Synthesis and Magnetic Properties of Novel Poly(*N*-2-thiazolyl(meth)acrylamide)-Fe(II) Complexes

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ABSTRACT: *N*-2-thiazolyl(meth)acrylamides were polymerized by a radical route to obtain polymers in good yields. The polymers, with a pendent heterocyclic group, are soluble in common organic solvents, which allow the corresponding metal complexes with higher loads to be prepared easily. FTIR, ^{1}H NMR, and energy-dispersive X-Ray spectroscopy (EDX) were applied to characterize these materials. The magnetic behavior of poly(*N*-2-thiazolyl(meth)acrylamide)-Fe(II) complexes was examined as a function of applied magnetic field at 4 K and as a function of temperature (4 ~ 300 K) at an applied magnetic field of 1 ~ 3 kOe, exhibiting the characteristics of a ferromagnet. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 83–87, 2005

Key words: *N*-2-thiazolyl(meth)acrylamide; polymer; polymeric complex; magnetic property; synthesis

INTRODUCTION

In recent years, organic ferromagnets have drawn growing attention due to their characteristics of structural diversities, low density, and ready processing.[1–5] Design and synthesis of magnetic polymers are one of the great challenges in today's magnetic material research, and some significant achievements have been made in this field.[6–8]

According to Hoffmann and coworkers,[9] polymers built from sulfur, carbon, and nitrogen, containing five-membered rings, would theoretically display magnetic ordering. Several years ago, we proposed and started the design and synthesis of bithiazole-based polymers and corresponding metal complexes. A variety of novel polymer-metal complex materials incorporating bithiazole moieties in the main chain have been obtained, and some of them showed interesting magnetic behaviors.[10–14] These materials should have potential applications in the fields of microwave absorbance and electromagnetic shield technique. However, the main drawback of this kind of polymeric matrices is that their solubility is usually poor in common solvents and thereby decreases their processability. In a recent attempt, we successfully prepared magnetic composite films by *in situ* blending of bithiazole-based polymeric complexes with polyvinyl alcohol.[15]

In this article, we describe the synthesis of acrylamide-type polymers with pendent thiazolyl groups (Scheme 1). The as-prepared polymers exhibited better solubility in common organic media as compared to the main chain-type bithiazole-based polymers, as well as good complexing ability to metal ions. The formation of polymeric Fe(II) complexes was characterized by IR and EDX, and their magnetic property was also investigated using a Physical Properties Measurement System.

EXPERIMENTAL

Materials

2-Aminothiazole was purchased from MERCK-Schuchardt. Triethylamine and ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were purchased from Shanghai Chem. Reagent Co. Acryloyl chloride and methacryloyl chloride were prepared from thionyl chloride and corresponding carboxylic acids. Tetrahydrofuran (THF) was dried over a benzophenone-sodium complex for several days and distilled prior to use. 2, 2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol.

Measurements

FTIR spectra were recorded with a Bruker Vector 22 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance AMX-500 NMR instrument in DMSO-d_6 with tetramethylsilane (TMS) as the internal standard. Chemical composition of metal complexes was determined by energy-dispersive X-ray spectroscopy (EDX) (Finder 1000 X-ray spectrometer, Cam-

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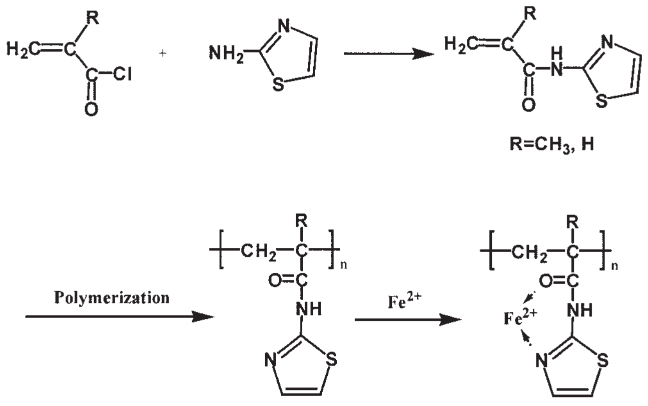

