

Synthesis and Magnetic Properties of Novel Complexes of Poly(*N*-2-thiazolylmethacrylamide) with Nd(III), Pr(III), and Sm(III)

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ABSTRACT: *N*-2-Thiazolylmethacrylamide (NTMA) was polymerized by a radical route to obtain the polymer in good yields. The complexes of PolyNTMA with three rare earth ions Nd(III), Pr(III), and Sm(III) were prepared for the first time. FTIR and ¹H NMR were applied to characterize these materials. The magnetic behavior of PolyNTMA–metal 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 30 kOe. It was found that Pr(III)

complex exhibits an antiferromagnetic property, while Nd(III) and Sm(III) complexes exhibit a special magnetic property different from the typical magnet. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1289–1293, 2006

Key words: poly(*N*-2-thiazolylmethacrylamide); metal-polymer complexes; magnetic polymers; functionalization of polymers

INTRODUCTION

In recent years there has been much interest in the preparation of organic ferromagnets.^{1–5} Compared to common inorganic ferromagnets, the organic ferromagnets possess the characteristics of structural diversities, lower density, and readily processing. 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 Genin and Hoffmann,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 incorporating bithiazole moieties in the main chain have been obtained, and some of them showed interesting magnetic behaviors.^{10–16} However, the main drawback of these kinds 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 acrylamide-type polymers with pendent thiazolyl groups and prepared the corresponding ferrous complexes.¹⁷ The polymers showed better solubility than previously reported main-chain bithiazole-based polymers, which enhance their complexing ability to metal ions.

On the basis of the preliminary studies mentioned earlier, we describe here further results on the magnetic property of three novel acrylamide-type polymer–rare earth complexes (Scheme 1). The corresponding polymer–rare earth complexes were successfully prepared for the first time, and their magnetic property was investigated.

EXPERIMENTAL

Materials

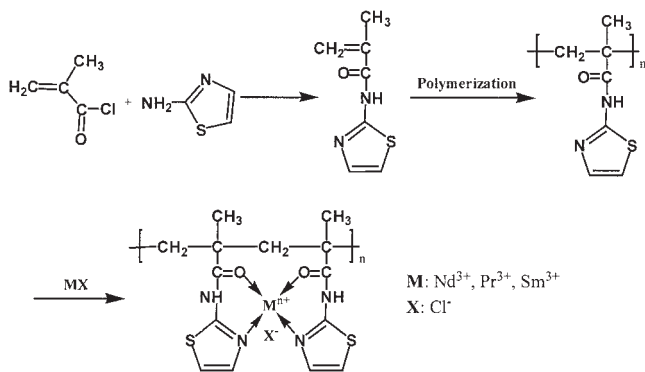
2-Aminothiazole was purchased from Merck-Schuchardt (Shanghai, China). Triethylamine were purchased from Shanghai Chem. Reagent Co. (Shanghai, Chian) NdCl₃, PrCl₃, and SmCl₃ were prepared from HCl and Nd₂O₃, Pr₂O₃, Sm₂O₃, respectively. Methacryloyl chloride was prepared from thionyl chloride and methacrylic 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 was recorded with a Bruker Vector 22 spectrometer. ¹H NMR spectra were recorded on a

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

Bruker Avance AMX-500 NMR instrument in DMSO- d_6 , with tetramethylsilane (TMS) as internal standard. The metal content of the complexes was determined by complexometric titration. 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. The amounts of samples used in magnetic measurements are about 50 – 100 mg, and was held by the specific plastic tube.

Monomer synthesis

N-2-thiazolylmethacrylamide (NTMA)

A THF (20 mL) solution of methacryloyl chloride (4.18 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 off. Then, the filtrate was poured into a large amount of hexane to give a white product, followed by washings with dilute solution of NaHCO_3 and deionized water. 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 ($\text{H}_2\text{C}=\text{C}$), 5.65($\text{H}_2\text{C}=\text{C}$), 2.12 (CH_3), ~ 11.8 (NH).

Polymerization

Polymerization of N-2-thiazolylmethacrylamides (0.5 g) was carried out with AIBN (0.005 g) as an initiator in dry THF at 70°C for 20 h. 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. IR (KBr, cm^{-1}): 3237(N—H), 2929(C—H), 1675(C=O), 1535(N—H), 1478, 1390, 1320(thiazole), 1063, 942; 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 (NH).

Preparation of polymer–rare earth complexes

The preparation of polymeric complexes was performed by mixing corresponding rare earth salt with polymer 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 metal ions. The isolated complexes were dried under vacuum at 60°C for 24 h.

