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Synthesis of novel copolymers containing tri(ethylene oxide) segments and bithiazole rings on the backbone and magnetic properties of their complexes

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Abstract

Two novel copolymers containing bithiazole rings and ethylene oxide on the skeleton (PPOBTz and PNOBTz) were synthesized via Schiff reaction and Ullmann reaction, respectively. The copolymers were characterized by FTIR, ^{1}H NMR. Their polymeric complexes with Cu^{2+} and Nd^{2+} were prepared. The magnetic behavior of these polymeric complexes was measured as a function of magnetic field strength (0−60 kOe) at 4 K and as a function of temperature (4−300 K) at a magnetic field strength of 30 kOe, indicating that they all exhibited features of soft ferromagnet.

Keywords: Bithiazole and tri(ethylene oxide) containing polymer; Polymeric complex; Magnetic properties

1. Introduction

Polymeric complexes with magnetic properties have been receiving considerable interest due to their potential applications in a wide range of areas. Organic polymers containing paramagnetic species may provide a new kind of magnetic material owing to the magnetically long-range ordering of unpaired electrons through spin−spin interaction [1]. The ability to control the sign and magnitude of the magnetic-exchange interaction between adjacent metal ions in a polymeric complex is of fundamental importance for the design and synthesis of new magnetic materials based on polymeric coordination complexes [2−5]. It was found that polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form a stable five-member ring. The crystal structure of metal complexes of the monomer, 2,2′-diamino-4,4′-bithiazole (DABT) has been characterized by X-ray diffraction [6,7]. In 2000, three poly(Schiff base)-Fe^{2+} complexes containing bithiazole rings were prepared for the first time and found to be soft ferromagnets [8]. Subsequently, a series of polymeric complexes containing bithiazole rings were prepared and exhibited different types of magnetic behaviors [9−12].

In this paper, we introduced bithiazole rings and tri(ethylene oxide) segments into the polymer backbone as two coordinating centers. Their complexes with Cu^{2+} and Ni^{2+} were prepared and the magnetic behaviors of the complexes were preliminarily studied.

2. Experiment

2.1. Materials

All the chemicals used were of AR grade. Pyridine was distilled over CaH_2 before use. Thionyl chloride, triethylene glycol, 4-hydroxybenzaldehyde and dimethyl sulfoxide (DMSO) were purchased from Shanghai Chemical Reagent Company. 2,2′-Diamino-4,4′-bithiazole (DABT) was prepared according to the literature [13].

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2.2. Measurements

^{1}H NMR spectra were recorded on a Bruker Advance AMX-500NMR instrument in DMSO-d_6 with tetramethyl silane (TMS) as internal standard. A Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra in KBr pellets. The intrinsic viscosity [η] was measured with an Ubbelohde type viscometer (The diameter and length of the capillary are 0.5–0.6 mm and 11 cm, respectively.) in DMSO at 30 °C and the value is an average of three measurements. Thermogravimetric analyses (TGA) were carried out with a Perkin–Elmer thermogravimetric apparatus. The content of ions was measured by complexometry using EDTA. The magnetic properties of the complex were measured with a physical properties measurement system (PPMS-9T) magnetometer (Quantum Design).

2.3. Monomer and polymer preparations

The synthetic approach of the polymers (PPOBTz and PNOBTz) and the corresponding monomers is outlined in Scheme 1.

2.3.1. 1,8-Dichloro-3,6-dioxaoctane (**1**)

1,8-Dichloro-3,6-dioxaoctane was synthesized according to the method reported by Pedersen [14]. The yield was 90%.

IR (KBr, ν, cm^{-1}): 665 (Cl–C), 1125 (C–O–C), 2870 (CH$_2$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.75 (t, 4H, ClCH$_2$), 3.62 (t, 4H, ClCH$_2$CH$_2$), 3.67 (s, 4H, OCH$_2$CH$_2$O).

