

Magnetic Properties and Morphology of Block Copolymer Templated Ferrimagnetic CoFe_2O_4 Nanoparticles

Sufi R. Ahmed, Satish B. Ogale, and Peter Kofinas

Abstract—We synthesized the block copolymer of poly(norbornene-dicarboxylic acid) and poly(norbornene) at room temperature, using ring opening metathesis polymerization. We then templated the CoFe_2O_4 nanoparticles within the polymer matrix, utilizing the self-assembled nature of the block copolymer. We used transmission electron microscopy, superconducting quantum interference device magnetometry, and X-ray powder diffraction to investigate the morphology and magnetic properties of the nanocomposites. The nanocomposite films are ferrimagnetic at room temperature. The CoFe_2O_4 nanoparticles are spherical and have an average radius of 8.7 ± 0.4 nm. The nanoparticles are uniformly distributed within the polymer matrix with a nanoparticle density of 110^9 particles/cm².

Index Terms—Block copolymer, CoFe_2O_4 , ferromagnetic, nanoparticle.

I. INTRODUCTION

THE synthesis of uniformly distributed single-domain magnetic nanoparticles are of current interest because of their potential applications in ultrahigh-density magnetic memory devices. Cobalt ferrite, CoFe_2O_4 is a well-known hard magnetic material with very high cubic magnetocrystalline anisotropy, high coercivity, and moderate saturation magnetization. These properties make it a promising material for high-density magnetic recording devices. For such an application, it is necessary to produce stable single-domain particles with uniform distribution. Several methods to produce submicrometer CoFe_2O_4 particles have been reported in literature [1]–[6]. All these techniques require high-temperature treatments to produce CoFe_2O_4 particles, and the resulting nanoparticles are often agglomerated. We have previously reported the room-temperature synthesis and magnetic properties of a superparamagnetic CoFe_2O_4 -polymer nanocomposite [7], [8]. In this paper, we report on the magnetic properties of a ferrimagnetic CoFe_2O_4 -polymer nanocomposite synthesized using wet chemical methods. Block copolymer used in this study had a different block ratio (NOR : NORCOOH = 400 : 150) than the polymer used in our previous work, which had a block

ratio of (NOR : NORCOOH = 400 : 50). The polymer used in this study also had a narrower polydispersity index (PDI) than the polymer used earlier. The use of diblock copolymers with a narrow PDI as self-assembled nanotemplates enable the synthesis of CoFe_2O_4 nanoparticles at room temperature. The self-assembled nanoscale morphology of the diblock copolymer also results in the formation of uniformly distributed spherical nanoparticles within the polymer matrix. Due to the uniformly distributed high nanoparticle density and their ferrimagnetic nature, this nanocomposite has the potential for high-density memory and magnetic recording applications.

II. EXPERIMENTAL SETUP

Ring opening metathesis polymerization (ROMP) of norbornene (NOR) and 2-norbornene-5,6-dicarboxylic acid bis(trimethylsilyl) ester (NORCOOTMS) was used to synthesize diblock copolymers of $[\text{NORCOOTMS}]_{150}/[\text{NOR}]_{400}$ [9]. The $[\text{NORCOOTMS}]_{150}/[\text{NOR}]_{400}$ diblock copolymer was converted to $[\text{NORCOOH}]_{150}/[\text{NOR}]_{400}$ by precipitating the polymer solution in a mixture of methanol, acetic acid, and water, and was dried under vacuum for 24 h. The polymer was then dissolved in THF, and FeCl_3 and CoCl_2 were mixed with the polymer solution (polymer: FeCl_3 : CoCl_2 = 1 : 75.0 : 37.5 mole). Due to the high affinity of these metals toward the COOH group, FeCl_3 and CoCl_2 were directly attached to the $[\text{NORCOOH}]$ block [8]. Solid films were formed by static casting. The films were then washed with NaOH and water. FeCl_3 and CoCl_2 reacted with NaOH and water within the NORCOOH domains and formed CoFe_2O_4 nanocrystals [8]. The films contained 11.47% CoFe_2O_4 by weight.

The molecular weight of the polymer was determined by gel permeation chromatography (GPC). GPC was performed with a Wyatt Technology Mini-DAWN light scattering detector, Waters 2410 RI detector, Waters 515 pump, and a Rheodyne 7125i injector with a 200 μL loop. THF was the mobile phase at a flow rate of 1.0 mL/min, through Waters 10^4 , 10^5 , and 10^6 Å columns. The structure of the CoFe_2O_4 nanoparticles was characterized using a Bruker D8 Advance Powder X-ray diffractometer as described in our previous work [7]. The morphology of the polymer samples were studied using a Hitachi H-600 transmission electron microscope operated at 100 keV. The transmission electron micrograph (TEM) images were analyzed using the NIH Image software. The magnetic properties of the block copolymer samples were measured

Manuscript received October 11, 2002; revised February 27, 2003. This material was based upon work supported by the National Science Foundation under Grant CTS-9875001 and Grant MRSEC DMR-008008.

