

SYNTHESIS AND MAGNETIC PROPERTIES OF COMPLEXES OF A CONJUGATED HYPERBRANCHED POLYMER CONTAINING BITHIAZOLE RINGS*

Neng-wen Ding^a, Wei-lin Sun^{a**}, Yan Lin^b and Zhi-quan Shen^a

^a Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^b Ningbo City College of Vocational Technology, Ningbo 315100, China

Abstract A novel conjugated hyperbranched polymer containing bithiazole rings (PBTADB) was synthesized by polycondensation of 1,3,5-benzenetricarboxaldehyde and 2,2'-diamino-4,4'-bithiazole (DABT). The structure of the hyperbranched polymer was confirmed by FT-IR and ¹H-NMR. PBTADB dissolved in organic polar solvents such as DMSO and NMP. Bithiazole rings were introduced to provide bidentate N-donor sites for binding metal ions. The metal complexes were prepared by chelation of the polymer with Co²⁺ and Sm³⁺. The magnetic behavior of coordination compounds was measured as a function of magnetic field strength (0–4.8 × 10⁶ A/m) at 5 K and as a function of temperature (5–300 K) at magnetic field strength of 2.4 × 10⁶ A/m. The magnetic hysteresis loops of PBTADB-Sm³⁺ and PBTADB-Co²⁺ showed the typical 'S' shape at 5 K with the Curie-Weiss temperature T_{θ} = 96 K and 41 K respectively. The results show that they exhibit properties of soft ferromagnetic materials.

Keywords: Bithiazole; Conjugated hyperbranched polymer; Magnetic properties.

INTRODUCTION

In the past decades, the hyperbranched polymers, a special type of dendritic polymers, had completely attracted scientists' attention. The researchers took great challenges to synthesize the hyperbranched polymers partly because of the branched structure and the large number of functional groups. To date, many kinds of chemical reactions had been found available to design beautiful macromolecules. Jikei *et al.*^[1] successfully obtained a soluble hyperbranched aromatic polyamide from diamines and trimesic acid. Fomina *et al.*^[2] prepared fully conjugated hyperbranched polymers by a Heck reaction. With high selectivity and good yields, cycloaddition reactions contributed a lot to the syntheses of hyperbranched polymers^[3]. Hyperbranched polyamines containing unsaturated units were synthesized by ring-opening multibranching polymerization using cyclic carbamates with palladium catalysis^[4]. Ferrocene-functionalized hyperbranched polyphenylenes were successfully prepared *via* new catalyst systems, and their complexes furnished magnetic ceramics with high magnetizabilities ($M_s \approx 83 \text{ A}\cdot\text{m}^2/\text{kg}$)^[5]. Excellent reviews covering synthetic strategies and major characterization aspects of the hyperbranched polymers were finished by Viot and Lederer in 2009^[6]. Obviously, much attention has been paid to the hyperbranched polymers due to their different chemical and physical properties from one another. Many potential applications in commercial products have been in practice such as coatings^[7], additives^[8] and solvent extraction^[9].

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21174129 and 20674071).

** Corresponding author: Wei-lin Sun (孙维林), E-mail: opl_sunwl@zju.edu.cn

Received February 13, 2012; Revised March 4, 2012; Accepted March 7, 2012

doi: 10.1007/s10118-012-1162-y

Genin and Hoffmann suggested that polymers structured by sulfur, carbon and nitrogen-containing five-member rings should theoretically display magnetic ordering^[10]. To obtain new organic magnetic materials, our group prepared kinds of polymers containing bithiazole ring and their coordination compounds. A novel polymer containing bithiazole rings was first synthesized by polycondensation of 2,2'-diamino-4,4'-bithiazole (DABT) with terephthalaldehyde^[11]. We^[12] designed three polymer-Fe²⁺ complexes that were synthesized from Fe²⁺ and poly(Schiff base)s. The poly(Schiff base)s were prepared from 2,2'-diamino-4,4'-bithiazole (DABT) with phthalaldehyde, 5,5'-methylenebis (salicylaldehyde) (MBSA) and terephthalaldehyde. These polymer-Fe²⁺ complexes presented the magnetic hysteresis loop at 200 K. The values of remanence magnetization and coercivity were 0.0095 A·m²/kg and 1.25×10^3 A/m, respectively. After that, the investigations about polymers containing bithiazole rings were carried out, and their complexes have been reported with the different types of magnetic properties^[13–17].

In our previous work, a hyperbranched aromatic polyamide containing bithiazole rings and its coordination compounds were prepared. The coordination compounds are potential magnetic materials with good solubility. But magnetic behaviors of the polyamide is unsatisfied, especially the hysteresis loop^[18]. In this article, we synthesized a novel conjugated hyperbranched polymer containing bithiazole rings. Among the π -conjugated polymers, those with electron-withdrawing imine nitrogen(s) (C=N) are attracting interest, they have the electron-accepting ability and are wonderful reactive for metal-complex, which can modify their optical and electric properties^[19, 20]. Here, we are focused on magnetic properties of the coordination compounds prepared by chelation of the polymer with Co²⁺ and Sm³⁺. Finally, an interest magnetic phenomenon is founded by exploring magnetic properties of them.

