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IRON-SCHIFF BASE MAGNETIC POLYMERS. SYNTHESIS AND CHARACTERIZATION

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Abstract A magnetically active organometallic iron-Schiff base polymer, molecular weight was between about 4,000 and 50,000 daltons, was synthesized. This polymer comprised a multiplicity of Schiff base tridentate chelating groups having the capacity to combine with the iron (II) or iron (III) ion of an organic salt. A magnetic susceptibility (χ_g) of this organic polymer was between about 1×10^{-6} cc/g and 1×10^{-2} cc/g at an ambient temperature. When this polymer, which was a useful tough film, was heated up to about 200 °C and held for approximately 1 minute, the magnetic susceptibility increased from 1×10^{-4} cc/g to 6×10^{-4} cc/g. The surprising permanent residual enhancement of the magnetic susceptibility of this polymer should be useful in the storage of information in optical magnetic devices.

INTRODUCTION

A number of researchers have examined metal containing materials for use as magnetic films for information storage devices.[1,2] Specifically, Lions ad Martin disclosed the preparation of Schiff base polymers in aqueous solution having fairly low molecular weight. To our knowledge, this was the first example of molecular based-magnets with ferromagnetic exchange.[3] Sugano et al. disclosed the aqueous preparation of low molecular weight powders from reactions of Schiff base polymers to which were added various iron salts in aqueous solution.[4] Sugano et al. further carried out the re-examination of preparation of Schiff base polymers in aqueous solution, which were fairy low molecular weights. When the Schiff based polymer was added to the aqueous iron solution, iron ion became coordinated to the polymer and the combination displayed magnetic capabilities.[5]

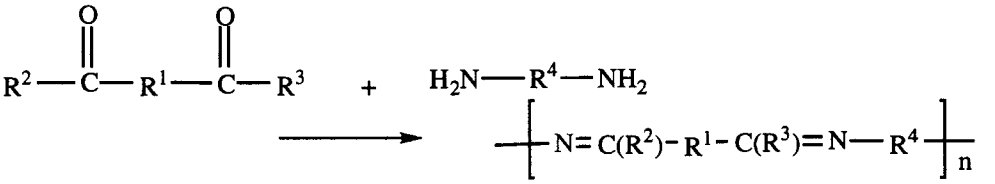
Previously we have synthesized hetelopoly metal tetrathiolates(poly(M1TM2) , T: tetrathiolate) with ferromagnetic properties facilitated by superexchange.[6,7,8] In this work, magnetic polymers consisting of Schiff base were synthesized in order to obtain new molecular based magnetic materials. We found a process to prepare a

magnetically enhanced iron-Schiff base polymer as a useful film and demonstrated that the magnetic susceptibility increases by six times with the Laser heating of the polymers. Implications of these results are discussed in relation to magnetic storage of information.

SYNTHESIS

(A) Synthesis

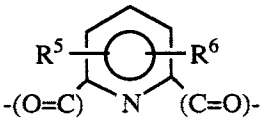
The Schiff base polymer under anhydrous conditions which, most importantly, also involved continuous removal of any water produced during the polymerization were produced. When the solution cast on a surface, flexible useful films were observed to form. After $FeSO_4.7H_2O$ was added in an organic solvent such as DMF, DMAC, etc. or water or aqueous mixtures of solvents, the organometallic polymer produced by removal of the solvent was tough yet flexible, with interesting magnetic properties. The Schiff base reaction in the present work is a reaction of diketone (or dialdehyde) with diamine as shown below:



R^2, R^3 are alkyl groups each independently having from 1 to 12 carbon atoms in it.

R^1 is 

which is obtained from a nitrogen aromatic compound having the carbonyl groups in the 2,6-positions, e.g.:



The aromatic ring is substituted with R^5 and R^6 which are each independently selected from CH_3-, CH_3CH_2-, $CH_3CH_2CH_2$-, -F, Cl, or Br.

In the above Schiff bases, a diketone or dialdehyde is coupled with a diamine to produce a Sciff base polymer. Also, an aldehyde-ketone, where one R^2-(C=O) and

R^3-(C=O) is an aldehyde and the other is a ketone, is contemplated in the present work.