Scheme 1 Synthetic route for monomer, polymer, and polymeric complexes.

bridge). Viscosity measurements were made in DMSO with an Ubbelohde type viscometer at 30°C. The magnetic measurements were carried out by a PPMS-9T magnetometer (QUANTUM DESIGN); the temperature is ranged from 4 to 300 K, and the intensity of magnetic field is ranged from –50 to 50 kOe.

Monomer synthesis

N-2-Thiazolylacrylamide (NTA)

A THF (20 mL) solution of acryloyl chloride (4.2 g, 0.04 mol) was slowly added into a stirred THF solution of 2-aminothiazole (4 g, 0.04 mol) containing triethylamine (4.04 g, 0.04 mol) at 0°C. The resulting mixture was stirred for 20 h, and the formed solid was removed. Then, the filtrate was poured into a large amount of hexane to give a white product, followed by washings with a dilute solution of $NaHCO_3$ and deionized water. Yield: 52%. Mp: 101–102°C.

IR (KBr, cm^{-1}): 3161 (N–H), 2921 (C–H), 1682 (C=O), 1640 (C=C), 1575 (*N*-H), 1483, 1364, 1332 (thiazole). ^1H NMR (500 MHz, DMSO-d_6): δ 7.51 (thiazole-*H*), 7.26 (thiazole-*H*), 6.53 (=C*H*CO), 6.41 (H_2C=), 5.90 (H_2C=), 12.36 (N*H*).

N-2-Thiazolylmethacrylamide (NTMA)

Monomer NTMA was prepared similarly to NTA from the corresponding methacryloyl chloride and 2-aminothiazole. Yield: 85%. Mp: 125–127°C.

IR (KBr, cm^{-1}): 3137 (N–H), 2923 (C–H), 1671 (C=O), 1628 (C=C), 1551 (N-H), 1491, 1390, 1323 (thiazole). ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (thiazole-H), 6.98 (thiazole-H), 5.92 (H_2C=), 5.65 (H_2C=), 2.12 (CH_3), ~ 11.8 (NH).

Polymerization

Polymerization was carried out with AIBN as an initiator in dry THF at 70°C for 20 h under the following conditions: $[\text{monomer}]_0 = 0.11M$, [initiator] = 0.87 mM. After the completion of polymerization, the reaction mixture was poured into a large amount of methanol to precipitate the formed polymer. Then, the polymer was filtered off, washed with methanol, and dried under vacuum. Both of the products (PolyNTA and PolyNTMA) are white powder.

*Poly(*N*-2-thiazolylacrylamide), PolyNTA IR (KBr, cm^{-1}).* 3171 (*N*-H), 2924 (C-H), 1685 (C=O), 1553 (*N*-H), 1483, 1367, 1320 (thiazole); Yield: 84%; $[\eta] = 0.21$ dL/g (DMSO, 30°C). ^1H NMR (500 MHz, DMSO-d_6): δ ~ 7.42 (thiazole-*H*), 1.8 (CH_2), 2.5(C*H*), ~ 12.0 (N*H*).

*Poly(*N*-2-thiazolylmethacrylamide), PolyNTMA IR (KBr, cm^{-1}).* 3237 (*N*-H), 2929 (C-H), 1675 (C=O), 1535 (*N*-H), 1478, 1390, 1320 (thiazole); Yield: 81%; $[\eta] = 0.27$ dL/g (DMSO, 30°C). ^1H NMR (500 MHz, DMSO-d_6): δ 7.43 (thiazole-*H*), 7.08 (thiazole-*H*), 2.10 (CH_2), 1.30 (CH_3), ~ 11.7 (N*H*).

