Synthesis and Properties of Polymeric Complexes Containing Bithiazole Rings and Carbazole Units

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ABSTRACT: A novel polymer (poly[2,2′-(4,4′-bithiazolylene)][N-(2-ethylhexyl)-3,6-carbazylene] (PBTCA) was first synthesized from 2,2′-diamino-4,4′-bithiazole and *N*-(2-ethylhexyl)-3,6-diformylcarbazole. The structure of the polymer was determined with IR and ^{1}H-NMR spectroscopy. The PBTCA–Nd^{3+} complex was prepared via the mixing of neodymium trichloride hexahydrate and PBTCA in dimethyl sulfoxide under a nitrogen atmosphere. The magnetic behaviors of the Nd^{3+} complex of a poly(Schiff base) were measured as a function of the magnetic field strength (0–50 kOe) at 4 K and as a function of the temperature (4–300 K). The results show that PBTCA–Nd^{3+} is a ferromagnet when the temperature is below 15 K, and above that, it is a diamagnet. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 443–446, 2006

Key words: bithiazole; poly(Schiff base); polycondensation; conjugated polymers; magnetic polymers

INTRODUCTION

For several decades, aromatic heterocyclic polymers, because they have good mechanical properties, thermal stability, radio resistance, and anticorrosion properties, have been studied for broad use in electronics, chemical engineering, mechanical engineering, and so forth. They are used not only as structural materials but also as functional materials.[1–3]

Aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five-membered rings. The crystal structure of metal complexes of the monomer 2,2′-diamino-4,4′-bithiazole (DABT) has been characterized with X-ray diffraction.[4,5] In recent years, our group has been working on the synthesis and properties of bithiazole-based polymers and their metal complexes for developing functional polymeric materials, and we have reported a series of novel polymers and their metal complexes, which display some interesting results.[6–10]

In this article, we report a new bithiazole-based polymer (Scheme 1), in which carbazole moieties are linked together by a conjugated bithiazole segment, and its Nd^{3+} complex. Carbazole is a compound that has been the subject of many studies because of its photoconductive properties and its ability to form charge-transfer complexes due to its inherent electron-donating nature arising from the nitrogen atom through the conjugated aromatic rings. It is quite likely that carbazole-containing polymers will possess electro- and photochemical properties as well as high thermal stability because of the carbazole-conjugated system.[11–15] The main focus of this article is a discussion of the synthesis and magnetic properties of the complex.

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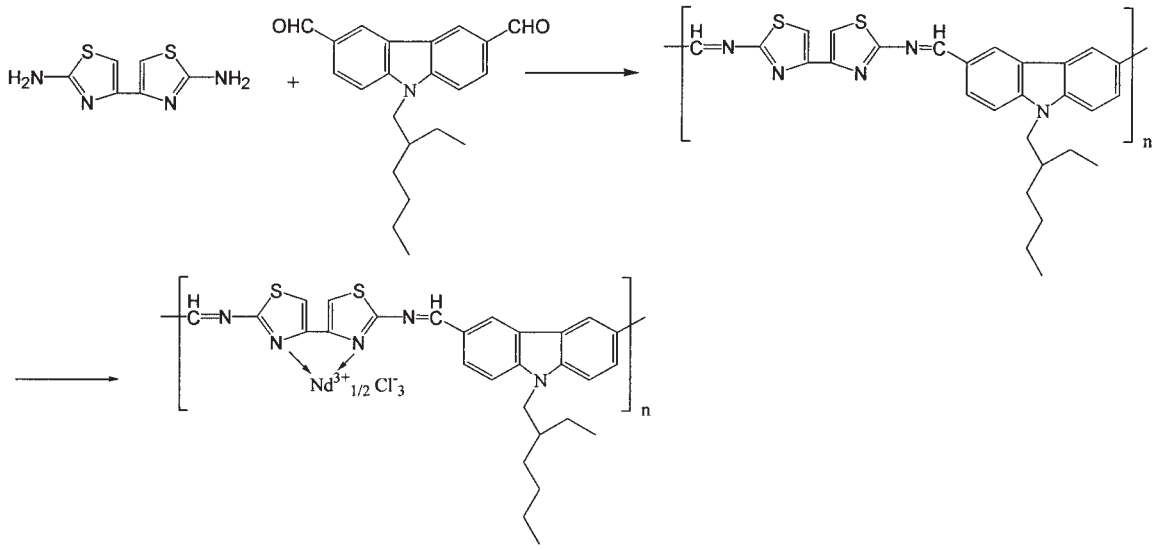
EXPERIMENTAL

Materials

N-(2-Ethylhexyl)-3,6-diformylcarbazole (NDC)[14,16] and DABT[17] were prepared according to the literature. Dimethyl sulfoxide (DMSO) was handled as usual. Neodymium trichloride hexahydrate ($NdCl_3 \cdot 6H_2O$)[18] was prepared according to the literature procedure.

