Synthesis and Magnetic Properties of Bithiazole-Based Polyamide Complexes

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ABSTRACT: A new polyamide containing bithiazole moieties (polythiazole amides, PTA) was synthesized by the polycondensation of 2,2′-diamino-4,4′-bithiazole and oxalyl chloride. The rare-earth metal complexes of the polymer were prepared from PTA and rare-earth chloride in DMSO. The structures of the polymer and the complexes were characterized through IR spectra. The preliminary magnetic properties of the complexes were investigated; it was found that these materials are ferromagnets at low temperature. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 554–557, 2008

Key words: polyamide; bithiazole; synthesis; metal–polymer complexes; magnetic property

INTRODUCTION

The study on polymers containing bithiazole moieties has been more than half a century. During 1944–1946, Erlenmeyer published some articles concerning these polymers, but left the polymers uncharacterized.[1–4] Later, because the thiazole nucleus has excellent thermal and chemical stability, polymers containing bithiazole moieties were extensively studied by several groups in the world.[5–9] It is well known that bithiazole could coordinate with many kinds of metal ions. In 1996, Sun et al. found that when the polymers containing bithiazole moieties chelated with transition metal ions, the polymer complexes obtained possess fairly ferromagnetism. It is a new method to prepare polymeric ferromagnet.[10–15] In this article, we report the synthesis and characterization of a new polyamide containing bithiazole moieties and its rare-earth complexes. The preliminary magnetic properties of the polymeric complexes were investigated.

EXPERIMENTAL

Materials

Dimethylformamide (DMF), dimethylsulfoxide (DMSO), and triethylamine were dried and purified by usual methods. 2,2′-Diamino-4,4′-bithiazole (DABT) was prepared according to literature[5] followed by several recrystallizations. Oxalyl chloride was a commercial product of Shanghai Chemical Reagent.

Measurements

IR spectra were recorded with a Bruker Vector 22 using KBr pellets. The intrinsic viscosity of polymer was measured by an Ubbelohde-type viscometer at 30°C using sulfuric acid as a solvent. Magnetic measurements were carried out by a PPMS-9T magnetometer (Quantum Design). The magnetization with the applied magnetic field was measured at 4 K, and the temperature dependence of the magnetization was measured from 4 to 300 K at an applied magnetic field of 30 kOe.

The contents of rare-earth metals were determined by complexometry using EDTA (Scheme 1).

Synthesis of polymer

A three-necked flask equipped with a dropping funnel and gas inlet tube was charged with a solution of 2,2′-diamino-4,4′-bithiazole (5 mmol) in DMF (40 mL). Oxalyl chloride (5.02 mmol) diluted with DMF (5 mL) was added dropwise to the solution at 0°C under a stream of N_2. After the mixture stirring at ambient temperature for 8 h, it was poured into methanol and the light yellow solid obtained was filtered off, washed with methanol, redissolved in a minimum amount of DMF and again precipitated in methanol, filtered and dried under vacuum at 80°C for 12 h, then the polymer polythiazole amides (PTA) was obtained. Yield: 86%, [η]: 0.12 dL/g.

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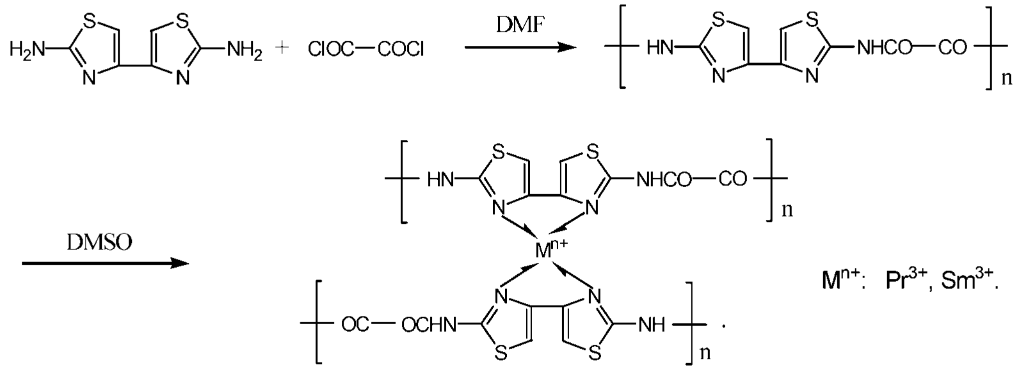

Scheme 1 Synthesis route of PTA and suggested structure for the corresponding complexes.