2.3.2. 1,8-Bis(4-formalphenoxy)-3-oxaoctane (**2**) [15]

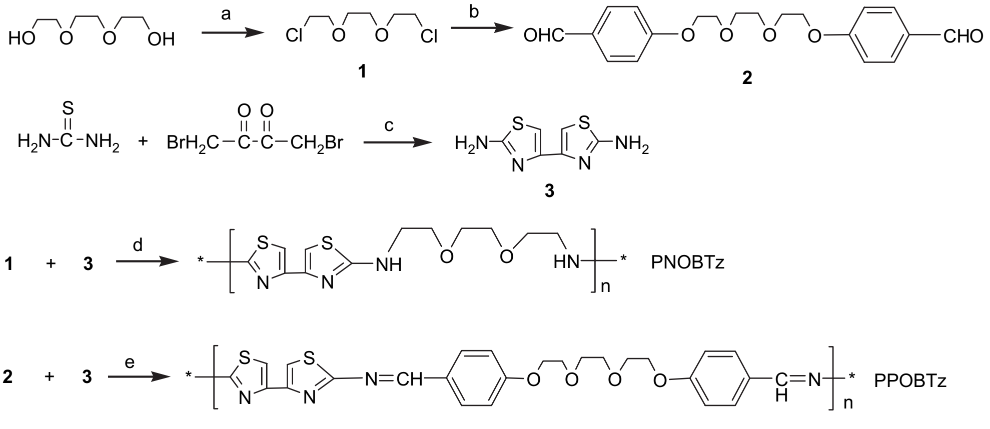
A mixture of 4-hydroxybenzaldehyde (3.42 g, 0.028 mol), sodium hydroxide (1.2 g, 0.03 mol) and diethylene glycol monomethylether (60 ml) was stirred and heated to reflux under nitrogen atmosphere for 30 min, and 1,8-dichloro-3,6-dioxaoctane (2.6 g, 0.014 mol) in 15 ml of diethylene glycol monomethylether was added dropwise. Reflux was continued for 24 h. After it cooled to room temperature, the solvent was removed at a reduced pressure, and the residue was recrystallized twice in ethanol. The yield was 30%. Mp: 148–150 °C. IR (KBr, ν, cm^{-1}): 1136, 1154 (C–O–C), 1256 (Ar–O), 1601 (C=C), 1686 (–C=O), 2800–3000 (CH$_2$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.9 (2H, CHO), 7.7 (4H, ArH), 6.95 (4H, ArH), 4.27 (4H, ArOCH$_2$), 3.85 (4H, ArOCH$_2$CH$_2$), 3.75 (4H, OCH$_2$CH$_2$O).

2.3.3. Synthesis of PPOBTz

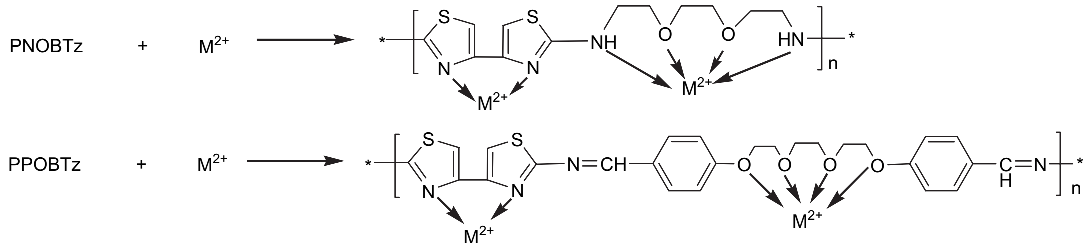
An equimolar ratio of 1,8-bis(4-formalphenoxy)-3-oxaoctane and DABT was dissolved in DMSO to get 10% solid content. The solution was magnetic stirred and kept at 120 °C under nitrogen atmosphere and red (brown) solution was obtained after two days. After it cooled to room temperature, the solution was precipitated in water, and then the brown solid polymer was collected by filtration. The crude polymer was thoroughly washed with water, methanol and acetone, and then dried at 60 °C for 24 h in a vacuum oven. The yield is 70%. IR (KBr, ν, cm^{-1}): 1112, 1161 (C–O–C), 1252 (Ar–O), 1510 (C=N of bithiazole rings), 1600 (C=C), 1680 (C=N), 2924, 2872 (CH$_2$), 3187, 3309 (NH$_2$). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.85 (2H, CH=N), 7.85 (4H, Ar–H), 7.05–7.15 (6H, Ar–H and protons of bithiazole rings), 4.19 (4H, ArOCH$_2$), 3.77 (4H, ArOCH$_2$CH$_2$), 3.62 (4H, OCH$_2$CH$_2$O) (see Fig. 2). Intrinsic viscosity (η) = 0.12 dL g^{-1} (DMSO, 30 °C).