Preparation of polymeric complex

The preparation of polymeric complexes was performed by mixing $FeSO_4{\cdot}7H_2O$ (0.452 g, 1.6 mmol) with the polymer (0.15 g) in DMSO at 80°C under a purified N_2 atmosphere. The resulting solution was stirred for 20 h, producing the precipitate, which was collected by suction filtration and washed thoroughly with deionized water to remove excess physisorbed $FeSO_4$ (the filtrate was treated by H_2O_2 solution and then detected with NH_4SCN titration). The isolated complexes (brick-red powder) were dried under vacuum at 60°C for 2 days.

PolyNTA-Fe^{2+} IR (KBr, cm^{-1}). 3256 (*N*-H), 2925 (C-H), 1685 (C=O), 1547 (*N*-H), 1483, 1368, 1320 (thiazole). Yield: 87%.

PolyNTMA-Fe^{2+} IR (KBr, cm^{-1}). 3377 (*N*-H), 2928 (C-H), 1672 (C=O), 1536 (*N*-H), 1479, 1390, 1320 (thiazole). Yield: 91%.

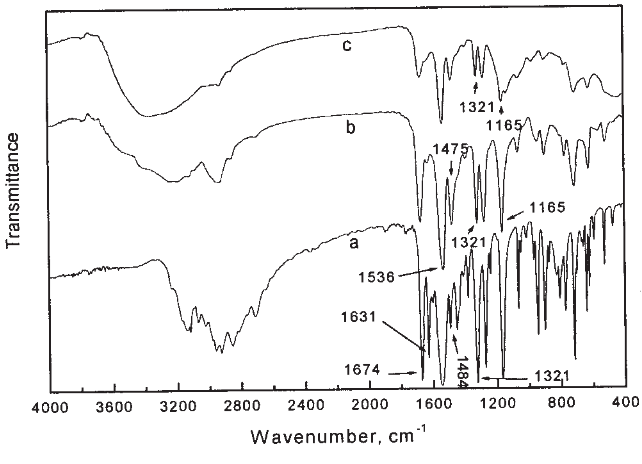

Figure 1 IR spectra of (a) NTMA, (b) PolyNTMA, and (c) PolyNTMA-Fe^{2+} complex.

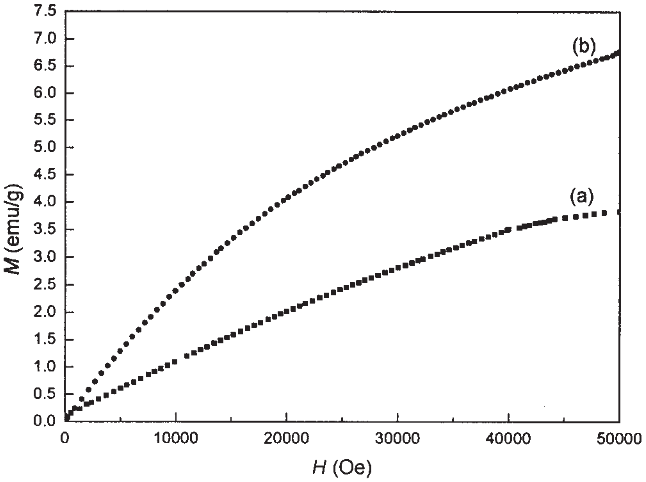

Figure 2 Magnetization curve (*M*) versus applied field (*H*) at 4 K for the complexes PolyNTA-Fe^{2+} (a) and PolyNTMA-Fe^{2+} (b).

