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Synthesis and Magnetic Properties of Fe(II) and Nd(III) Complexes of Poly(N-2-thiazolylacrylamide)

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Abstract: *N*-2-Thiazolylacrylamide (NTA) was polymerized by a radical route to obtain the polymer in good yield. The polymer with a pendent heterocyclic group is soluble in common organic solvents, which allow to prepare the corresponding metal complexes with higher loads easily. FTIR, ^{1}H NMR, elemental analysis, and energy-dispersive X-Ray spectroscopy (EDX) were applied to characterize these materials. The magnetic behavior of Fe(II) and Nd(III) complexes of poly(N-2-thiazolylacrylamide) was examined by a PPMS-9T magnetometer, exhibiting the characteristics of a soft ferromagnet. It is found that the Nd(III) complex has an extremely high relative saturation magnetization of 35 emu/g.

Keywords: N-2-Thiazolylacrylamide, polymer, polymeric complex, magnetic property, synthesis.

In recent years, the organic ferromagnets have drawn growing attention due to their characteristics of structural diversities, low density, and readily processing[1-3]. Design and synthesis of magnetic polymers are one of great challenges in today′s magnetic material research, and some significant achievements have been made in this field[4,5].

In this article, we describe the synthesis of acrylamide-type polymer with pendent thiazolyl groups (**Scheme 1**). The as-prepared polymer exhibited better solubility in common organic media compared to the main chain-type bithiazole-based polymers as well as possesses good complexing ability to metal ions. Fe(II) and Nd(III) complexes of poly(N-2-thiazolylacrylamide) were prepared for the first time. The formation of the complexes was characterized by IR and EDX, and their magnetic property was also investigated using a physical properties measurement system.

FTIR spectrum was recorded with a Bruker Vector 22 spectrometer. ^{1}H NMR spectrum was recorded on a Bruker Avance AMX-500 NMR instrument in DMSO-d_6 with tetramethylsilane (TMS) as internal standard. Chemical composition of metal complexes was determined by energy-dispersive X-ray spectroscopy (EDX) (Finder 1000 X-ray spectrometer, Cambridge). Viscosity measurements were made in DMSO with an Ubbelohde type viscometer at 30 °C. The magnetic measurements were carried out by 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.

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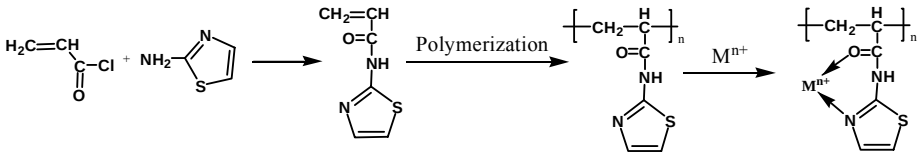
Scheme 1 Synthetic route for the monomer, polymer, and polymeric complexes



The preparation of N-2-thiazolylacrylamides[6] (NTA) is as follows: a THF (20 mL) solution of acryloyl chloride (4.2 g, 0.04 mol) was slowly added into the 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 hours and the formed solid was removed off. The filtrate was poured into a large amount of hexane to precipitate the white product, followed by washing with 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). ^{1}H-NMR (500 MHz, DMSO-d_6, δ ppm): 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*). Elemental analysis calculated for PolyNTA ($C_6H_6N_2OS$): C, 46.74%; H, 3.92%; N, 18.17%. Found: C, 46.83%; H, 4.03%; N, 17.95%.

Polymerization of N-2-thiazolylacrylamides (0.5 g) was carried out with AIBN (0.005 g) as an initiator in dry THF at 70 °C for 20 h. After polymerization was completed, the reaction mixture was poured into a large amount of methanol to precipitate the formed polymer. Then, the polymer was filtered, washed with methanol, and dried under vacuum. IR (KBr, cm^{-1}): 3171(N-H), 2924(C-H), 1685(C=O), 1553 (N-H), 1483, 1367, 1320 (thiazole); [η] = 0.21 dL/g (DMSO, 30 °C).

The preparation of polymeric complexes was performed by mixing excessive $FeSO_4$ or $NdCl_3$ with the polymer in DMSO at 80°C under a pure N_2 atmosphere. The resulting solution was stirred for 20 h to obtain the precipitate, which was collected by suction filtration, washed thoroughly with deionized water to remove excess physisorbed metal ions. The isolated complexes were dried under vacuum at 60 °C for 24 h. IR (PolyNTA-Fe^{2+}, KBr, cm^{-1}): 3256(N-H), 2925(C-H), 1685(C=O), 1547(N-H), 1483, 1368, 1320(thiazole). IR (PolyNTA-Nd^{3+}, KBr, cm^{-1}): 3256(N-H), 2925(C-H), 1685 (C=O), 1554(N-H), 1483, 1368, 1319(thiazole).