Preparation of the polymeric complex

In a three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas inlet tube, was charged with 0.5 g PTA prepared earlier and 50 mL DMSO as solvent. After the inner air was removed with nitrogen through the gas inlet tube, the stoichiometric $PrCl_3 \cdot 6H_2O$ or $SmCl_3 \cdot 6H_2O$ was added to the polymer solution. While stirred under N_2 atmosphere, the mixture was heated to 80°C and stirred at this temperature for another 24 h. After cooling down, the reaction mixture was poured into cold methanol. The precipitate was collected in a Bush funnel, washed with methanol and deionized water thoroughly, and then dried at 80°C under vacuum for 12 h.

RESULTS AND DISCUSSION

Synthesis of polymer and its complexes

Scheme 1 shows the synthesis route for PTA and their rare-earth complexes. To prepare the polymer successfully, we paid special attention to drying the solvents used and kept the reaction temperature at 0°C, for the high activity of carbonyl chloride group. The corresponding complexes were prepared by reacting with PTA with rare-earth chloride in DMSO. The appearance of precipitate accompanying with color changing from light yellow to dark green indicates the formation of the rare-earth complexes. It should be noted that the collected powder product must be washed with deionized water thoroughly to ensure the removing of the excessive rare-earth ions.

The IR spectra of DABT, PTA, PTA–Pr^{3+}, and PTA–Sm^{3+} are shown in Figure 1, The absorption bonds in the spectra of DABT at 3300–3500 cm^{-1} and 3100–3300 cm^{-1} (double) can be attributed to the vibration of N—H of the amino groups. It is found that in the case of PTA those peaks are dramatically weakened, and the characteristic absorptions of skeletal vibration of thiazole appear at 1531, 1359, 1280, 851 cm^{-1}, which indicate that the amino group of DABT has reacted with the carbonyl chlo-

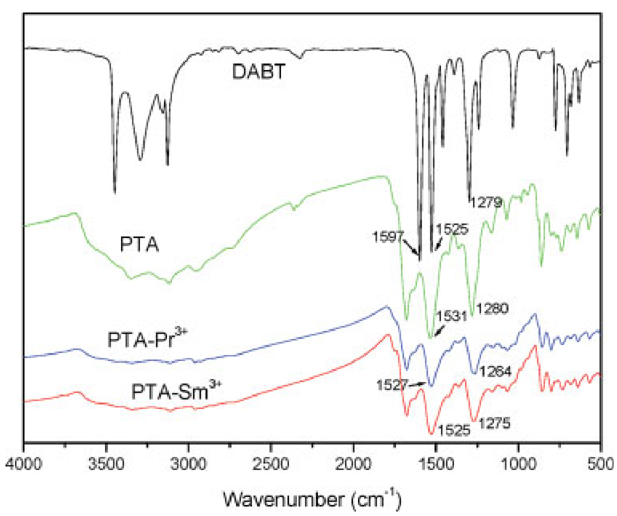

Figure 1 IR spectra of DABT, PTA, PTA-Pr^{3+}, and PTA-Sm^{3+}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