EXPERIMENTAL

Materials

Most of the reagents were purchased from Shanghai Chemical Reagent Company, like bromine (liquid), 2,3-butyldione, *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), 2-thiourea and 1,3,5-trimethylbenzene, *etc.* 1,3,5-Benzenetricarboxaldehyde was synthesized in our laboratory. DABT was prepared according to the literature^[10]. SmCl₃ was prepared by heating a mixture of hydrated samarium chloride and ammonium chloride under reduced pressure^[21]. CoCl₂ was obtained by heating a mixture of cobaltous chloride hexahydrate and ammonium chloride under reduced pressure.

Measurements

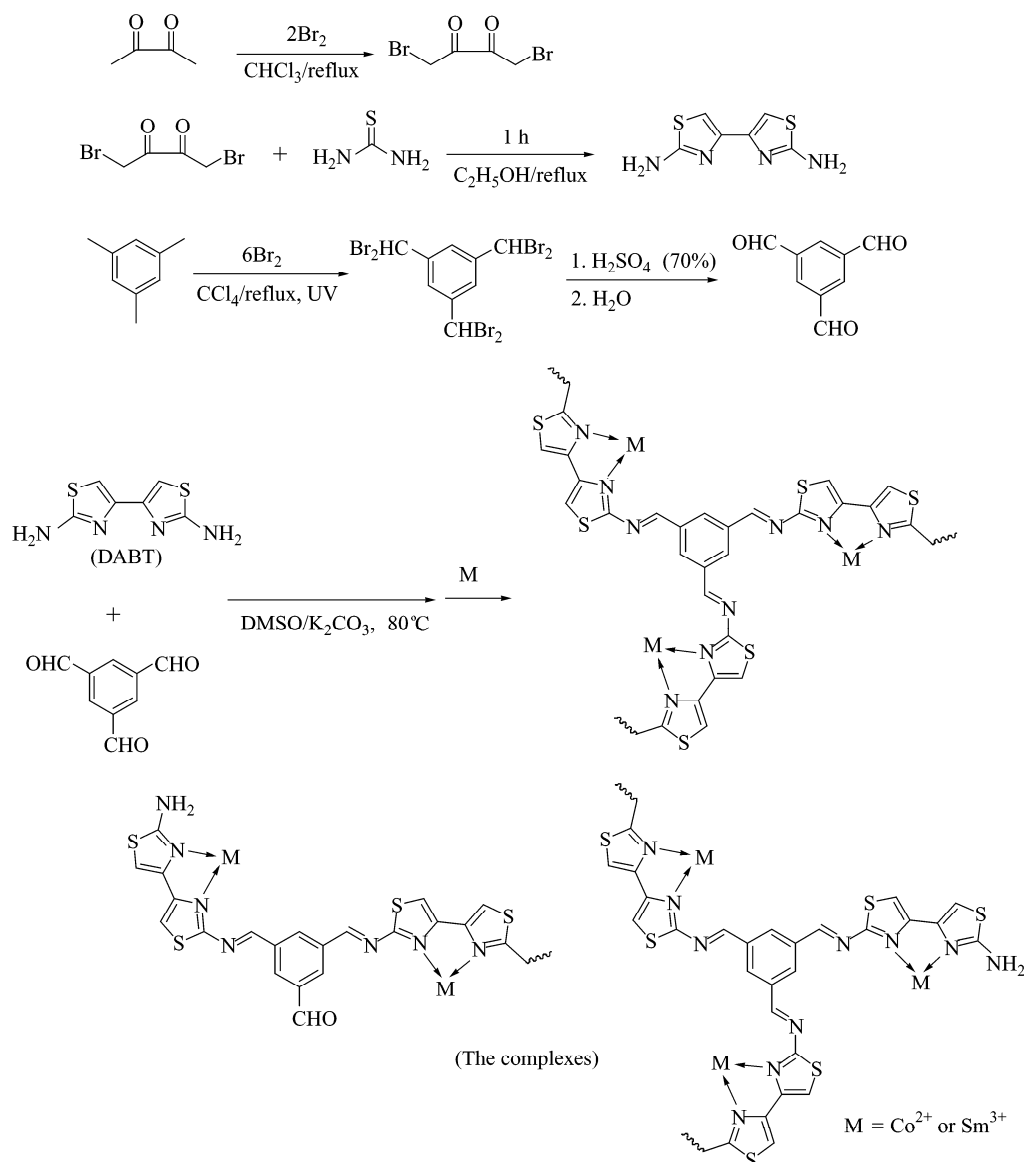
A Bruker Vector 22 Fourier transform infrared (FT-IR) spectrometer was used to record IR spectra with KBr pellets. ¹H-NMR spectra were recorded on a Bruker Advance AMX-400NMR instrument in DMSO with tetramethyl silane (TMS) as internal standard. Thermo gravimetric analyses (TGA) were carried out with a Pyris-1 thermo gravimetric apparatus at the heating rate of 10 K/min. The intrinsic viscosity [η] was measured in DMSO at 30°C. The content of metal 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).

Synthesis of Monomers and the Hyperbranched Polymers

The route of the synthesis of the monomers and the hyperbranched polymers is showed in Scheme 1.