PolyNTMA- Nd^{3+} white powder. IR (KBr, cm^{-1}): 3243(N—H), 2980(C—H), 1679(C=O), 1536(N—H), 1480, 1390, 1320(thiazole), 1061, 1022, 953. Yield: 85%.

PolyNTMA- Pr^{3+} green powder. IR (KBr, cm^{-1}): 3115(N—H), 2989(C—H), 1676(C=O), 1535(N—H), 1479, 1390, 1318(thiazole), 1018, 950. Yield: 77%.

PolyNTMA- Sm^{3+} yellow powder. IR (KBr, cm^{-1}): 3241(N—H), 2979(C—H), 1678(C=O), 1535(N—H), 1479, 1389, 1319(thiazole), 1058, 1020, 951. Yield: 82%.

RESULTS AND DISCUSSION

Characterization of polymer and polymeric complex

The structure of the polymer–rare earth complexes were characterized by IR spectroscopy. In comparison with PolyNTMA, a significant change in absorption was observed in the region of 1100 – 900 cm^{-1} . The absorption at 1020 cm^{-1} for polymer–rare earth complexes was not observed in the spectroscopy of PolyNTMA. A small blue-shift of absorption band at 1675 cm^{-1} of carbonyl group was also observed in the spectroscopy of polymer–rare earth complexes. This indicates the coordination between polymer and rare earth metal ions.

According to the data of complexometric titration, the metal contents for complexes of PolyNTMA with Nd^{3+} , Pr^{3+} , Sm^{3+} were calculated. Thus, the formula of the polymeric complexes may be suggested as shown in Table I. The metal content of polymer–rare earth complexes was compared with that of polymer–Fe(II) complex observed in our previous study.¹⁷ It is obvious that the polymer shows poor coordinative ability with rare earth and we get only polymeric rare earth complexes with lower loads. How to prepare polymer–rare earth complexes with higher metal content remains a challenge and we are still working on it. Although we proposed an intrachain structure for the polymeric complexes as shown in Scheme 1, the possibility of the coordination from different chains also cannot be excluded.

TABLE I
Metal Content of Polymer–Metal Complexes

Polymeric complex	Metal content ^a (wt %)	Suggested formula
PolyNTMA-Fe ²⁺	16.7 ^b	[C ₇ H ₈ N ₂ OS(FeSO ₄) _{0.916}] _n
PolyNTMA-Nd ³⁺	0.79	[C ₇ H ₈ N ₂ OS(NdCl ₃) _{0.009}] _n
PolyNTMA-Pr ³⁺	1.7	[C ₇ H ₈ N ₂ OS(PrCl ₃) _{0.021}] _n
PolyNTMA-Sm ³⁺	0.43	[C ₇ H ₈ N ₂ OS(SmCl ₃) _{0.005}] _n

^a Percentage to the respective dried samples.

^b Ref. 17.

Magnetic property of polymeric complexes

Figure 1 presents a typical relationship between magnetization (M) and applied magnetic field (H) for the complexes at 4 K. It can be seen that the magnetization increases with an increase of applied magnetic field for all samples. The value of relative saturation magnetization for PolyNTMA-Fe²⁺ (~6.8 emu/g) is obviously larger than that of PolyNTMA-Nd³⁺, PolyNTMA-Pr³⁺, and PolyNTMA-Sm³⁺, which accords with their load of metal ions.

The temperature dependence of the magnetic susceptibility is also studied at an applied magnetic field

of 30 kOe from 4 to 300 K for the complexes. For PolyNTMA-Fe²⁺ [Fig. 2(a)], the magnetic susceptibility (χ) follows the Curie–Weiss relationship, $\chi = C/(T - \theta)$, in a temperature range from 300 to 200 K. This means that the complex exhibits paramagnetic behavior at high temperatures. The positive Curie–Weiss temperature ($\theta = 102$ K) indicates the existence of mainly ferromagnetic coupling in PolyNTMA-Fe²⁺ complex.¹⁸ While for the complex of PolyNTMA-Pr³⁺, a typical antiferromagnetic property was found [Fig. 2(c)]. The negative Curie–Weiss temperature ($\theta = -21.8$ K) also implies the existence of antiferromagnetic interaction in this complex.