2.3.4. Synthesis of PNOBTz

A mixture of DABT (1.98 g, 0.01 mol), 1,8-dichloro-3,6-dioxaoctane (1.87 g, 0.01 mol), sodium bicarbonate (0.52 g, 0.006 mol) and DMSO (100 ml) was stirred and heated at 120 °C under nitrogen atmosphere. A brown solution was obtained after reacting for 24 h, and the solution was precipitated in water after cooling, and then the brown solid polymer was collected by filtration. The crude polymer was thoroughly washed with water, methanol and acetone, and then dried at 60 °C for 24 h in a vacuum oven. The yield was 65%. IR (KBr, ν, cm^{-1}): 1103 (C–O–C), 1297 (C–N), 1521 (–C=N of bithiazole rings), 1620 (C=C) 3175, 3304 (NH and NH$_2$). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.38–7.16 (4H, NH and protons of bithiazole rings), 4.37 (4H, NHCH$_2$), 3.80 (4H, ArNHCH$_2$O), 3.57 (4H, OCH$_2$CH$_2$O). Intrinsic viscosity (η) = 0.09 dL g^{-1} (DMSO, 30 °C).



Scheme 1. The synthetic route of monomers and polymers. Reagents and conditions: a = SOCl$_2$, benzene, pyridine, reflux, 20 h; b = 4-hydroxybenzaldehyde, CH$_3$OCH$_2$CH$_2$OH, NaOH, reflux, 24 h; c = CH$_3$CH$_2$OH, reflux, 1 h; d = NaHCO$_3$, DMSO, 120 °C, 24 h; e = DMSO, 120 °C, 48 h.



Scheme 2. Preparation of the complexes (M = Cu, Ni). (The bithiazole and ethylene oxide on the backbond are partially chelating with the metals and the details are shown in Table 1.)

2.4. Preparation of polymeric complexes

The preparation of the complexes (PPOBTz–Cu^{2+}, PPOBTz–Ni^{2+}, PNOBTz–Cu^{2+} and PNOBTz–Ni^{2+}) is shown in Scheme 2.

$CuSO_4 \cdot 5H_2O$ (0.5 g, 2.0 mmol) and PPOBTz (0.5 g, 1.0 mmol) were dissolved in DMSO and stirred at 80 °C for 4 h under nitrogen atmosphere. The resulting brown solution was poured into water, and then a dark brown precipitate of PPOBTz–Cu^{2+} was obtained. The precipitate was collected by filtration, and then washed with water and methanol to remove unreacted $CuSO_4 \cdot 5H_2O$. The same procedure was applied for the preparation of PPOBTz–Ni^{2+}, PNOBTz–Cu^{2+} and PNOBTz–Ni^{2+}. The metal content in the complexes was determined by complexometric titration. The results are shown in Table 1.