2,2'-Diamino-4,4'-bithiazole

1,4-Dibromobutyldione (19.5 g, 80 mmol) and 2-thiourea (12.2 g, 160 mmol) were mixed in ethanol (400 mL). The mixture is refluxed for 6 h, then it was poured into H₂O (1600 mL) and the solution was neutralized with ammonium hydroxide. The yellow crystal formed and was collected by filtration. The resultant crystal was purified by recrystallization in the DMF and H₂O (1:2) solution. The product was dried in a vacuum at 60°C for 24 h. The yield is 12 g (83%). IR: 3447, 3289, 3154, 3127, 1598, 1528, 1461, 1298, 1035, 776, 704 cm⁻¹; ¹H-NMR (DMSO-*d*₆): δ = 6.9 (4H, NH₂), 6.64 (2H, -thiazole).



Scheme 1 The synthetic route of the monomers and the hyperbranched polymeric complexes

1,3,5-Tris (dibromomethyl) benzene

A 500 mL three-necked flask was equipped with a magnetic bar, dropping funnel and a reflux condenser, the top of which was connected to a gas absorption. A 500 W ultraviolet lamp was clamped in such a position that its bulb was within 5 cm of the flask. The flask was filled with 30 g of dry 1,3,5-trimethylbenzene and 250 mL of dry carbon tetrachloride. Then the stirring was started and the flask was heated in an oil bath to keep the temperature at 80°C . 240 g of bromine was gradually added through the dropping funnel at such a rate that there was no large amount of unreacted bromine in the flask when it starts boiling. Stirring and heating were continued throughout the reaction, which required 3 h. When the bromine reacted completely, the carbon tetrachloride was removed by reduced-pressure distillation, and then a pale yellow product was obtained. The product was dissolved in 100 mL of hot chloroform. The chloroform solution was cooled in an ice bath and the product was removed by filtration. After the second recrystallization, light-gray crystals melting at $167\text{--}168^\circ\text{C}^{[22]}$ were obtained. The yield was 80 g (53%).

1,3,5-Benzenetricarboxaldehyde

A round-bottomed flask was equipped with a still head, capillary ebullition tube, and receiver in an assembly for vacuum distillation. The flask was filled with 42 g of finely powdered 1,3,5-tris (dibromomethyl) benzene and 100 mL of concentrated sulfuric acid (70%). The reactants were thoroughly mixed by shaking. A vacuum was applied by means of a water pump, and a stream of air was allowed to pass through the capillary tube in order to facilitate the rapid removal of hydrogen bromide. The flask was heated in an oil bath to 70°C, and, as the evolution of gas became less vigorous, the temperature of the bath was gradually raised to 110°C. The reaction was completed when a crystal clear solution was obtained and no more gas was evolved (about 2 h). The flask was then cooled and the solution was poured into 300 g of crushed ice. The crystalline solid was collected on a filter, washed with a little water, and recrystallized from 300 mL of 10% methanol with the aid of 1 g of decolorizing carbon to remove the yellow color. The yield of pure product melting at 160–161°C^[22] is 10.8 g (80%). ¹H-NMR (CDCl₃): δ =8.6 (3H, -ph), 10.2 (3H, CHO).

Synthesis of the Hyperbranched Polymer (PBTADB)

2,2'-Diamino-4,4'-bithiazole (2.97 g, 15 mmol) and 1,3,5-benzenetricarboxaldehyde (1.62 g, 10 mmol) were dissolved in dry DMSO (20 mL) with anhydrous potassium carbonate (5 g). The mixture was heated at 80°C for 8 h. Then the inorganic salt was filtered from the heterogeneous solution. When the filtrate was poured into deionized water, the yellow solids were precipitated immediately. To get rid of the oligomers after filtration, the product was dissolved in DMSO and precipitated in deionized water once again. And this procedure was repeated twice. Finally, the product was dried in a vacuum oven at 60°C for 24 h.

Preparation of the Coordination Compounds

The PBTADB's complexes were prepared by mixing equimolar ratios of SmCl₃ (or CoCl₂) and the hyperbranched polymer in DMSO with stirring at 80°C for 48 h under nitrogen atmosphere. The solution was precipitated with methanol, and then filtered and washed with plenty of methanol to remove the surplus of metal ion. To confirm that there were no reduce surplus metal ions, the filtrate was added into aqueous silver nitrate, until there was no participate. Then the solids were dried at 60°C for 24 h in a vacuum oven. According to the data of complexometric titration, the metal contents for complexes are shown in Table 3.

RESULTS AND DISCUSSION

Synthesis and Characterization

Polymerization of bifunctional monomers (A₂) and trifunctional monomers (B₃) generally could lead to branching, cross-linking and cyclization reactions. To obtain a soluble hyperbranched product, the most likely method was controlling the polycondensation conditions^[1]. Based upon the Schiff reaction, the soluble hyperbranched polymers were successfully prepared by controlling the reaction time and the stoichiometric ratio of amino and aldehyde groups (see Table 1). When the mole ratio of 2,2'-diamino-4,4'-bithiazole to 1,3,5-benzenetricarboxaldehyde was 3:2, the product could not become a gel. Three kinds of solvents were used

Table 1. The reaction conditions of the polycondensation of 1,3,5-benzenetricarboxaldehyde and DABT