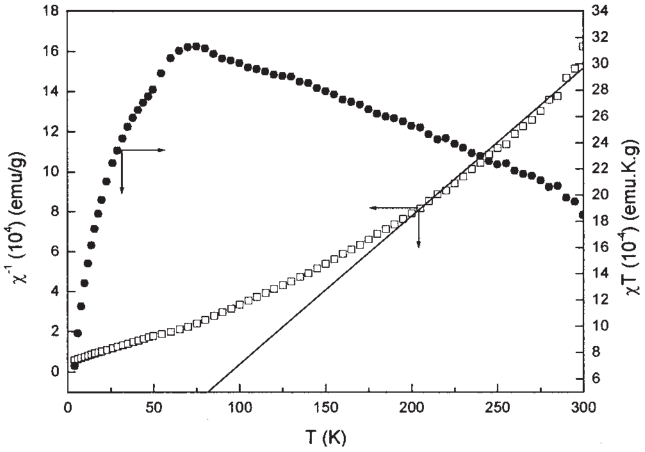

Figure 4 The product of magnetic susceptibility (χ) and temperature (*T*), and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (*T*) for PolyNTMA-Fe^{2+} at an applied magnetic field of 1000 Oe. The straight line is a fit to the Curie–Weiss law in the temperature range 200–300 K.

RESULTS AND DISCUSSION

Characterization of polymer and polymeric complex

As shown in Scheme 1, the radical polymerization of *N*-2-thiazolyl(meth)acrylamides was carried out under mild conditions, producing desired polymers in good yields. The polymers were obtained as white powders and exhibited relatively low molecular weights based on their specific viscosity values ([η] = 0.2 ~ 0.27 dL/g, DMSO, 30°C). In contrast to the bithiazole-based polymers previously synthesized in our laboratory, the polyamides with a pendent thiazole group are readily soluble in DMSO and DMF but slightly soluble in tetrahydrofuran. This difference may be attributed to the fact that the main chain of the polyamides is much more flexible than that in the former cases. In our previous study, the bithiazole-containing polymers have a rigid conjugate structure and usually showed a poor solubility.[10,11] The better solubility of polymers is favorable for obtaining metal complexes with higher loads. However, the resulted Fe(II)-complexes cannot dissolve in the above solvents. In fact, these complexes gradually precipitated from the medium with the elongation of complexing reaction time.

The structure of both polymers (PolyNTA and PolyNTMA) was characterized by IR and ^{1}H NMR spectroscopy. As a representative, Figure 1 shows the IR spectra of monomer NTMA, PolyNTMA, and

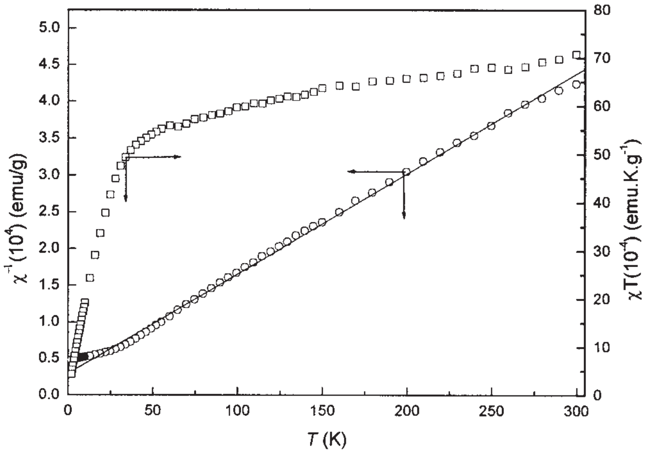

Figure 3 The product of magnetic susceptibility (χ) and temperature (*T*), and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (*T*) for PolyNTA-Fe^{2+} at an applied magnetic field of 1000 Oe. The straight line is a fit to the Curie–Weiss law in the temperature range 40–300 K.