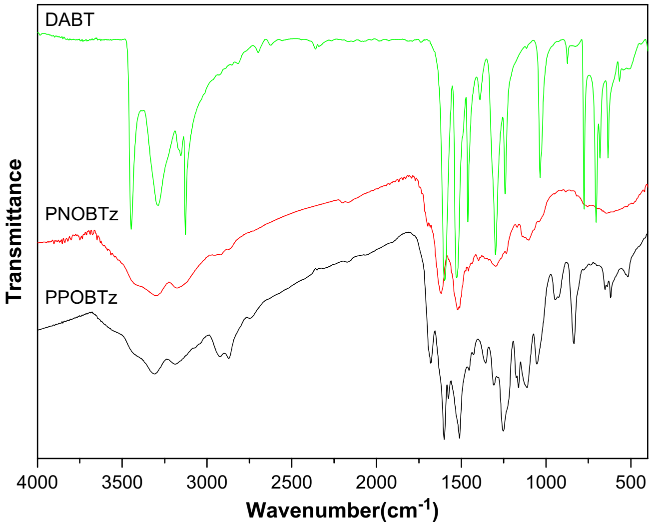


Fig. 1. The IR spectra of DABT, PNOBTz and PPOBTz.

3. Results and discussion

3.1. Characterization of polymers

The basic strategies employed for the synthesis of PNOBTz and PPOBTz are based on polycondensation by the methods of Ullmann reaction [16] and Schiff reaction [17], respectively. The polymers were characterized by IR, ^1H NMR. The IR spectra of PPOBTz and PNOBTz compared with the monomer DABT, are shown in Fig. 1, which reveals that the two polymers give characteristic peaks in the range of 1400–1550 cm^{-1}, which is due to the vibration of bithiazole rings. The reduction of the broad absorption in the range of 3300–3000 cm^{-1} of the N–H stretching vibration of a secondary amine, and the new peaks in the range of 1000–1250 cm^{-1} which correspond to stretching band of Ar–O and C–O reveal the successful reaction. In the IR spectrum of PPOBTz, the stretching oscillation of the new C=N bond appeared at about 1676 cm^{-1}. The wide peak of PNOBTz at 1297 cm^{-1} which corresponds to C–O illustrated the effect of the inner molecular hydrogen bond, and the wide peaks in 7.38–7.16 ppm in the ^1H NMR spectra of PNOBTz confirmed this conclusion.

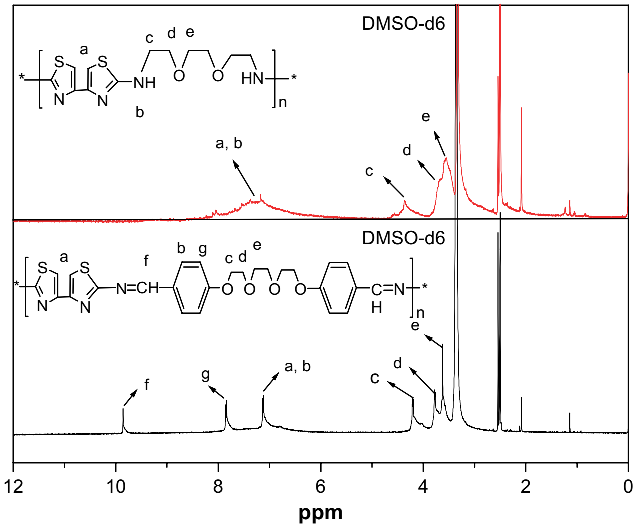


Fig. 2. ^1H NMR spectra of PPOBTz and PNOBTz in DMSO-d_6 at 500 MHz.

Table 1
Metal content of polymer–metal complexes

Polymeric complex	Metal content[a] (wt.%)	Suggested formula
PNOBTz–Cu^{2+}	8.5	$[C_{12}H_{16}N_4O_2S_2(CuSO_4)_{0.45}]_n$
PNOBTz–Ni^{2+}	7.1	$[C_{12}H_{16}N_4O_2S_2(NiSO_4)_{0.46}]_n$
PPOBTz–Cu^{2+}	6.2	$[C_{20}H_{24}N_4O_4S_2(CuSO_4)_{0.51}]_n$
PPOBTz–Ni^{2+}	3.2	$[C_{20}H_{24}N_4O_4S_2(NiSO_4)_{0.26}]_n$

[a] Percentage to the respective dried samples.