Polymers	DABT/1,3,5-benzenetricarboxaldehyde	Solvent	Reaction time (h)	Gel	$[\eta]$ (dL/g)	Yield (%)
1	9:4	DMSO	8	Y	—	—
2	3:2	DMSO	8	N	0.061	65
3	1:1	DMSO	8	N	0.037	51
4	3:2	Ethanol	8	N	0.017	38
5	3:2	THF	8	N	0.009	33
6	3:2	DMSO	2	N	0.024	36
7	3:2	DMSO	6	N	0.053	56
8	3:2	DMSO	10	N	0.063	67
9	3:2	DMSO	12	Y	—	—

during the polymerization. We found that the yield is high in DMSO, when compared to THF or ethanol. The reason is that the polymer can dissolve in DMSO and continue to react with monomers, while the product may be precipitated in THF or ethanol and stop the reaction. The reaction time played an important role during the process of the polycondensation. As the reaction time went on, three-dimensional structure was developed, and a gel would be formed over 12 h. From Table 1, we successfully obtained the appropriate polycondensation conditions. The hyperbranched product dissolved in ordinary organic polar solvents like DMSO, DMAc, and NMP (see Table 2).

Table 2. The Solubility tests of the polymers

Polymers	CHCl ₃	DMF	DMAc	DMSO	NMP
2	–	+	+	+	+
3	±	+	+	+	+
4	±	+	+	+	+
5	±	+	+	+	+
8	–	+	+	+	+

±: swell; +: soluble; –: not soluble

To characterize the structures of the product, FT-IR and ¹H-NMR were employed. From the Fig. 1, the FT-IR spectra reveal that the polymer gives characteristic peaks in the range of functional group region, in which the absorption peaks of benzene rings and bithiazole rings were overlapped. However a new peak at about 1624 cm^{–1} is the stretching oscillation of the ν_{C=N} of the polymer, while the ν_{C=N} of DABT is at 1598 cm^{–1}. Two absorption peaks at 3385 and 1697 cm^{–1} are belonging to the ν_{N–H} and ν_{C=O} respectively, which show that there are a little unreacted amino and aldehyde groups. Moreover, the unreacted groups can be detected by ¹H-NMR spectra. As shown in Fig. 2, the peak at δ = 10.2 (a) belongs to the proton on aldehyde. And the chemical shift of the protons on amino is δ = 6.3 (g). There are four peaks in the field of δ = 8.7–9.1 (d, c, b, h) belonging to the protons of benzene rings.

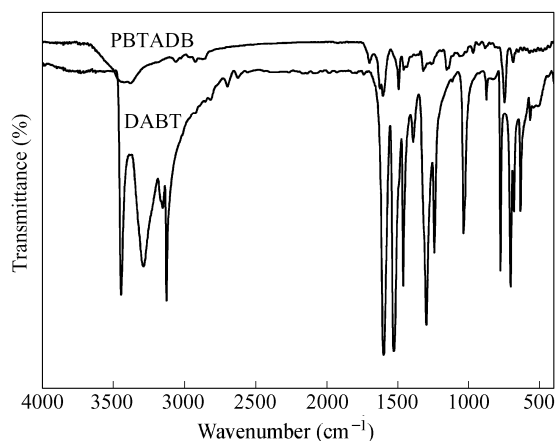


Fig. 1 FT-IR spectra of the PBTADB polymer and the DABT monomer

However, the two peaks at δ = 7.9 and 7.6 are attributed to the protons of Schiff's base and bithiazole ring respectively. To better define the chemical structures of the hyperbranched polymer, Fréchet and co-workers quantified the degree of branching (DB) using Eq. (1)^[23, 24]:

$$DB = (N_D + N_T) / (N_D + N_T + N_L) \quad (1)$$

where N_D , N_T , and N_L refer to the numbers of dendritic, terminal and linear units in the hyperbranched polymers, respectively. The ¹H-NMR spectrum of hyperbranched polyamides showed that the resonances from the hydrogens in the D, L and T units had different shifts due to the difference in their chemical environments (see

Fig. 2). Based on the relative percentages of those units, the calculated DBs ranged between 45% and 55%. According to the equation, the calculated DB of our product was 51%.

