Chinese Chemical Letters Vol. 16, No. 8, pp 1113-1116, 2005 1113
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Magnetic Properties of Polyamide Complex Containing Bithiazole Moieties

Hong Zhou GAO, Wei Lin SUN*, Zhi Quan SHEN

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027

Abstract: A new polyamide containing bithiazole moieties (PTA) was synthesized by the polycondensation of 2, 2′-diamino-4, 4′-bithiazole (DABT) and oxalyl chloride. The polymer complex was prepared from PTA and $NdCl_3$ in DMSO. They were characterized through IR and elemental analysis. The preliminary magnetic properties of the complex PTA-Nd^{3+} was investigated, it was found that the material is a ferromagnet at low temperature.

Keywords: Polyamide, bithiazole, rare earth ion, magnetic property.

The study on polymers containing bithiazole moieties has been more than half a century. During 1944-1946, Erlenmeyer published some articles concerning these polymers, which formed from the reaction of a bisthioamide and a bis-a-haloketone, but left the polymers uncharacterized[1]. Later, because the thiazole nucleus has excellent thermal and chemical stability, polymers containing bithiazole moieties were extensively studied by several groups in the world[2-4]. In recent years, Sun *et al*. found that when the polymer containing bithiazole moieties chelate with transition metal ions, the polymer complex possessed fairly ferromagnetism[5-7]. It is a new method to prepare the polymeric ferromagnet. In this paper, we report the synthesis and characterization of a new polyamide containing bithiazole moieties. The preliminary magnetic properties of the PTA-Nd^{3+} complex were investigated.

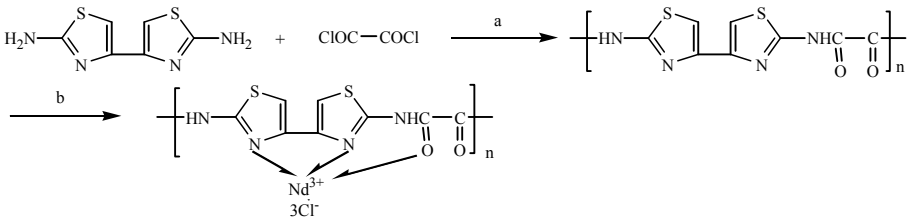
Experimental

Materials

Dimethylformamide (DMF), dimethylsulfoxide (DMSO) and triethylamine were dried and purified by usual methods. 2, 2′-Diamino-4, 4′-bithiazole (DABT) was prepared according to literature[5] followed by several recrystallizations. Oxalyl chloride was a commercial product of Shanghai Chemical Reagent Company. IR spectra were recorded with a Bruker Vector 22 using KBr pellets. The intrinsic viscosity of polymer was measured by an Ubbelohde–type viscometer at 30°C using sulfuric acid as a solvent.

* E-mail: opl_sunwl@emb.zju.edu.cn

Scheme 1 Preparation of PTA and PTA-Nd^{3+}



a) DMF, triethylamine, 0°C, 6 h. b) $2NdCl_3 \cdot 6H_2O$, DMSO, 80°C, 24 h

Magnetic measurements were carried out by a PPMS-9T magnetometer (Quantum Design). The content of Nd is determined by complexometric titration using EDTA. Elemental analysis for C, H, N, were performed using a Flash EA112 elemental analyzer.

Preparation of polymer

To a three-necked 100 mL flask equipped with a mechanical stirrer was added 5 mmol DABT and 50 mL DMF. The mixture was stirred at room temperature for 15 min. After dissolving the monomer, 10 mmol triethylamine was added, and then 5.02 mmol oxalyl chloride was added dropwise. The mixture was stirred at 0°C for 6 h, and then poured into 200 mL methanol to isolate the polymer. The precipitated polymer was separated by filtration and washed with hot methanol, then dried at 80°C under vacuum for 12 h, a yellow powder of PTA was obtained, the yield is 86%, and the intrinsic viscosity is 0.12 dL/g.

Preparation of the polymer complex

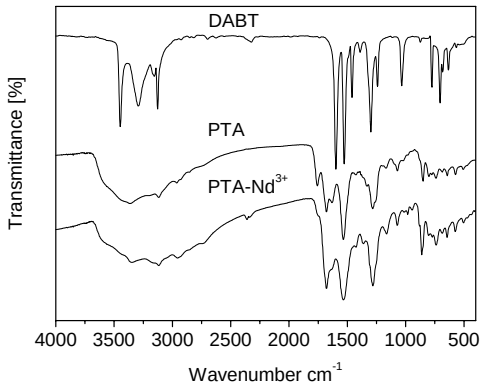
To a three-necked 100 mL flask equipped with a mechanical stirrer was added 0.5 g PTA prepared above，and 50 mL DMSO as solvent. After the inner air was removed with nitrogen through the gas inlet tube, the needed $NdCl_3 \cdot 6H_2O$ was added to the polymer solution. The mixture was heated to 80°C and stirred at the same temperature for 24 h, then poured into 200 mL methanol. The precipitate was collected in a Bush funnel, washed with methanol and ion-free water thoroughly, and then dried at 80°C in a vacuum for 12 h. A yellow green powder of PTA-Nd^{3+} was obtained, and the yield is 78%. Elemental analysis for $[C_8H_4N_4S_2O_2(NdCl_3)_{0.188}]$: C, 32.07%; H, 1.34%; N, 18.71%. Found: C, 31.56%; H, 2.22%; N, 16.58%, Nd, 9.11%.