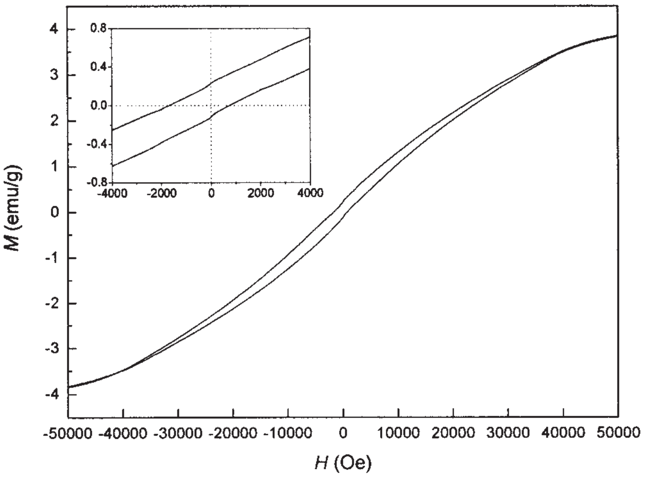

Figure 5 Magnetic hysteresis loop of PolyNTPA-Fe^{2+} at 2 K. Insert: Expanded view of the region from −4000 to 4000 Oe.

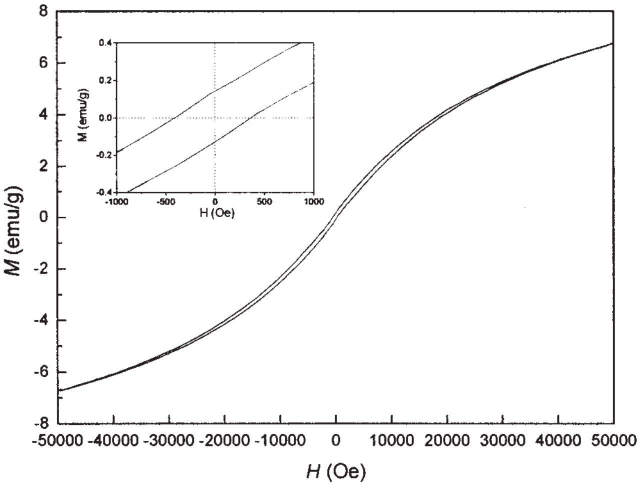

Figure 6 Magnetic hysteresis loop of PolyNTMA-Fe^{2+} at 4 K. Insert: Expanded view of the region from –1000 to 1000 Oe.

PolyNTMA-Fe^{2+} complex. The characteristic absorptions of the thiazole ring and skeletal vibration are observed at 1484, 1321, and 1165cm^{-1}.[16] The peaks at 1674 and 1536cm^{-1} are attributed to amido linkage, and they have no variation in all the spectra. In comparison with the monomer, a significant change is the disappearance of the C=C stretching vibration (1631cm^{-1}) in the IR spectrum for PolyNTMA. These results indicate that the polymerization took place in the C=C double bond of the acryl skeleton, and the thiazole group retained its integrity. We can also find in Figure 1 that the spectrum of polyNTMA-Fe^{2+} (c) is almost identical with that of its polymer matrix (b), except for some differences in the region of 1165–400 cm^{-1}.

According to the data from energy-dispersive X-ray spectroscopy (EDX), the Fe contents were about 14.9 wt % and 16.7 wt % for PolyNTA-Fe^{2+} and PolyNTMA-Fe^{2+}, respectively. Thus, the formula of the polymeric complexes may be suggested as $[C_6H_6N_2OS(FeSO_4)_{0.69}]_n$ and $[C_7H_8N_2OS(FeSO_4)_{0.92}]_n$. This means that in the PolyNTA skeleton, there are about three repeating units on average matching two Fe^{2+} ions, while for the latter case, one repeating unit nearly matches one Fe^{2+} ion. Comparison of the results and those observed in our previous study indicates that the two polymers possess greater coordinative ability,[11,17] which may be relative to the good solubility of polymer matrices to a certain extent. Although we proposed an intrachain structure for the polymeric complexes as shown in Scheme 1, the possibility of coordination from different chains also cannot be excluded. However, the exact structure has not yet been confirmed and remains to be elucidated.