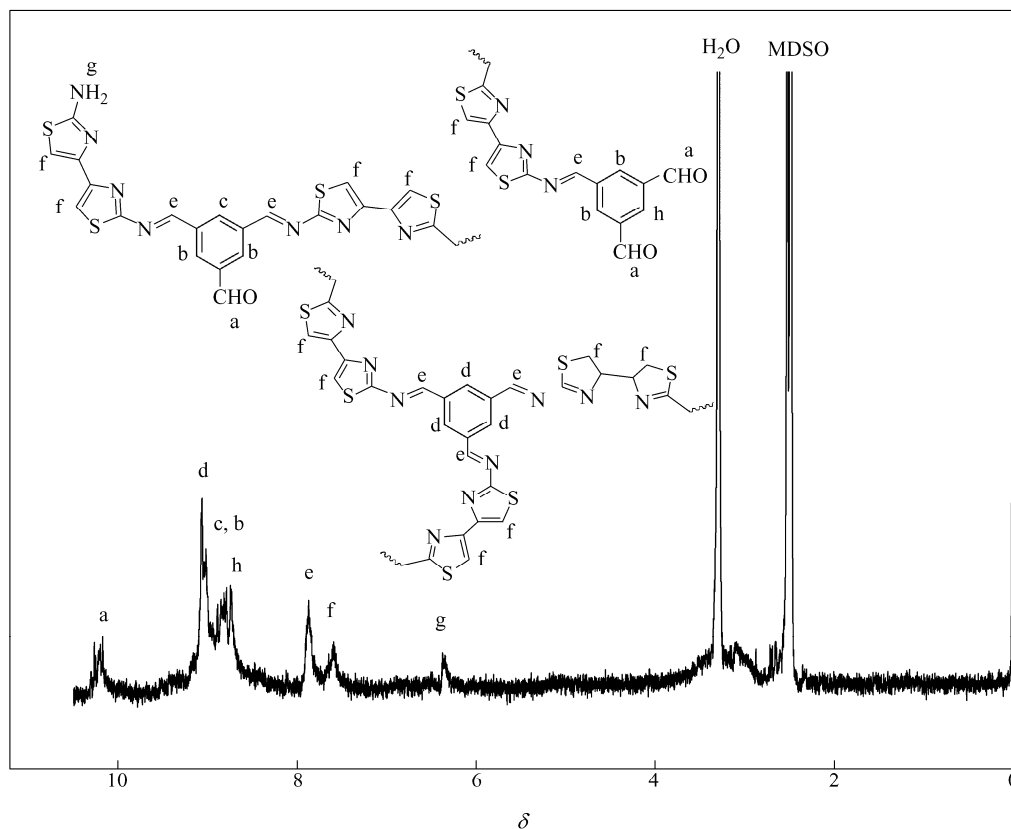


Fig. 2 ^1H -NMR spectrum of the PBTADB

FT-IR spectra of the complexes and the polymer are shown in Fig. 3. By comparing FT-IR spectra of the polymer and their corresponding metal complexes, it can be found that the absorption remarkably changes between 1000 cm^{-1} and 1660 cm^{-1} . A weak peak at about 1526 cm^{-1} , attributed to the skeleton vibrating peak of bithiazole ring, appears again in their complexes, which disappears in the hyperbranched polymer. But a strong absorption peak at 1528 cm^{-1} belongs to $\nu_{\text{C-N}}$ of the bithiazole ring of DABT. The formation of coordinate bond changes the skeleton vibrating energy of bithiazole ring. That is why the peak at 1526 cm^{-1} reappears in the spectrum of the complexes. These results indicate that the chelation between metal ions and the polymer skeleton is formatted *via* nitrogen atoms in bithiazole rings.

Thermal stability of the polymers in nitrogen atmosphere at the heating rate of 10 K/min was evaluated by thermo gravimetric analysis (TGA). The thiazole ring with heteroaromatic structure would have excellent stabilities derived from its molecular symmetry and aromaticity^[25]. Due to the bithiazole rings and the benzene rings, the hyperbranched polymer shows good thermal stability. The temperature of degradation is 275°C for 5% of weight loss (see Fig. 4).

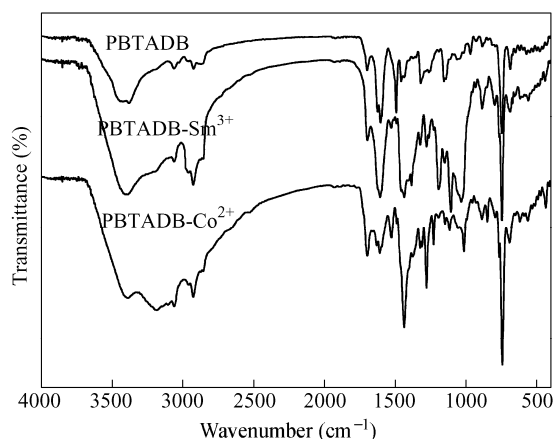


Fig. 3 FT-IR spectra of PBTADB, PBTADB-Sm³⁺ and PBTADB-Co²⁺

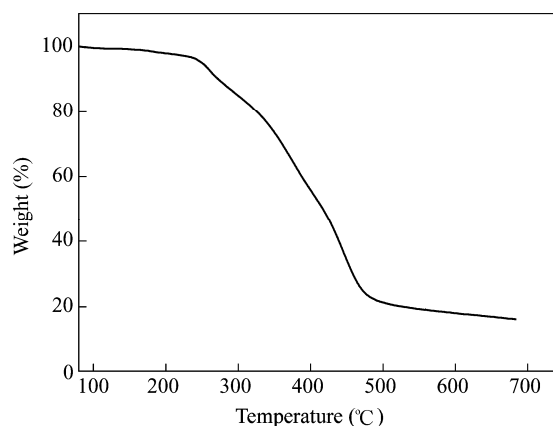


Fig. 4 The thermogravimetric curve for PBTADB

Magnetic Properties of the Complexes

In the past two decades, much attention has been focused on the quest for organic and polymeric magnets because of their advantages compared with traditional magnets, such as the diversity of structures, low density, low magnetic loss, process of preparation without metallurgy at high temperature, *etc.* The design and preparation of organic ferromagnets are great challenges in the field of molecular-based magnetic materials^[26–29]. Here, the preliminary magnetic properties of the two complexes were investigated. To make sure that metal complex is a magnetic material, we explored the temperature dependence of the magnetization for the polymeric complexes over the temperature range of 5–300 K at an applied magnetic field of 2.4×10^6 A/m (see Fig. 5).