The ^1H NMR spectra of PPOBTz and PNOBTz are shown in Fig. 2. In the ^1H NMR spectrum of PPOBTz, the single peak appeared at 9.85 ppm belonging to CH=N, and the aryl protons appeared in the range of 7.0–8.0 ppm. The peak of the protons of bithiazole rings was overlapped with the peaks of the phenyl in 7.05–7.15 ppm with an integral of 2.97 (6H) which is 1.5 times to the integral of the peak (4H, 1.96) appearing at 7.85 ppm. And the two polymers have similar peaks in the range of 3.0–5.0 ppm, which belong to the protons of EO segment. In the ^{1}H NMR spectrum of PNOBTz, the peak of NH appears with a wide shape in the range of 7.38–7.16 ppm, which is due to the hydrogen bond effect and overlapped with the peaks of bithiazole protons.

The comparison of IR spectra of the complexes and polymers is shown in Figs. 3 and 4. It can be found that the absorption remarkably changed between 1200 and 1500 cm^{-1}, indicating the formation of the complex. For instance, in comparison with PPOBTz, significant changes were observed in the IR spectrum of PPOBTz–Cu^{2+}, the obvious shift of bands within the 1510–1358 cm^{-1} range are due to the coordination between Cu^{2+} ions and the nitrogen atoms of bithiazole ring. The skeletal vibrations of bithiazole rings become less flexible owing to coordination. Similar changes were observed within the region of 2000–400 cm^{-1} in the IR spectra of other polymers and their corresponding complexes. The ion content of the complexes was measured by complexometry using EDTA.

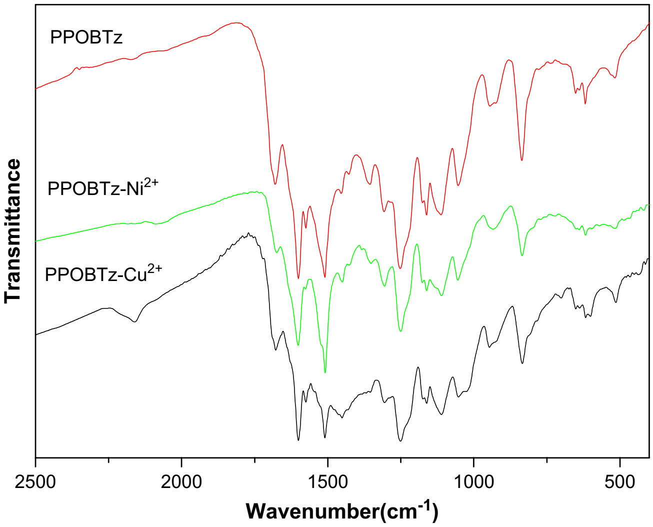


Fig. 3. The IR spectra of PPOBTz, PPOBTz–Ni^{2+} and PPOBTz–Cu^{2+}.

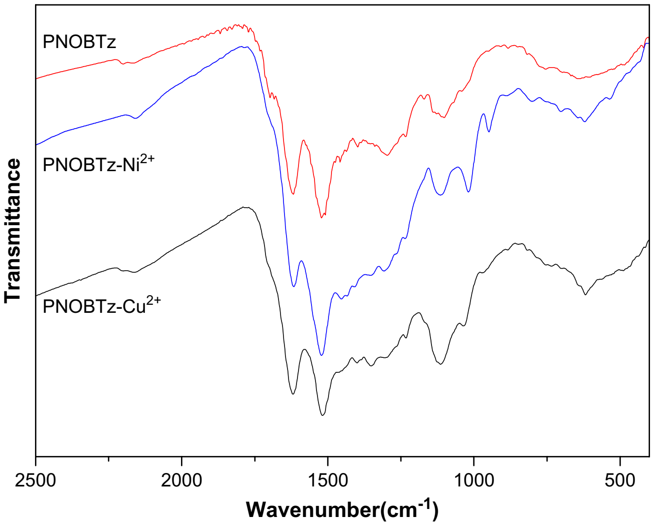


Fig. 4. The IR spectra of PNOBTz, PNOBTz–Ni^{2+} and PNOBTz–Cu^{2+}.

