

# Synthesis And Magnetic Properties Of Block Copolymer-CoFe<sub>2</sub>O<sub>4</sub> Nanoclusters

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## ABSTRACT

The overall goal of this research is to explore techniques for the development of novel binary magnetic oxide nanoclusters uniformly distributed within a polymer matrix. These  $\text{CoFe}_2\text{O}_4$  nanoclusters were synthesized at room temperature, and are confined within the self-assembled nanoscale structure exhibited by block copolymers templates. The diblock copolymers were synthesized by ring opening metathesis polymerization of norbornene and norbornene trimethylsilane and the binary magnetic oxide was introduced through a nanoreaction scheme using wet chemical methods. Transmission electron micrographs of microtomed thin sections of these nanocomposites show that the metal oxide nanoclusters are ellipsoidal in shape and are uniformly distributed within the polymer matrix. A SQUID magnetometer was used to study the magnetic properties of the polymeric nanocomposites at applied fields up to 5 Tesla and at a temperature range between 300K and 5°K. Mössbauer spectroscopy was used to study the structure of the nanoconfined metal oxide, and confirmed the synthesis of  $\text{CoFe}_2\text{O}_4$  nanoclusters exhibiting an inverse spinel structure. This study provided a better understanding of the nucleation, growth and distribution of metal oxide nanoclusters within block copolymers and indicated ways to control the magnetic properties of polymeric based nanocomposite materials. The development of such binary metal oxide - block copolymer nanocomposites is targeting the functionalization of such nanostructures into magnetic device technologies.

## INTRODUCTION

Metal nanoclusters are subject of current interest because of their unusual optical, electronic and magnetic properties, which often differ from their bulk properties. Recently metal nanoclusters of Cu, Ag, Pd, Pt[1,2,3] and metal oxide nanoclusters of  $\text{Fe}_3\text{O}_4$  and CuO have been synthesized within microphase separated domains of diblock copolymers. The self-assembled nature of the microdomains allows very good control over the shape and size of the nanoclusters. The interface between the blocks of the diblock copolymers play an important role in the nucleation and growth of clusters, and induce a narrow size distribution. The polymer matrix also provides kinetic hindrance to aggregation of nanoclusters.

Cobalt ferrite,  $\text{CoFe}_2\text{O}_4$  is a well known hard magnetic material with very high cubic magnetocrystalline anisotropy, high coercivity and moderate saturation magnetization. In this paper we describe the synthesis and the magnetic properties of polymer based  $\text{CoFe}_2\text{O}_4$  nanocomposites. This is the first report on the room temperature synthesis of mixed metal oxide nanoclusters dispersed within a polymer matrix.

## EXPERIMENTAL

Polymer synthesis and mixed metal oxide formation: Diblock copolymers were synthesized by ring opening metathesis polymerization (ROMP) of norbornene (NOR) and norbornene trimethylsilane (NORCOOTMS). This reaction scheme is shown in Figure 1.

Figure 1. Synthesis of the  $[\text{NOR}]_{400}[\text{NORCOOH}]_{50}$  diblock copolymer

$[\text{NOR}]_{400}[\text{NORCOOH}]_{50}$  was dissolved in THF, and  $\text{FeCl}_3$  and  $\text{CoCl}_2$  were mixed with the polymer solution (polymer:  $\text{FeCl}_3$ : $\text{CoCl}_2$  = 1:25.0:12.5 mole). Due to the high affinity of these metals towards the COOH group,  $\text{FeCl}_3$  and  $\text{CoCl}_2$  were attached to the  $[\text{NORCOOH}]$  block. Films were formed by static casting over a period of 3 days. The films were then washed with NaOH and water.  $\text{FeCl}_3$  and  $\text{CoCl}_2$  reacted with NaOH and water inside the NORCOOH nanospheres. As a result,  $\text{CoFe}_2\text{O}_4$  nanocrystals were formed inside the NORCOOH block, as depicted schematically in Figure 2.

Magnetic Characterization: The experiments were carried out between 5 °K and 300 °K and in fields up to 50 kOe. The Mössbauer spectra were obtained using a conventional constant acceleration Ranger Electronics Corporation Mössbauer spectrometer, driven by a triangular waveform.

Figure 2. Formation of  $\text{CoFe}_2\text{O}_4$  nanoclusters within diblock copolymers.

## RESULTS AND DISCUSSION

Gel permeation Chromatography (GPC) confirmed that the distribution of the synthesized block copolymer was unimodal, and was relatively narrow as given by the Poly Dispersity Index (PDI) of 1.15. The templating procedure that we employed is markedly different from previous work, in that the metal salt is introduced while the polymer is in solution, before any microphase separation of the two blocks can occur. Earlier block copolymer nanoreactor synthesis schemes [1-4] have introduced the metal salt by diffusion of a metal salt solution into a spin-cast or static-cast microphase separated solid film. The advantages which our templating process presents, are rapid diffusion and attachment of the metal to the polymer since both are in the liquid state, and resultant self - assembled nanostructures at room temperature through wet chemical methods, thus making this an appropriate process to integrate in the fabrication of novel magnetic devices without additional thermal cycling steps.

Morphology: The morphology of the polymer- $\text{CoFe}_2\text{O}_4$  nanocomposite was investigated using a HITACHI H-600 transmission electron microscope operated at 100 keV. The TEM image shown in Figure 3, indicates that the  $\text{CoFe}_2\text{O}_4$  nanoclusters are almost spherical and have an average diameter of 15 nm.

Figure 3. TEM of  $\text{CoFe}_2\text{O}_4$  nanoclusters uniformly distributed within the polymer matrix

Mössbauer spectraThe room temperature and 4.2K Mössbauer spectra are shown in Figure 4. The room temperature spectra are complex. They exhibit a quadrupolar component at the center of the spectrum and a magnetically split component at the outer parts of the spectrum.

Figure 4. Mössbauer spectra of polymer- $\text{CoFe}_2\text{O}_4$  at (a) 300K, and (b) 4.2K.