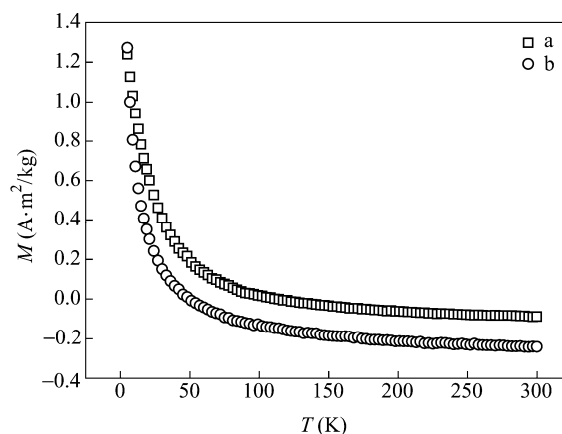


Fig. 5 Magnetization as function of temperature at an applied magnetic field of 2.4×10^6 A/m for PBTADB-Sm³⁺ (a) and PBTADB-Co²⁺ (b)

It is found that the magnetization increases slowly with the decreasing of temperature and then increases sharply in the range of 40–60 K. From Fig. 5, the curves also show that M increases with decreasing temperature from negative values to positive values, which does not follow the traditional ferromagnetism. The results indicate that the strong magnetic interaction arises among coordinated metal ions at low temperature. The PBTADB-Sm³⁺'s χ^{-1} - T curve has a hyperbola that is a significant transition like a switch around 112 K in Fig. 6. The magnetic exchange interaction between adjacent metal ions in polymeric complexes is of fundamental importance for the design and synthesis of new magnetic materials based on polymeric coordination

complexes^[30]. It means that it is probable to explore the origin of hyperbolic signals of the complexes. Above 112 K, the magnetism derived from the Sm^{3+} is too weak to compensate the diamagnetism of the polymer, thus the complexes behaves as diamagnetism; but below 112 K, due to the superexchange interaction between metal ion and conjugated polymer chain, the χ^{-1} - T curve also has a positive Curie-Weiss temperature, $T_\theta = 96$ K, which implies the existence of ferromagnetic coupling in the material. With this interest magnetic phenomenon, the polymeric complexes will not only contribute to the research concerning the relationship of structure and magnetism, but also provide some useful information for designing the magnetic materials. And further investigation is in progress in our group.

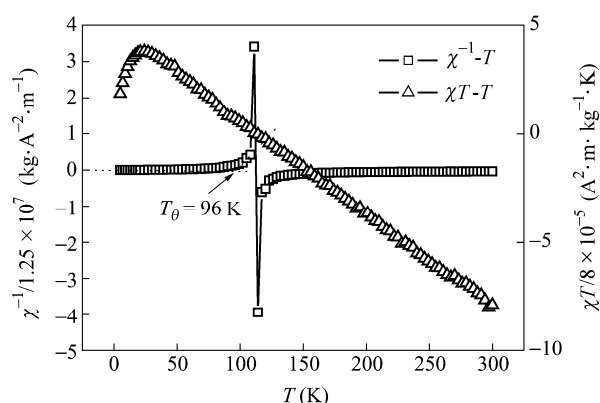


Fig. 6 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PBTADB- Sm^{3+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 100 K and 110 K.

The same reason could explain what happened in Fig. 7. The temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PBTADB- Sm^{3+} and PBTADB- Co^{2+} are shown in the Figs. 6 and 7, respectively. The magnetic susceptibility (χ) of these two complexes follows the Curie-Weiss relationship, $\chi = C/(T - \theta)$, in the range of 100–110 K and 42–50 K. In accordance with the Curie Weiss law, a straight line is fitted. According to the intersection of the extension line and the horizontal axis, the Curie-Weiss temperature of PBTADB- Sm^{3+} is 96 K (see Fig. 6), and the Curie-Weiss temperature of PBTADB- Co^{2+} is 41 K (see Fig. 7). The positive Curie-Weiss temperature indicates that these two complexes are ferromagnets. To get complementary information on the magnetization of PBTADB- Sm^{3+} and PBTADB- Co^{2+} , the magnetic hysteresis loops of PBTADB- Sm^{3+} and PBTADB- Co^{2+} at 5 K (see Figs. 8 and 9) show their characteristics of ferromagnetic interactions. Due to the 2D structure, this ferromagnetic interaction maybe stronger between metal ions and the hyperbranched conjugated polymer chain compared with the line conjugated one^[31]. At 5 K, the observed coercive field (H_c) of PBTADB- Sm^{3+} and PBTADB- Co^{2+} is 4620 A/m and 1016 A/m respectively (see Table 3). The remnant magnetization (M_r) of two complexes is $0.1 \text{ A}\cdot\text{m}^2/\text{kg}$ and $0.0085 \text{ A}\cdot\text{m}^2/\text{kg}$ respectively. The typical 'S' shape and such low coercive field (H_c) and remnant magnetization (M_r) indicate that the polymeric complexes are organic soft ferromagnetic polymers. In addition, the corresponding data are listed at Table 3. As shown in Table 3, although the metal contents of the complexes are different, the magnetic behaviors of them are similar. That is to say, the superexchange interaction between different metal ions and conjugated polymer chains has similar process. The probable reason that leads to the different metal contents of the polymer is the complexing ability of metal ions.