3.2. Thermal properties of polymers

Thermal stability of the polymers in nitrogen atmosphere at heating rates of 10 °C/min was evaluated by thermogravimetric analysis (TGA). As shown in Fig. 5, both of the two polymers had a small weight loss at the beginning. The weight loss of more than 10% began at about 300 °C. At 500 °C, PPOBTz and PNOBTz retained 65% and 61% of their weight, respectively. The better weight retention of PPOBTz compared with PNOBTz can be explained by the phenylene group in the backbone. The result suggests that two polymers have good thermal stability due to the bithiazole rings.

3.3. Magnetic properties of the polymer complexes

The preliminary magnetic properties of four complexes were investigated. The temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PPOBTz–Ni^{2+} and PNOBTz–Ni^{2+} at an applied magnetic field of 30 kOe are shown in Figs. 6 and 7, respectively. It can be seen that the magnetic susceptibility (χ) of these two complexes followed the Curie–Weiss relationship, $\chi = C/(T-\theta)$, in the range of 250–300 K, with the Curie–Weiss temperature θ at about 160 K. The positive Curie–Weiss temperature indicates that the two complexes are ferromagnets. The magnetic hysteresis loop of PPOBTz–Ni^{2+} and PNOBTz–Ni^{2+} at 4 K is shown in Figs. 8 and 9, respectively. From the typical S shape and small area of hysteresis loop, it can be deduced that PPOBTz–Ni^{2+} and PNOBTz–Ni^{2+} are soft ferromagnets.

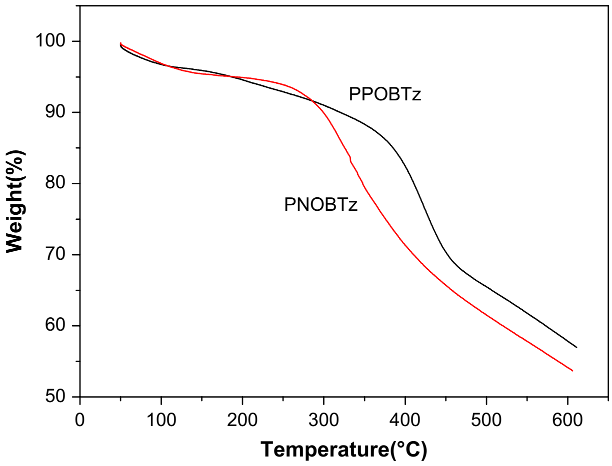


Fig. 5. The TGA curves of PPOBTz and PNOBTz in N_2.

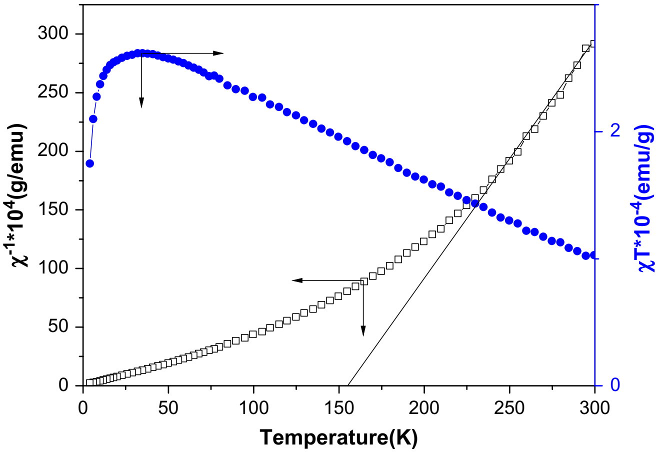


Fig. 6. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PPOBTz–Ni^{2+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law between 250 and 300 K.