It is noteworthy that the magnetic behavior for PolyNTMA-Nd³⁺ and PolyNTMA-Sm³⁺ is different from the other two complexes. From 4 to 115 K, PolyNTMA-Nd³⁺ behaves as a ferromagnetic complex, while at 115 K, an abrupt change of magnetic property can be observed and the complex exhibits a typical diamagnetic property above 115 K [Fig. 2(b)]. PolyNTMA-Sm³⁺ has a similar property, with a transition temperature of 74 K [Fig. 2(d)]. This phenomenon does not follow the traditional ferromagnetism and a similar example has been found in our group.¹⁹

To obtain complementary information on the magnetic properties, the hysteresis loops have been detected at 4 K for the complexes. Figure 3 is the hysteresis loop of PolyNTMA-Nd³⁺; the magnetization curve as a function of applied field exhibits a hysteresis cycle at low temperature, which is a characteristic of ferromagnetic interactions. The other two complexes have a similar hysteresis loop and the basic data of magnetic property can be found in Table II.

Table II summarizes magnetic parameters of the four complexes, together with that of main-chain type complexes previously synthesized in this laboratory for comparison. Compared to the main-chain-type bi-thiazole-based complexes (PMD-Fe²⁺ and PMBD-Fe²⁺), PolyNTMA-Fe²⁺ have higher values of relative saturation magnetization, while the other three polymeric rare earth complexes show very little magnetization. On the other hand, the four polymeric complexes also showed some difference in magnetic properties. The results imply that the content of metal ions in polymeric skeleton and the different metal ions

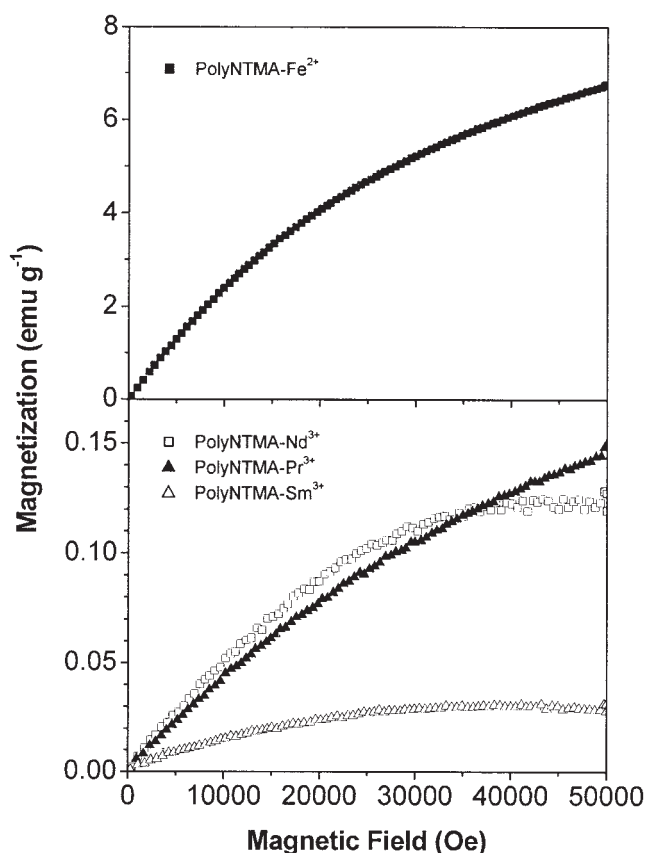


Figure 1 Magnetization curve (M) versus applied field (H) at 4 K for the polymeric complexes PolyNTMA-Fe²⁺ (■), PolyNTMA-Nd³⁺ (□), PolyNTMA-Pr³⁺ (▲), and PolyNTMA-Sm³⁺ (△).