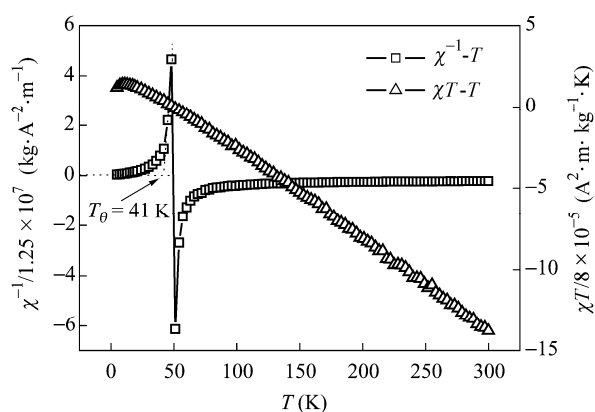


Fig. 7 Temperature dependence of χT and reciprocal magnetic susceptibility (χ^{-1}) for PBTADB- Co^{2+} at an applied magnetic field of 2.4×10^6 A/m. The straight line is a fit to the Curie-Weiss law between 42 K and 50 K.

Table 3. Magnetic properties of PBTADB-2- Sm^{3+} and PBTADB-2- Co^{2+}

PBTADB-2-M	Metal content (wt%)	T_θ (K)	Coercive field (A/m)	Transition temperature (T_i) (K)	Remnant magnetization $\times 10^3$ ($\text{A} \cdot \text{m}^2/\text{kg}$)
PBTADB-2- Sm^{3+}	7.3	96	4620	112	100
PBTADB-2- Co^{2+}	4.5	41	1016	50	8.5

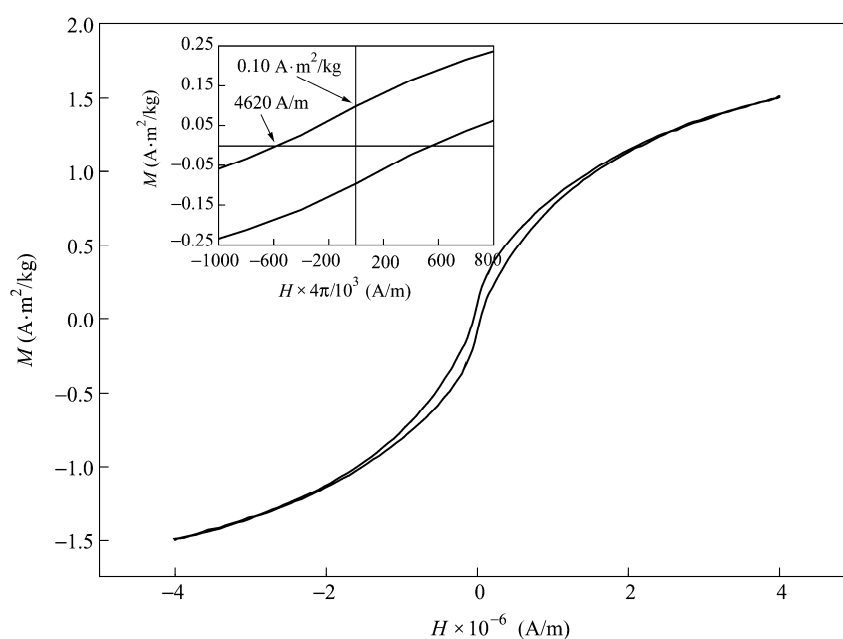


Fig. 8 Hysteresis loop (M versus H) at 5 K for PBTADB- Sm^{3+} complex. Inset: expanded view of the region from -8000 A/m to 8000 A/m.

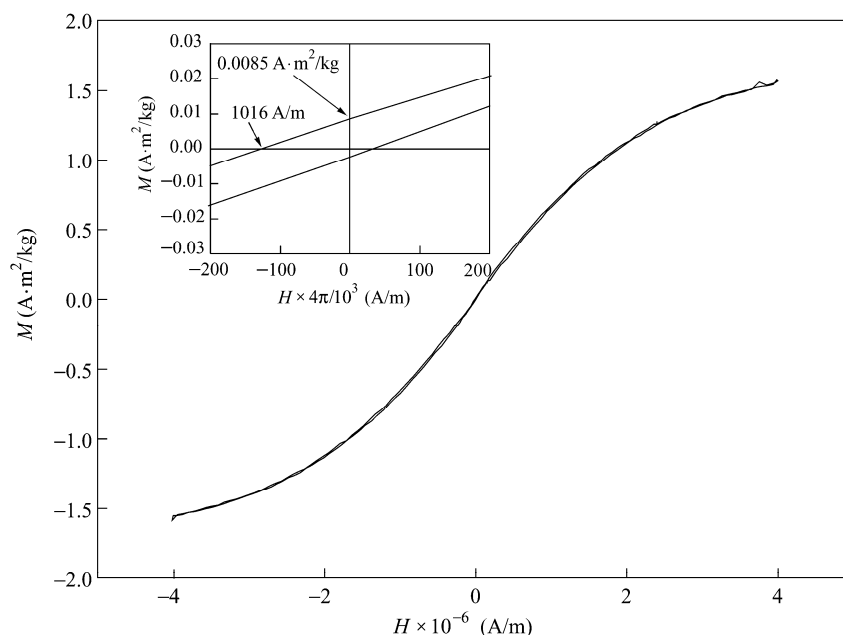


Fig. 9 Hysteresis loop (M versus H) at 5 K for PBTADB- Co^{2+} complex
Inset: expanded view of the region from -1600 A/m to 1600 A/m