Magnetic property of Fe^{2+}-complexes

Figure 2 presents a typical relationship between magnetization (*M*) and applied field (*H*) for the complexes at 4 K. It can be seen that the magnetization increases with an increase of applied field for both samples. The value of relative saturation magnetization for PolyNTMA-Fe^{2+} (~ 6.75 emu/g) is obviously larger than that of PolyNTA-Fe^{2+}, which accords with their load of Fe(II) ions.

The temperature dependence of the magnetic susceptibility is also studied at an applied magnetic field of 1000 Oe from 4 K to 300 K for the complexes (Figs. 3 and 4). For PolyNTA-Fe^{2+}, the magnetic susceptibility (χ) follows the Curie–Weiss relationship, $\chi = C/(T - \theta)$, in a larger temperature range (300 ~ 40 K). This means that the complex exhibits paramagnetic behavior at high temperatures. However, from 4 to 40 K, the magnetic susceptibility deviated from the Curie–Weiss law as a typical antiferromagnetic curve fashion, indicating the presence of exchange interaction at a low temperature scope. The negative Curie–Weiss temperature (θ = –21.4 K) also implies the existence of antiferromagnetic interaction in this complex.

It is noteworthy that the magnetic behavior for PolyNTMA-Fe^{2+} is different from that of PolyNTA-Fe^{2+} (Fig. 4). The positive Curie–Weiss temperature (θ = 80.1 K) indicates the existence of mainly ferromagnetic coupling in the PolyNTMA-Fe^{2+}complex.[18] The value of χT increases with a decrease of temperature, and an abrupt increase is observed below 70 K. This suggests that the system approaches a magnetic phase transition at 70 K.[11]

To obtain complementary information on the magnetic properties, the hysteresis loops have been de-

TABLE I
Magnetic Properties of Polymeric Fe(II)-Complexes

Polymeric complex	Relative saturation magnetization (emu/g)	Remanence magnetization (emu/g)	Coercivity (Oe)	Ref.
PolyNTA-Fe^{2+}	3.9 (4K)	0.22 (4 K)	1650 (4 K)	this work
PolyNTMA-Fe^{2+}	6.8 (4K)	0.13 (4 K)	400 (4 K)	this work
PMD-Fe^{2+}	3.25 (5K)	0.02 (50K)	158 (50K)	10
PMBD-Fe^{2+}	1.8 (5K)	0.014 (5 K)	360 (5 K)	11

tected at 4 K for the materials. As shown in Figures 5 and 6, the magnetization curve as a function of applied field exhibits a hysteresis cycle at low temperature, which is a characteristic of ferromagnetic interactions.

Table I summarizes magnetic parameters of both Fe(II)-complexes together with those of main-chain type complexes previously synthesized in this laboratory for comparison. Compared to the main chain-type bithiazole-based complexes (PMD-Fe^{2+} and PMBD-Fe^{2+}), both PolyNTA-Fe^{2+} and PolyNTMA-Fe^{2+} have higher values of relative saturation magnetization. On the other hand, the Fe^{2+}-complexes of PolyNTA and PolyNTMA also showed some differences in magnetic property. The results imply that the structure of the repeating unit in the polymeric skeleton has a subtle effect on their magnetic behaviors. Further investigation for this is in progress.

CONCLUSIONS

Polymers of (meth)acrylamides with a pendent thiazole group and their ferrous complexes have been prepared in good yields. The polymers showed better solubility than previously reported main-chain bithiazole-based polymers, which enhances their complexing ability to metal ions. From the field and temperature dependence of magnetization and hysteresis loop, it can be concluded that the Fe(II)-complex PolyNTA-Fe^{2+} is an antiferromagnet, whereas PolyNTMA-Fe^{2+} is a soft ferromagnet. The values of remanence magnetization and coercivity of PolyNTMA-Fe^{2+} are lower than those of the former. This difference in magnetic behavior between the two complexes may be related to their repeating-unit structure in the main chain, except for the content of bound Fe(II) ions.

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