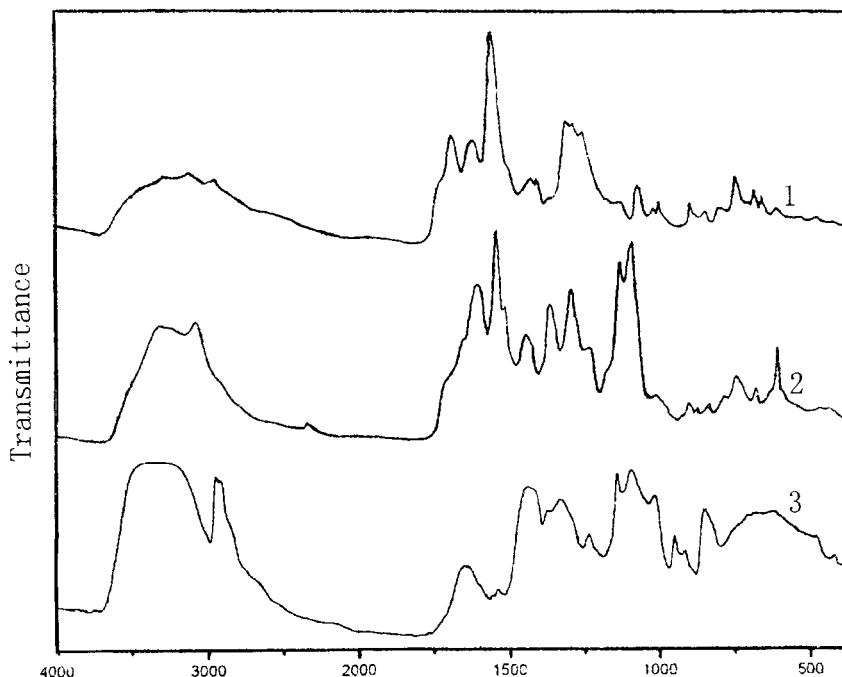
Figure 2 IR spectra of (1) DTTPA, (2) DTTPA–Cu^{2+}, and (3) DTTPA–Cu^{2+} composite film.

netization increase. The relationship between the magnetization and the applied field for its PVA composite film at 2.5, 7.5, and 15 K is shown in Figure 4. Compared with DClAI–Fe^{2+}, there is a similar trend between M and H. As the temperature decreases, the values of the relative saturation magnetization increase. At 2.5 K the value of the relative saturation magnetization is about 0.78 emu/g but at 15 K it is only 0.35 emu/g, which means that the

film has a relatively stronger magnetization at lower temperature. For both DClAI–Fe^{2+} and the film, the value of M increases sharply until about 20 kOe, although an increasing trend is slow above 25 kOe. This is a typical characteristic of a ferromagnet, which suggests that the magnetic property of this composite film is similar to that of the polymeric complex.
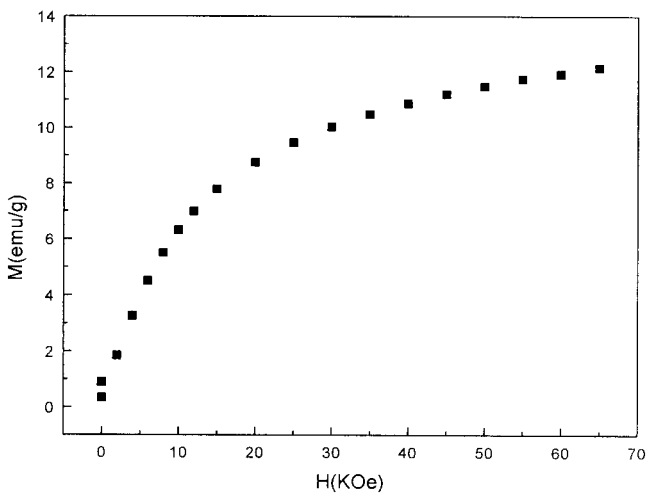

Figure 3 Magnetization curve M versus H at $T = 1.5$ K for DClAI–Fe^{2+}.
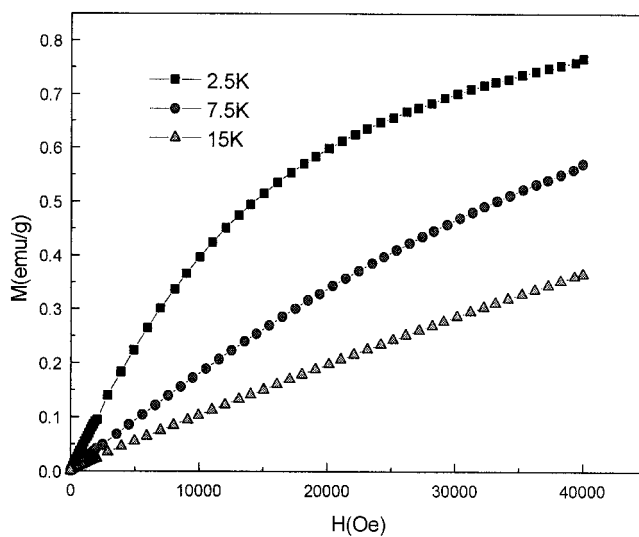