Synthesis of the polymer (PBTCA) and polymeric complex

The polymer was synthesized via a condensation reaction as follows. An equimolar ratio of DABT to NDC was dissolved in DMSO to obtain a 5% concentration. The solution was magnetically stirred and kept at 80°C under a nitrogen atmosphere. After 24 h, a red-brown solution was obtained. The polymer was precipitated by the addition of toluene, and then the brown solid was filtered, washed with toluene, water, methanol, and acetone, and dried



Scheme 1 Synthetic route of PBTCA and suggested structure for the corresponding Nd^{3+} complex (PBTCA–Nd^{3+}).

at 60°C for 24 h in a vacuum oven. The yield was 64.2%.

IR: 3302, 3179, 2922, 2859, 1604, 1521, 1484, 1313, 1211, 1130, 805, 739 cm^{-1}. ^{1}H-NMR (CF_3COOD-*d*): 0.8–1.5 (H of carbazole), 4.4, 7.3 (H of bithiazole), 7.8 (H of carbazole). Intrinsic viscosity: 0.18 dL/g (H_2SO_4, 30°C).

The PBTCA–Nd^{3+} complex was prepared via the mixing of $NdCl_3 \cdot 6H_2O$ and PBTCA (molar ratio = 2 : 1) in DMSO and stirring at 80°C for 24 h under a nitrogen atmosphere. The polymer complex was precipitated as a red-brown solid of PBTCA–Nd^{3+} by the addition of toluene to the black solution. The precipitate was filtered and washed with water until $NdCl_3$ was removed and then dried at 60°C for 24 h in a vacuum oven. The yield was 53.5%.

IR: 3293, 3168, 2955, 2922, 2866, 1622, 1522, 1484, 1310, 1211, 1015, 808, 736 cm^{-1}. Nd content: 7.62%.

Measurements

IR spectra were taken with KBr pellets with a Bruker Fourier transform infrared (FTIR) spectrometer (Germany). NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer. The content of metal (Nd) was obtained by complexometry.[19] The intrinsic viscosity was measured with an Ubbelohde viscometer at 30°C with concentrated H_2SO_4 as a solvent. The magnetic measurements were carried out with a magnetometer (Physical property measurement system (PPMS-9T)). The magnetization with an applied magnetic field was measured at 4 K, and the temperature dependence of the magnetization was measured from 4 to 300 K at an applied magnetic field of 30 kOe.

RESULTS AND DISCUSSION

Synthesis of the polymer and its complex

The structure of PBTCA was characterized with IR and ^{1}H-NMR spectra. Figure 1 shows the FTIR spectra of DABT, NDC, and PBTCA. A comparison of the FTIR spectra of the carbazole dialdehyde monomer and DABT with that of PBTCA shows that 1687 and 1597 cm^{-1}, which correspond to the strong aldehyde carbonyl absorption peaks of the dialdehyde monomer and the N—H bending vibration of DABT, respectively, disappear in the IR spectrum of PBTCA, and a new band appears at about 1604 cm^{-1}, which indicates the C═N bond of the polymer. The bonds in the region of 1521–1022 cm^{-1} reflect the skeletal oscillation of bithiazole rings, and those from 2922 to 2859 cm^{-1} indicate the long-chain alkyl in the carbazole monomer.

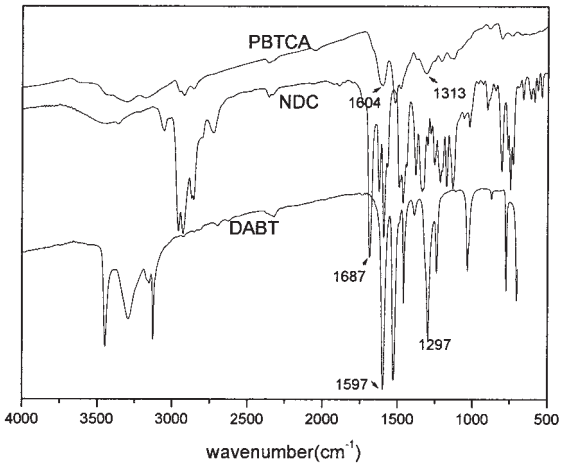


Figure 1 FTIR spectra of DABT, NDC, and PBTCA.