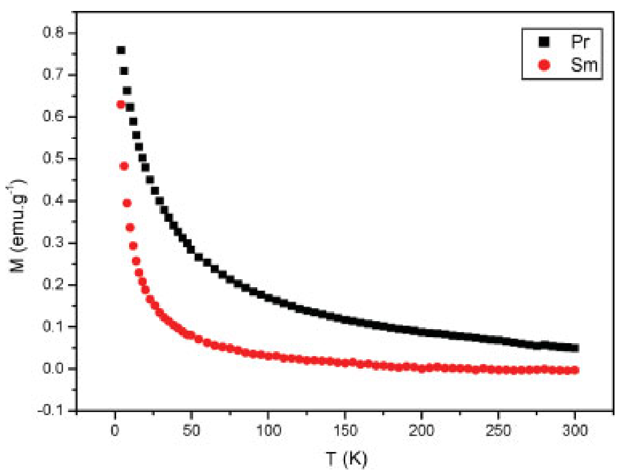

Figure 2 Magnetization as function of temperature at an applied magnetic field of 30 kOe for PTA–Pr^{3+} and PTA–Sm^{3+}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

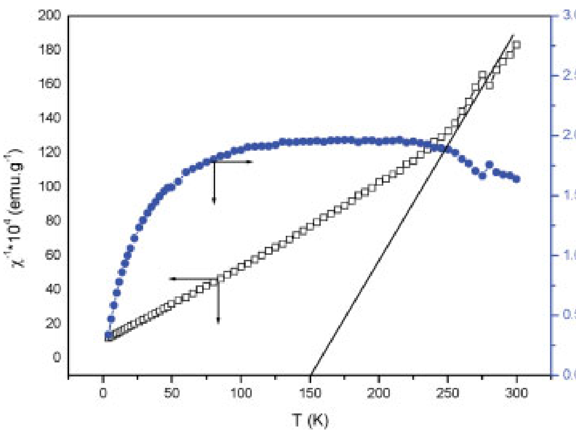

Figure 3 Temperature dependence of the product of magnetic susceptibility and temperature (χT), and reciprocal magnetic susceptibility (χ^{-1}) for PTA–Pr^{3+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law from 230 to 300 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

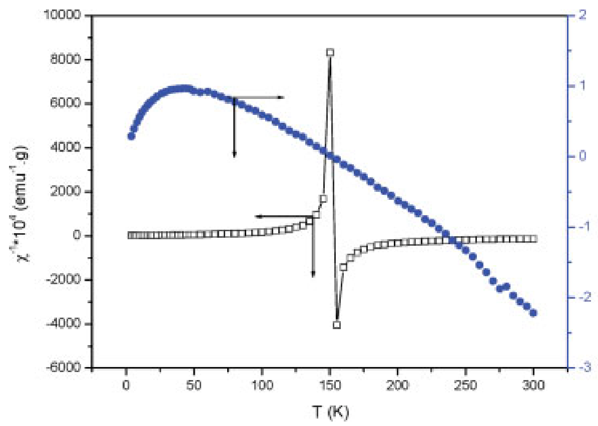

Figure 4 Temperature dependence of the product of magnetic susceptibility and temperature (χT), and reciprocal magnetic susceptibility (χ^{-1}) for PTA–Sm^{3+} at an applied magnetic field of 30 kOe. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ride. The spectrum of PTA–Pr^{3+} is similar to that of PTA except for some changes in absorption intensities, but the absorptions at 1531, 1280 cm^{-1} from the skeletal vibration of thiazole ring[16] shifts to 1527, 1264 cm^{-1}. This indicates the coordination between the nitrogen atoms of bithiazole moieties and the incorporated Pr^{3+}, because the skeletal vibrations of bithiazole moieties need lower energy to oscillate, because of the five-numbered ring coordination structure. Similar changes can be observed in IR spectra of PTA–Sm^{3+}, the bands at 1531, 1280 cm^{-1} of PTA shifted to 1525, 1275 cm^{-1} of PTA–Sm^{3+}.

Magnetic susceptibility of polymer complexes

First, it should be noted that PTA are diamagnetic because of the absence of paramagnetic sources, to make sure that their metal complex is a magnetic material, we examined the temperature dependence of the magnetization for the polymeric complexes over the temperature range of 4–300 K at an applied magnetic field of 30 kOe (Fig. 2). It can be found that the magnetization increases slowly with the decreasing of temperature and then increases sharply in the range of 40–60 K. The results indicate that the strong magnetic interaction arises among coordinated rare-earth ions at low temperature.