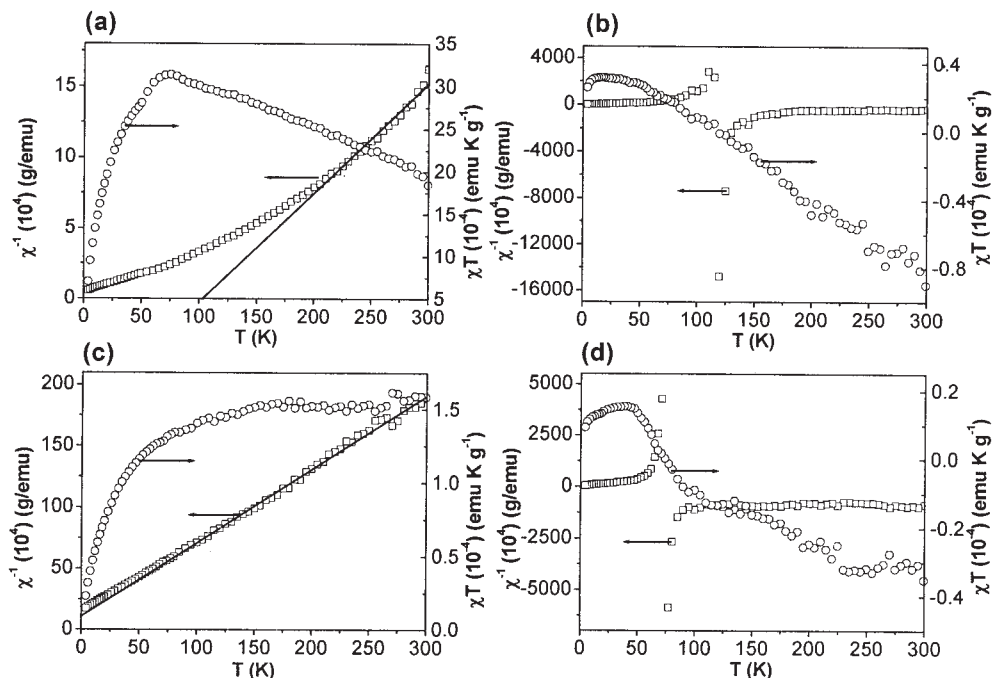


Figure 2 The product of magnetic susceptibility (χ) and temperature (T), and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PolyNTMA-Fe²⁺ (a), PolyNTMA-Nd³⁺ (b), PolyNTMA-Pr³⁺ (c), and PolyNTMA-Sm³⁺ (d) at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie-Weiss law.

have a subtle effect on their magnetic behaviors. Further investigation for this is in progress.

CONCLUSIONS

Polymers of acrylamide with a pendent thiazole group and their rare earth complexes have been prepared in good yields. The polymer showed better solubility

than previously reported main-chain bithiazole-based polymers, which enhance their complexing ability to metal ions. But the metal content of polymer-rare earth complexes is still very low. From the field and temperature dependence of magnetization and hysteresis loop, it can be concluded that PolyNTMA-Fe²⁺ is a ferromagnet, whereas PolyNTMA-Pr³⁺ is an antiferromagnet. PolyNTMA-Nd³⁺ and PolyNT-

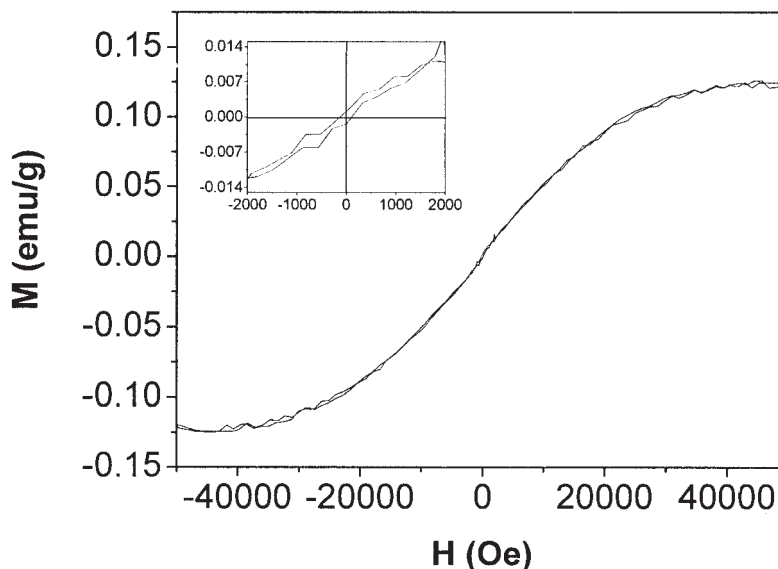


Figure 3 Magnetic hysteresis loop of PolyNTMA-Nd³⁺ at 4 K. Inset: Expanded view of the region from -2000 to 2000 Oe.

TABLE II
Magnetic Properties of Polymeric Complexes

Polymeric complex	Relative saturation magnetization at 4 K (emu/g)	Remanence magnetization at 4 K (emu/g)	Coercivity at 4 K (Oe)	Curie–Weiss temperature (K)	Ref.
PolyNTMA-Fe ²⁺	6.8	0.13	400	102	—
PolyNTMA-Nd ³⁺	0.13	0.001	120	—	—
PolyNTMA-Pr ³⁺	0.15	0.002	200	-21.8	—
PolyNTMA-Sm ³⁺	0.03	0.001	225	—	—
PMD-Fe ²⁺	3.25 ^a	0.02 ^b	158 ^b	81	10
PMBD-Fe ²⁺	1.8 ^a	0.014 ^a	360 ^a	—	11

^a Data obtained at 5 K.

^b Data obtained at 50 K.

MA-Sm³⁺ exhibit a special magnetic property: along with the decreasing of temperature, they change from diamagnet to ferromagnet with a transition temperature of 115 and 74 K, respectively. The difference in magnetic behavior among the four complexes may be related to the complicated interaction between metal ions, except for the content of corresponding metal ions.

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