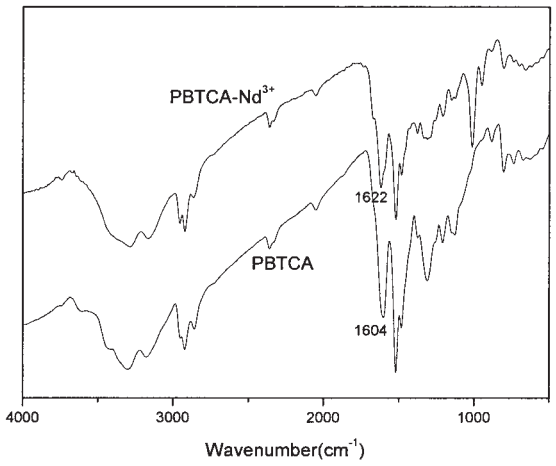


Figure 2 FTIR spectra of PBTCA and PBTCA–Nd^{3+}.

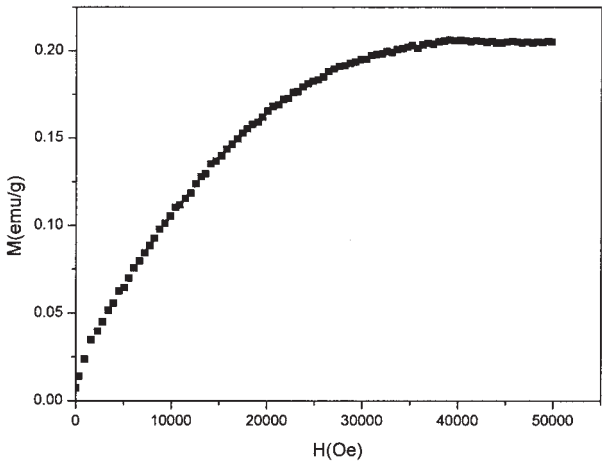


Figure 3 Magnetization (M) versus the applied magnetic field (H) at 4 K for PBTCA–Nd^{3+}.

With the two nitrogen atoms in the bithiazole rings, the polymer can chelate various metal ions by forming steady five-membered rings. The PBTCA–Nd^{3+} complex was synthesized and characterized with IR spectroscopy (Fig. 2). The IR spectrum of PBTCA–Nd^{3+} shows a slight difference from that of PBTCA, which is caused by chelation. The C═N bond, which appears at about 1604 cm^{-1} in the spectrum of PBTCA, shifts to 1622 cm^{-1} in that of PBTCA–Nd^{3+}, and the shifts of bonds in the region of 1521–1015 cm^{-1} may all be attributed to the skeletal vibrations of bithiazole rings, which become less flexible because of chelation.

As for the ^{1}H-NMR (CF_3COOD) spectrum, the polymer shows signals in the range of 0.8–1.5 due to the hydrogens of the alkyl of NDC and $\delta = = 7.3$ and $\delta = 7.8$, which can be attributed to the hydrogens of bithiazole rings and carbazole rings, respectively. Therefore, we insist that the structures of the polymer and its metal complex that we suggest in Scheme 1 are in accordance with the IR and ^{1}H-NMR spectra.

Magnetic properties of the complex PBTCA–Nd^{3+}

The curve of the magnetization versus the applied magnetic field at 4 K for PBTCA–Nd^{3+} is shown in Figure 3. The magnetization increases sharply when the applied field is less than 20 kOe, and then the increasing trend slows down; this is typical of a ferromagnet. The magnetization approaches saturation at about 40 kOe, and the relative saturation magnetization is about 0.2 emu/g.

Figure 4 shows the temperature dependence of the magnetization of PBTCA–Nd^{3+} at an applied magnetic field of 30 kOe from 4 to 300 K. The magnetization increases sharply with decreasing temperature below 50 K. The magnetization of PBTCA–Nd^{3+} has negative values above 15 K; this does not follow traditional ferromagnetism. A similar phenomenon was discovered by our group.[20]

The temperature-dependent curve of the reciprocal of the susceptibility for PBTCA–Nd^{3+} (Fig. 5) shows more obviously that a significant transition like a switch appears at about 15 K. When the temperature is less than 15 K, the PBTCA–Nd^{3+} complex is a ferromagnet, and above that temperature, it is a diamagnet. It is very favorable in the microwave and microelectronics industry as a magnetism switch because we can shift the magnetism of the complexes by changing the conditions, such as the temperature. Further investigation is in progress in our group.