Figure 4 Magnetization curve M versus H at $T = 2.5, 7.5,$ and 15 K for DClAI–Fe^{2+} composite film.
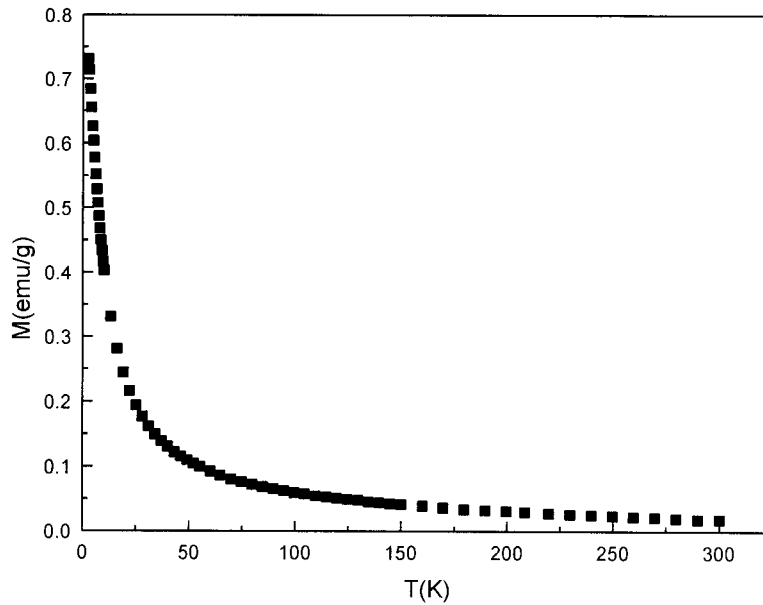
Figure 5   Magnetization versus temperature at H = 30 kOe for DClAI–Fe^{2+} composite film.

The temperature dependency of the magnetization of the film at an applied magnetic field of 30 kOe from 0 to 300 K is shown in Figure 5. The magnetization of the film decreases with increasing temperature. The temperature dependency of the χT products of the film is shown in Figure 6. The value of χT changes only slightly 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, which suggests that the system approaches a magnetic phase transition near 100 K.

Magnetization of the DTTPA–Cu^{2+} composite film

The typical relationships between the magnetization and the applied field for the DTTPA–Cu^{2+} composite film at 2 and 5 K are shown in Figure 7. It can be seen that as the temperature decreases, the values of the relative saturation magnetization increase. At 2 K the value of the relative saturation magnetization is 1.15 emu/g, but at 5 K it is only 0.75 emu/g, which means that, at lower temperature, the composite film has a relatively stronger magnetization.
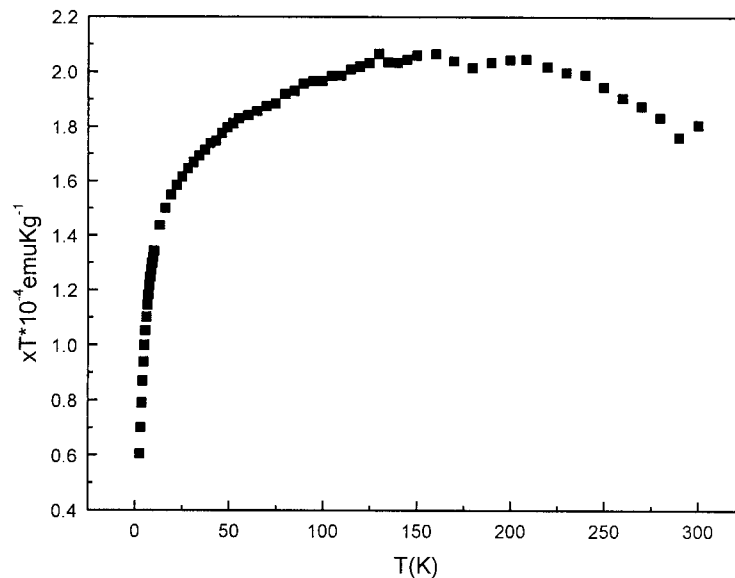