CONCLUSIONS

In summary, a novel conjugated hyperbranched polymer containing bithiazole rings was successfully synthesized by the method of polycondensation of bifunctional 2,2'-diamino-4,4'-bithiazole and trifunctional 1,3,5-benzenetricarboxaldehyde. Furthermore, the premier solution system of this reaction was obtained. The hyperbranched product could be dissolved in organic polar solvents like DMAc, DMSO and NMP. Metal complexes were also prepared by mixing equimolar ratios of SmCl_3 (or CoCl_2) and the polymer in DMSO, and characterized by FT-IR spectra. The metal contents of the two complexes are 7.3% and 4.5% respectively. From the field and temperature dependence of magnetization and hysteresis loop, both of them exhibit the properties of soft ferromagnets. And with a hyperbola in a certain temperature range, the complexes should provide some useful information for designing magnetic materials. Further investigations by our group are in progress.

REFERENCES

- 1 Jikei, M., Chon, S.H., Kakimoto, M., Kawauchi, S., Imase, T. and Watanabe, J., *Macromolecules*, 1999, 32: 2061
- 2 Fomina, L., Guadarrama, P., Fomine, S., Salcedo, R. and Ogawa, T., *Polymer*, 1998, 39: 2629
- 3 Voit, B., *New J. Chem.*, 2007, 31: 1139
- 4 Suzuki, M., Li, A. and Saegusa, T., *Macromolecules*, 1992, 25: 7071
- 5 Shi, J.B. and Tang, B.Z., *Macromolecules*, 2010, 43: 680
- 6 Voit, B. and Ledere, A., *Chem. Rev.*, 2009, 109: 5924
- 7 Staring, E., Dias, A.A. and van Benthem, R.A.T.M., *Prog. Org. Coat.*, 2002, 45: 101
- 8 Burkidnshaw, S.M., Froehling, P.E. and Mignaneooi, M., *Dyes Pigments*, 2002, 53: 229
- 9 Seiler, M., Köhler, D. and Arlt, W., *Sep. Purif. Technol.*, 2002, 29: 245
- 10 Genin, H. and Hoffmann, R., *Macromolecules*, 1998, 31: 444
- 11 Sun, W.L., Gao, X.S. and Lu, F.C., *Polymer*, 1997, 64: 2309
- 12 Weng, J., Jiang, L.M., Sun, W.L., Shen, Z.Q. and Liang, S.Q., *Polymer*, 2001, 42: 5491

- 13 Yang, J., Sun, W.L., Lin, W.H. and Shen, Z.Q., *Chinese J. Polym. Sci.*, 2009, 27(1): 131
- 14 Zhou, Z.X., Sun, W.L., Yang, J. and Shen, Z.Q., *Polymer*, 2005, 46: 9495
- 15 Yang, J., Sun, W.L., Lin, W.H. and Shen, Z.Q., *J. Polym. Sci. Polym. Chem.*, 2008, 46: 5123
- 16 Lin, W.H., Sun, W.L., Yang, J. and Shen, Z.Q., *Mater. Chem. Phys.*, 2008, 2: 617
- 17 Wu, L.B., Chen, Q., Lin, W.H., Bian, G.F., Sun, W.L. and Shen, Z.Q., *Acta Polymerica Sinica* (in Chinese), 2010, (3): 377
- 18 Ding, N.W., Lin, W.H., Sun, W.L. and Shen, Z.Q., *Sci. China Ser. B*, 2011, 2: 1
- 19 Yamamoto, T., Maruyama, T., Zhou, Z.H., Ito, T., Fukuda, T. and Yoneda, Y., *J. Am. Chem. Soc.*, 1994, 116: 4832
- 20 Wang, B. and Wasielewski, M.R., *J. Am. Chem. Soc.*, 1997, 119: 12
- 21 Taylor, M.D. and Carter, C.P., *J. Inorg. Nucl. Chem.*, 1962, 24: 387
- 22 Snell, J.M. and Weissberger, A., *Org. Synth.*, 1955, 3: 788
- 23 Hawker, C.J., Lee, R. and Fréchet, J.M.J., *J. Am. Chem. Soc.*, 1991, 113: 4583
- 24 Hawker, C.J. and Fréchet, J.M.J., *J. Am. Chem. Soc.*, 1990, 112: 7638
- 25 Zhao, X., Li, Y.F., Shao, Y., Ma, T., Gong, C.L. and Huang, C.S., *J. Appl. Polym. Sci.*, 2008, 107: 3119
- 26 Miller, J.S. and Epstein, A.J., *Angew. Chem., Int. Ed. Engl.*, 1994, 33: 385
- 27 Crayston, J.A., Devine, J.N. and Walton, J.C., *Tetrahedron*, 2000, 56: 7829
- 28 Rittenberg, D.K., Sugiura, K., Sakata, Y., Mikami, S., Epstein, A.J. and Miller, J.S., *Adv. Mater.*, 2000, 12: 126
- 29 Carmeli, I., Leitius, G., Naaman, R., Reich, S. and Vager, Z.J., *Chem. Phys.*, 2003, 118: 10372
- 30 Kahn, O., "Molecular magnetism", New York, VCH Publishers, 1993
- 31 Lin, W.H., Sun, W.L. and Shen, Z.Q., *Polym. Adv. Technol.*, 2007, 18: 959