To get more detailed information on the magnetic properties of the PBTCA–Nd^{3+} complex, it was necessary to detect the hysteresis loops. Figure 6 shows the hysteresis loops of the PBTCA–Nd^{3+} complex at 4 K, and Figure 7 shows an expanded view of the region from −500 to 500 Oe of the hysteresis loop of the

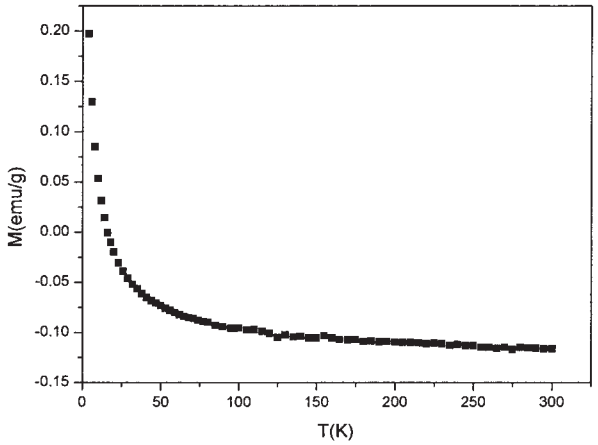


Figure 4 Magnetization (M) as a function of temperature (T) at an applied magnetic field of 30 kOe for PBTCA–Nd^{3+}.

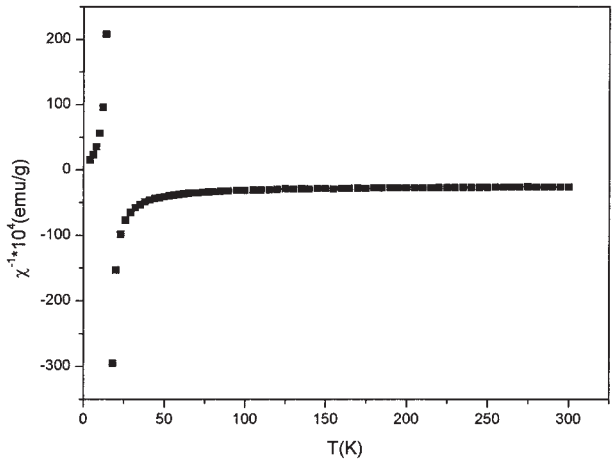


Figure 5 Reciprocal of the magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PBTCA–Nd^{3+} at an applied magnetic field of 30 kOe.

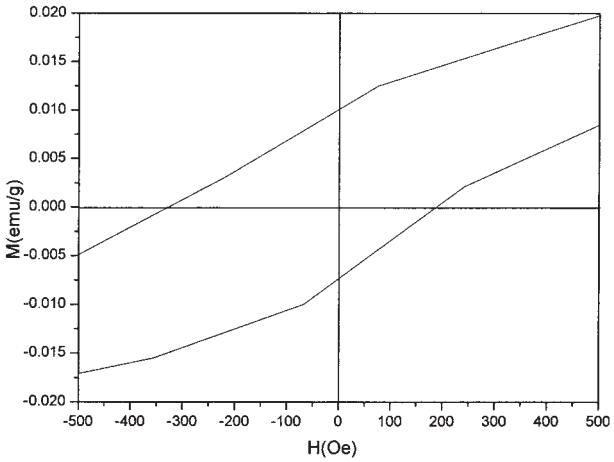


Figure 7 Expanded view of the region from −500 to 500 Oe of the hysteresis loop [the magnetization (M) versus the applied magnetic field (H)] at 4 K for the PBTCA–Nd^{3+} complex.

PBTCA–Nd^{3+} complex. From them, we determined that the observed coercive field was 184.85 Oe (4 K), and the remaining magnetization was 0.010 emu/g (4 K). The typical S shape of the hysteresis loop indicates that PBTCA–Nd^{3+} is a soft ferromagnet.

CONCLUSIONS

A poly(Schiff base) containing bithiazole rings and carbazole and its rare-earth complex were synthesized and characterized. The magnetic properties of the PBTCA–Nd^{3+} complex were studied. From the temperature and field dependence of the magnetization and hysteresis loop, we have concluded that PBTCA–Nd^{3+} is a soft ferromagnet with unusual temperature- and field-dependent magnetic behaviors.

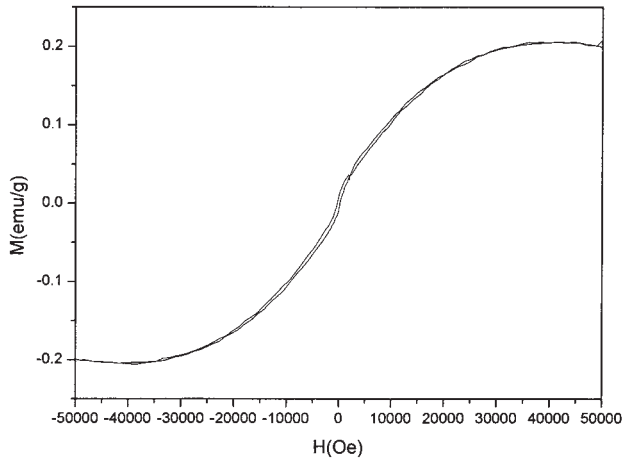


Figure 6 Hysteresis loop [the magnetization (M) vs the applied magnetic field (H)] at 4 K for the PBTCA–Nd^{3+} complex.

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