Figure 3 shows that the magnetic susceptibility (χ) of PTA–Pr^{3+} complex follows the Currie–Weiss relationship in the temperature range of 254–300 K, which means the polymeric complex exhibits paramagnetic behavior at high temperatures. However, the positive Currie–Weiss temperature (θ = 151 K) implies the existence of ferromagnetic coupling in the material. It can be also found that the product of magnetic susceptibility and temperature remains constant in the temperature range of 110–230 K. This can be interpreted as the realization of a ferromagnetic coupling among spins in short range at low temperature. For PTA–Sm^{3+}, its χ^{-1}–T curve is a hyperbola around 151 K, which is different from that of PTA–Pr^{3+} (Fig. 4). It means that above 151 K, the magnetism derived from the Sm^{3+} is too weak to compensate the diamagnetism of the polymer PTA, thus the complex behaves as diamagnetism; but below 151 K, the χ^{-1}–T curve also has a positive Currie–Weiss temperature, 138 K, which implies the existence of ferromagnetic coupling in the material. It can be also found that the value of χT monotonically increase with a decreasing T above 38 K, below 38 K, an abrupt increase in the slope of χT is observed, which suggested that the material approaches a magnetic transition at 38 K.

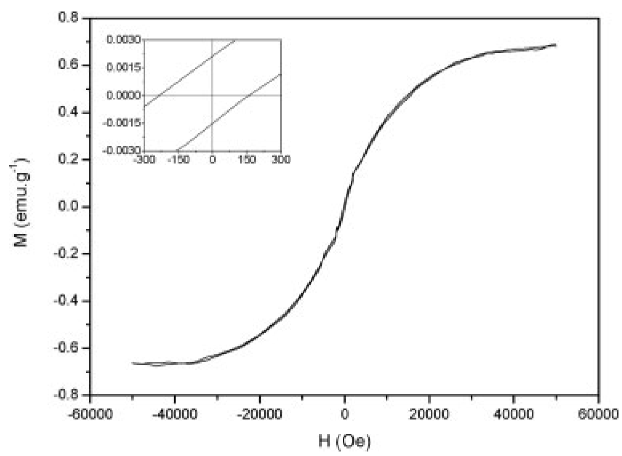

Figure 5 Hysteresis loop at 4 K for PTA02–Sm^{3+}. (Inset): Expanded view of the region from –300 to 300 Oe.

TABLE I
Magnetic Properties of Polymer Complexes and the Content of Rare Earth Metals

Complex	Relative saturation magnetization (emu/g)	Remanence magnetization (emu/g)	Coercivity (Oe)	Curie–weiss temperature T_p (K)	Content of rare earth metals (%)
PTA02-Sm^{3+}	0.68	0.002	233	134	4.9
PTA02-Pr^{3+}	1.07	0.123	239	151	7.1

Magnetization and hysteresis loop

At low temperature, the magnetization curve as function of applied field exhibits a hysteresis cycle for the polymeric complexes, Figure 5, which is characteristic of ferromagnetic interactions. From the typical S shape and small area of the hysteresis loops, we may conclude that the polymeric complexes are soft ferromagnets.

Table I summarizes the magnetic properties of PTA–Pr^{3+} and PTA–Sm^{3+}. The results indicate that both the complexes present the characteristics of a soft ferromagnet at low temperatures, and we can see that their Curie–Weiss temperature is relatively high. We notice that the relative saturation magnetization of PTA–Pr^{3+} is higher than that of PTA–Sm^{3+}, it maybe be explained that the rare-earth metal ions content of PTA–Pr^{3+} is higher than that of PTA–Sm^{3+}.

CONCLUSIONS

A new polythiazole amide and their rare-earth complexes have been studied. Both the complexes exhibites the characteristics of soft-ferromagnetic materials at low temperature, and have relatively high Curie–Weiss temperatures.

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