Figure 6   Magnetic susceptibility data for DClAI–Fe^{2+} composite film.
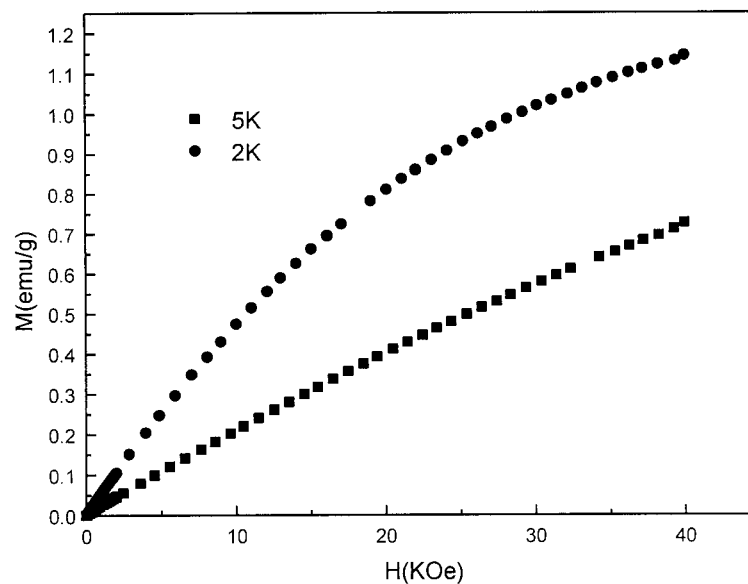
Figure 7 Magnetization curve M versus H at $T = 2$ and 5 K for DTTPA–Cu^{2+} composite film.

The temperature dependency of the magnetization of the film at an applied magnetic field of 30 kOe from 0 to 300 K is shown in Figure 8. As the temperature increases, the magnetization of the film decreases. The temperature dependency of the χT products of the film is shown in Figure 9. The value of χT increases with decreasing T above 60 K. As the temperature decreased from 60 to 10 K, the value of χT changed only slightly, which suggests that M has been saturated. Below 10 K, an abrupt increase of the value of χT is observed. Because at this time M reaches a maximum, the value of χT decreases as T decreases, which suggests that the system approaches a magnetic phase transition at 10 K.

CONCLUSIONS

Two polymers, DClAI and DTTPA, and their complexes were synthesized and characterized. Novel composite uniform films were also prepared by *in situ* compounding these metal complexes with PVA. The magnetization of the DClAI–Fe^{2+} and their related films was measured, and results indicated that the
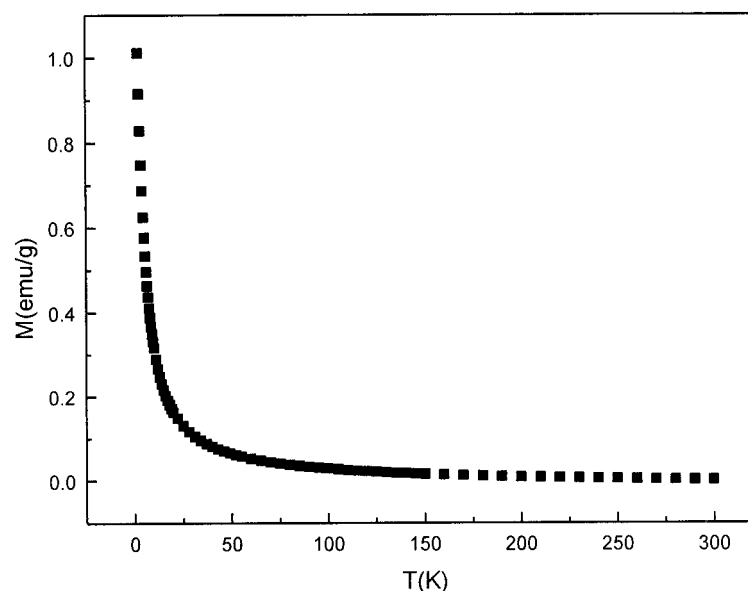

Figure 8 Magnetization versus temperature at $H = 30$ kOe for DTTPA–Cu^{2+} composite film.
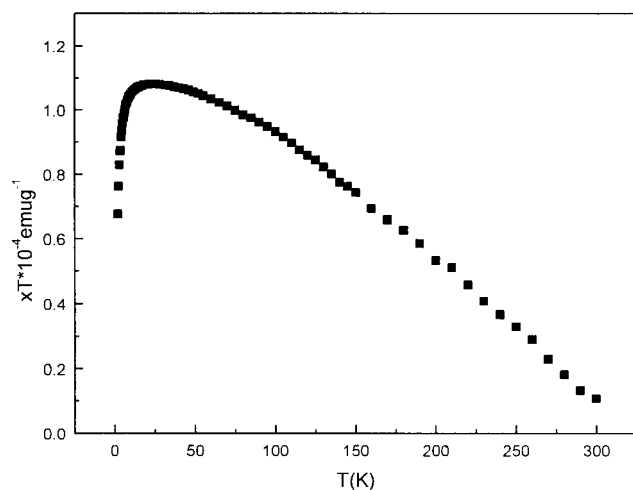
Figure 9 Magnetic susceptibility data for DTTPA–Cu^{2+} composite film.

properties of films are similar to those of their related polymeric complexes.

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