(B) Experimental details

In a 100 ml flask is added 2.0 g of 2, 6-diacetylpyridine, 1.42 g of 1, 6-diaminohexane, 50 ml of N-methylpyrolidone and 18 g of toluene. The flask is fitted with an azeotrope distillation head. The temperature of the head (pot) is allowed to achieve 120 °C and later 150 °C. The azeotrope is collected after about 20 ml of toluene is removed. The water fraction is about 0.5 ml. A gel like mass begins to precipitate at the last stage of the reaction. The precipitate is placed in methanol to remove solvent. The product is rubbery and easy to separate by filtration. The filtrate only has a light color. The precipitate is rinsed with methanol and derived in a vacuum, 2.97 g, 90 % yield as a tough rubbery substance. The molecular weight of this polymer is greater than 10000 daltons.[9]

This Schiff base polymer is treated with 2.5 g of $FeSO_4.2.5H_2O$ (dry) and the mixture is refluxed for two hr's. filtered and dried. A dark powder was obtained, 112.4 % yield having 15.2 % iron by atomic absorption.

MAGNETIC PROPERTY

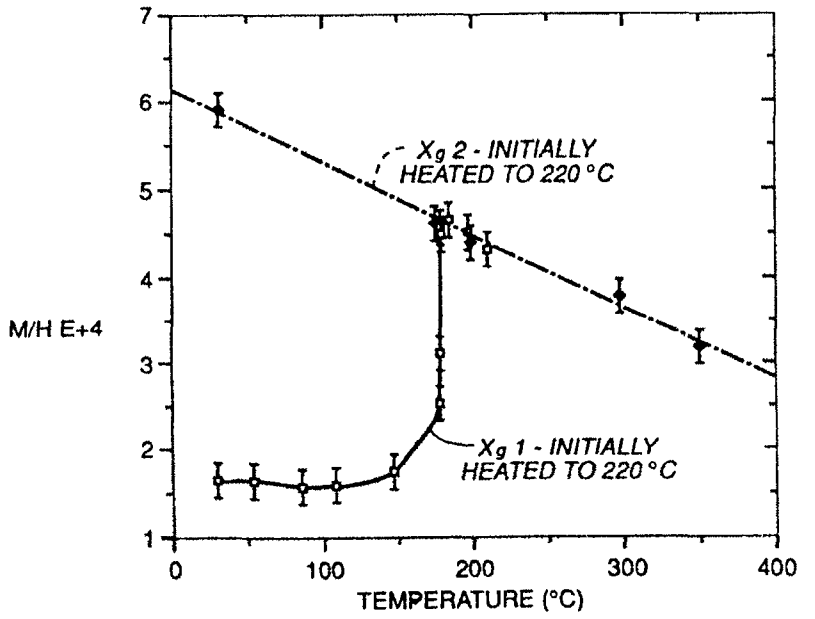


FIGURE 1 The plot of the magnetization of the iron (II) treated Schiff base polymer when heated from ambient (-20°C) to about 400 °C.

The Schiff-base polymer was attracted to a magnet at ambient temperature. The Schiff base-iron tough polymer has a magnetic susceptibility of about 1 x 10^{-4} cc/g. However, its magnetic susceptibility increased by Laser heating.

In Figure. 1 is shown the magnetic susceptibility at constant applied field (M/H) as a function of temperature for heating to 220 °C and holding for approximately 1 minute. Surprisingly, the magnetic susceptibility increased from about 1 x 10^{-4} to 6 x 10^{-4} cc/g by Laser heating. Upon cooling to ambient temperature, the enhanced magnetic susceptibility was retained at about 5 times of the original value before heating. However, the magnetic susceptibility had a peak at about 200 °C, and further heating (to 400 °C) caused a decrease in magnetic susceptibility because of degradation. We observed magnetite particles in the heated Schiff-base polymers by Mossbauer spectroscopy, but further investigation is now in progress.

The Schiff-base polymers have a unique magnetic property which is sensitive to Laser heating, and then their applications to thermal mode information storage materials are conceivable in several ways.

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