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Digital Object Identifier 10.1109/TMAG.2003.817074

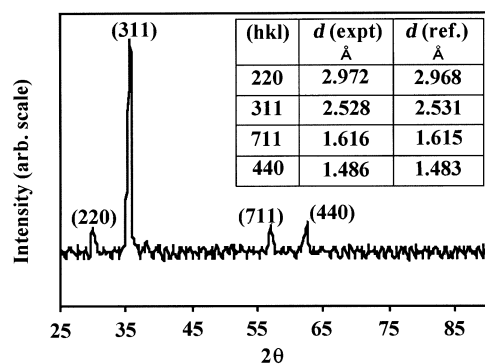


Fig. 1. Wide-angle X-ray diffraction pattern of the block copolymer- CoFe_2O_4 .

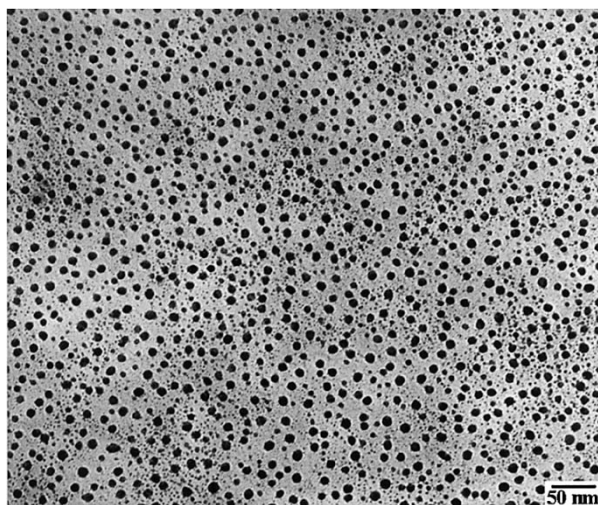


Fig. 2. TEM of the polymer- CoFe_2O_4 nanocomposite.

using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

The weight average molecular weight (M_w) of the $[\text{NORCOOH}]_{150}/[\text{NOR}]_{400}$ diblock copolymer was determined to be 73 030 g/mole with a polydispersity index (PDI) of 1.05. The self-assembled nanoscale morphology of the diblock copolymer was then used to template CoFe_2O_4 nanoparticles. The wide-angle X-ray diffraction pattern of the nanocomposite is shown in Fig. 1. The close match of our experimental values with literature values indicated successful room-temperature synthesis of CoFe_2O_4 .

In our previous work, we investigated diblock copolymer of $[\text{NOR}]_{400}/[\text{NORCOOH}]_{50}$, which had a PDI of 1.41. Nanoparticles synthesized using this polymer were oval shaped with an average radius of 4.8 ± 1.4 nm and were randomly distributed. In contrast, the TEM of the $[\text{NORCOOH}]_{150}/[\text{NOR}]_{400}$ polymer nanocomposite (Fig. 2) showed that CoFe_2O_4 nanoparticles formed within the diblock copolymer are spherical and have an average radius of 8.7 ± 0.4 nm. The CoFe_2O_4 nanoparticles are uniformly distributed within the polymer matrix with an average nanoparticle density of 110^9 particles/cm². Although the nanoparticles are not monodisperse, the TEM picture

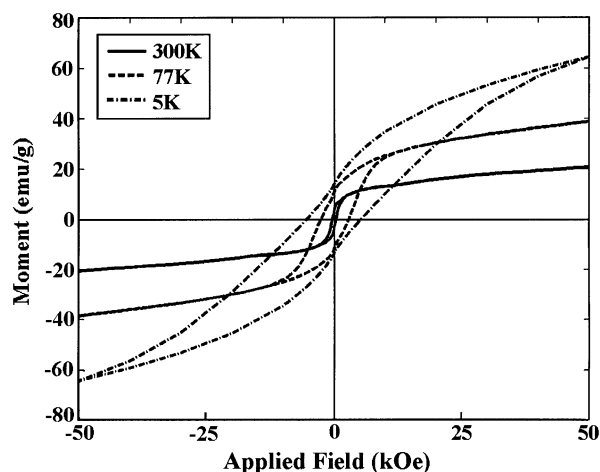


Fig. 3. Magnetization versus applied magnetic field for the block copolymer- CoFe_2O_4 nanocomposite at 300, 77, and 5 K.