Result and Discussion

Characterization

The IR spectra of monomer DABT, polymer PTA and its complex PTA-Nd^{3+} are shown in **Figure 1**. The absorption peaks in the spectra of DABT at 3300-3500 cm^{-1} and 3100-3300 cm^{-1} (double) can be attributed to the vibration of two N–H bands of the amino groups. It is found that in the case of PTA those peaks are dramatically weakened, which indicates that the amino group of DABT has reacted with the carbonyl

Figure 1 IR spectra of DABT, PTA and PTA-Nd^{3+}



chloride while polymerizing. The spectra of PTA-Nd^{3+} is similar to that of PTA except some changes in absorption intensities. But in the spectra of PTA-Nd^{3+}, the peak at 850.9 cm^{-1} in the spectra of the polymer, which is ascribed to the skeletal vibration of thiazole[8], has shifted to 862.7 cm^{-1}. These results reveal that PTA forms complex with Nd(Ⅲ) ions through coordination of N and O atom in polymer skeleton.

Magnetic properties

Figure 2 shows that the magnetic susceptibility (χ) of PTA-Nd^{3+} complex follows the Currie-Weiss relationship in the temperature range of 230-300 k, and the positive Currie-Weiss temperature (θ=130 k) implies the existence of ferromagnetic coupling in the material. The product of magnetic susceptibility and temperature (χT) remains constant in the temperature range of 50-130 k, below 50 k, an abrupt increase in the slope of χT was observed. This can be interpreted as the realization of a ferromagnetic coupling among spins in short range at low temperature.

Figure 2 Temperature dependence of χT and χ^{-1} for PTA-Nd^{3+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie-Weiss law from 230 k to 300 k.

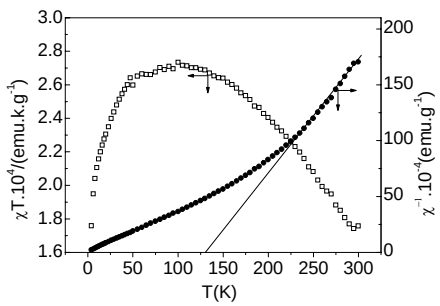
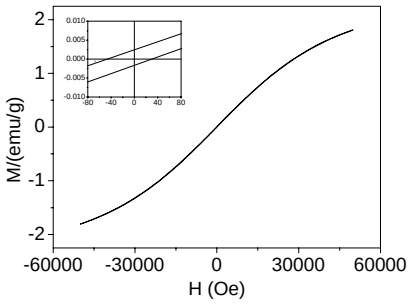


Figure 3 Hysteresis loop for PTA-Nd^{3+} at 4 k. The insert is the expanded view of the region from –80 Oe to 80 Oe.



At low temperature, the magnetization curve as function of applied field exhibits a hysteresis cycle for PTA-Nd^{3+}, **Figure 3**, which is characteristic of ferromagnetic interactions. At 4 k, the observed coercive field is H_c = 40 Oe and the remanent magnetization M_r = 0.003 emu/g. From the results, we may conclude that the PTA-Nd^{3+} complex is a soft ferromagnet.

Acknowledgment

The authors are indebted to the financial support of the National Natural Science Foundation of China (No: 20374044, 20434020).

References

1. H. Hehr, Erlenmeyer, *Helv. Chim. Acta*, **1944**, *27*, 489.
2. J. E. Mulvaney, C. S. Marvel, *J. Org. Chem*., **1961**, *26*, 95.
3. K. Inoue, *J. Polym. Sci: Part A*, **1995**, *33*, 2291.
4. W. L. Sun, X. S. Gao, F. C. Lu, *J. Appl. Polym. Sci.,* **1997**, *64*, 2309.
5. J. Weng, W. L. Sun, L. M. Jiang, Z. Q. Shen, *Maraomol Rapid Commun.*, **2000**, *21*,1099.
6. W. L. Sun, J. Weng, L. M. Jiang, Z. Q. Shen, *Synth. Met*., **2003**, *137*, 1341.
7. J. Weng, L. M. Jiang, W. L. Sun, Z. Q. Shen, *Polymer*, **2001**, *42*, 5491.
8. J. V. Metzger, *Comprehensive Heterocyclic Chemistry*, **1984**, *6*, 241, Pergamon press.

Received 28 September, 2004