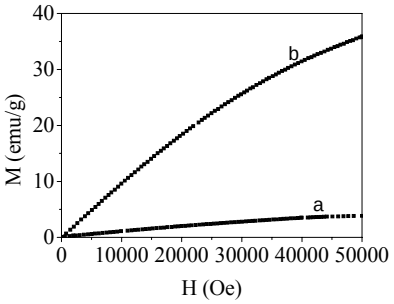
As shown in **Scheme 1**, the radical polymerization of N-2-thiazolylacrylamides was carried out under mild conditions to give desired polymers in good yields. The polymers obtained as white powders and exhibited relatively low molecular weights based on their specific viscosity values. In contrast to the bithiazole-based polymers previously synthesized in our laboratory[7,8], the polyamides with a pendent thiazole group are readily soluble in DMSO and DMF but slightly soluble in tetrahydrofuran.

According to the data from energy-dispersive X-ray spectroscopy (EDX), the metal contents were about 14.9 wt.%, 5.7 wt.% for PolyNTA-Fe^{2+}, PolyNTA-Nd^{3+}, respectively. Thus, the formula of the polymeric complexes may be suggested as $[C_6H_6N_2OS\ (Fe\ SO_4)_{0.69}]_n$ and $[C_6H_6N_2OS(NdCl_3)_{0.07}]_n$.

Figure 1 presents a typical relationship between magnetization (M) and applied field (H) for the complexes at 4 K.

Figure 1 Magnetization curve (M) *versus* applied field (H) at 4 K for the complexes PolyNTA-Fe^{2+} (a) and PolyNTA-Nd^{3+} (b).

Figure 2 Temperature dependence of χT and χ^{-1} for PolyNTA-Nd^{3+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie-Weiss law from 250 K to 300 K.



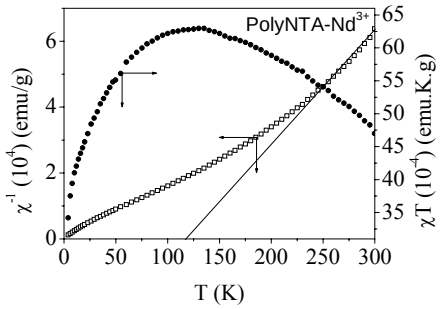


Figure 3 Magnetic hysteresis loop of PolyNTA-Nd^{3+} at 4 K. (Insert: Expanded view of the region from – 4000 to 4000 Oe.)

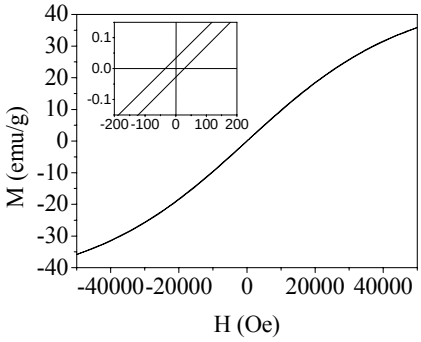


Table 1 Magnetic properties of polymeric complexes

Polymeric complex	Relative saturation magnetization(emu/g)	Remanence magnetization (emu/g)	Coercivity (Oe)	Curie-Weiss temperature(K)
PolyNTA-Fe^{2+}	3.9 (4 K)	0.22 (4 K)	1650 (4 K)	-
PolyNTA-Nd^{2+}	35 (4 K)	0.035 (4 K)	35 (4 K)	118
PMD-Fe^{2+} [7]	3.25 (5 K)	0.02 (50 K)	158 (50 K)	81
PMBD-Fe^{2+} [8]	1.8 (5 K)	0.014 (5 K)	360 (5 K)	-

The temperature dependence of the magnetic susceptibility is also studied at an applied magnetic field of 30 kOe from 4 K to 300 K for the complexes (**Figure 2** is the result of PolyNTA-Nd^{3+}).

To obtain complementary information on the magnetic properties, the hysteresis loops have been detected at 4 K for the materials. As shown in **Figure 3**, the magnetization curve as a function of applied field exhibits a hysteresis cycle at low temperature, which is a characteristic of ferromagnetic interactions.

Table 1 summarized magnetic parameters of both PolyNTA metal complexes together with that 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 PolyNTA-Nd^{3+} have higher values of relative saturation magnetization. The relative saturation magnetization of PolyNTA-Nd^{3+} is extremely high compared with all the other polymeric complexes which have been prepared before. The results imply that the structure of repeating unit in polymeric skeleton has a subtle effect on their magnetic behaviors. Further investigation is in progress.

Acknowledgments

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