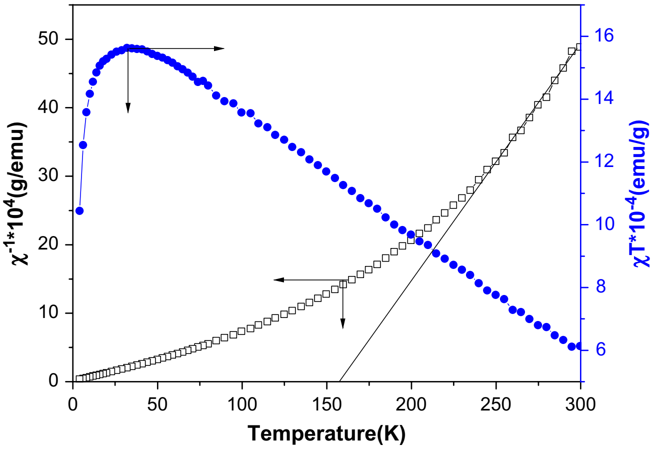


Fig. 7. Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PNOBTz–Ni^{2+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law between 250 and 300 K.

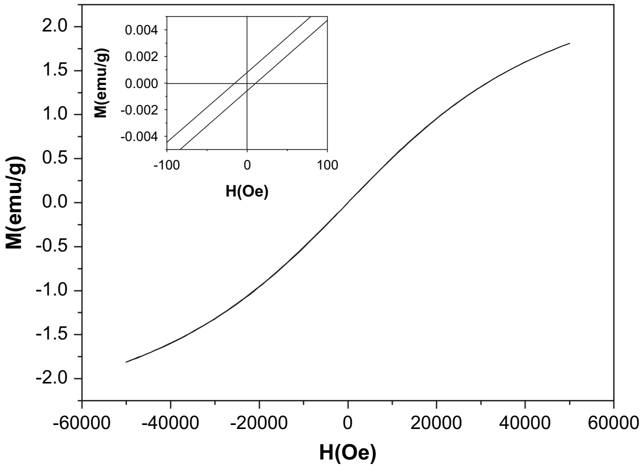


Fig. 8. Magnetic hysteresis loop of PPOBTz–Ni^{2+} at 4 K. (inset) Expanded view of the region from −100 to 100 Oe.

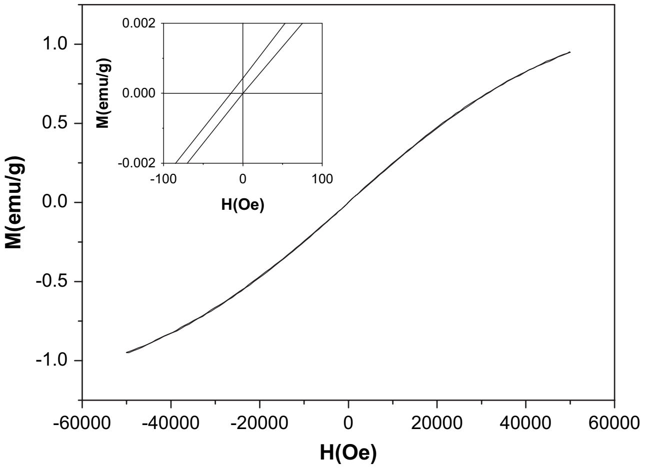


Fig. 9. Magnetic hysteresis loop of PNOBTz–Ni^{2+} at 4 K. (inset) Expanded view of the region from −100 to 100 Oe.

4. Conclusions

Two novel polymers containing bithiazole rings and ethylene oxide were synthesized and characterized. Good solubility in common organic solvents, high thermal stabilities were found for the two copolymers. The complexes of PPOBTz–Cu^{2+}, PPOBTz–Ni^{2+}, PNOBTz–Cu^{2+} and PNOBTz–Ni^{2+} were prepared and their preliminary magnetic properties were investigated.

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