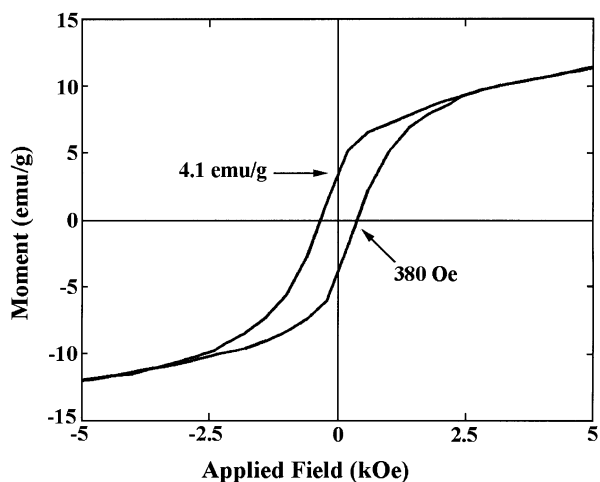


Fig. 4. Magnification of Fig. 3 showing the hysteresis loop of the block copolymer- CoFe_2O_4 nanocomposite at 300 K.

indicates a narrow size distribution ($\approx 4.6\%$) and uniform ordering of the nanoparticles. This is a result of the narrow PDI (1.05) of the diblock copolymer used in this study. The increase in the size of the nanoparticles is due to the increase in the NORCOOH block length.

The magnetic properties of the CoFe_2O_4 -polymer nanocomposite are shown in Figs. 3 and 4. The measured magnetization was divided by the total mass of the film used and the weight fraction of CoFe_2O_4 in the polymer (11.47%). At room temperature, the nanocomposite films were ferrimagnetic and the nanoparticles had a remanence (σ_r) = 4.1 emu/g of CoFe_2O_4 and a coercivity (H_c) of 380 Oe. The values of σ_r and H_c are smaller than that of bulk CoFe_2O_4 , which has $\sigma_r = 67.07$ emu/g and $H_c = 5.8$ kOe. We previously reported that the polymer nanocomposite containing CoFe_2O_4 nanoparticles with an average radius of 4.8 ± 1.4 nm exhibits no hysteresis, indicating that the nanoparticles are superparamagnetic. Both the remanence and coercivity were zero at 300 K. Therefore, the critical particle radius for superparamagnetic to ferrimagnetic transition lies in between 4.8 ± 1.4 nm and 8.7 ± 0.4 nm. The superparamagnetic nanoparticles had a

blocking temperature (T_B) of 80 K below which they became ferrimagnetic. Below the transition temperature, the 4.8 ± 1.4 nm nanoparticles also showed reductions in remanence and coercivity. Earlier studies on ferrite nanoparticles of γ -Fe₂O₃ [10], [11], NiFe₂O₄ [12], and CoFe₂O₄ [3]–[5] have also reported such reductions in remanence and coercivity, due to the finite size effects in nanometer-size particles, which results in noncollinear spin alignments [11]–[14]. The remanence and coercivity of the nanoparticles increased with decreasing temperature. At 77 K, the nanoparticles had a remanence (σ_r) = 12.5 emu/g and coercivity (H_c) = 5.3 kOe. At 5 K, the nanoparticles had $\sigma_r = 15.25$ emu/g and $H_c = 5.3$ kOe. The most remarkable feature of the magnetization curves is that the magnetization is far from saturation up to the highest field applied of 50 kOe. This is an indication of strong surface-spin pinning at the particle/support interface, resulting in a noncollinear spin structure within the CoFe₂O₄ particles [11]–[14].

IV. CONCLUSION

The diblock copolymer of [NORCOOH]₁₅₀/[NOR]₄₀₀ has been used to template CoFe₂O₄ nanoparticles at room temperature. The self-assembled nanoscale morphology of the diblock copolymer resulted in uniformly distributed spherical CoFe₂O₄ nanoparticles with an average radius of 8.7 ± 0.4 nm. The nanoparticle density within the polymer matrix was 110^9 particles/cm². CoFe₂O₄ nanoparticles were ferrimagnetic at room temperature with a remanence (σ_r) = 4.1 emu/g and coercivity (H_c) = 380 Oe. The remanence and coercivity increased with decreasing temperature. At 5 K, the coercivity of the nanocomposite was 5.3 kOe, which is equal to the coercivity of bulk CoFe₂O₄. At this temperature, the nanoparticles had a remanence (σ_r) = 15.25 emu/g of CoFe₂O₄. The magnetization of the nanoparticles remained unsaturated up to the highest field applied of 50 kOe. This is an indication of strong surface-spin pinning at the particle/support interface, resulting in a noncollinear spin structure within the CoFe₂O₄

particles. Due to the ferrimagnetic nature of the nanocomposite and uniformly distributed high nanoparticle density, this nanocomposite has potential uses in ultrahigh-density memory storage devices and magnetic recording applications.

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