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Magnetic properties and morphology of block copolymer-cobalt oxide nanocomposites

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Abstract

The morphology and magnetic properties of diblock copolymer templated ferrimagnetic cobalt oxide nanoparticles are reported. Ring opening metathesis polymerization (ROMP) was used to synthesize a novel cobalt diblock copolymer, where cobalt is directly attached to the polymer chain. Gel permeation chromatography (GPC) was performed to determine molecular weight distribution. Transmission electron microscope (TEM), UV–Vis, FTIR, and vibrating sample magnetometer (VSM) were used to characterize the block copolymer nanocomposite. The nanocomposite films were weakly ferrimagnetic at room temperature. The cobalt oxide nanoparticles were uniformly dispersed within the polymer matrix with an average radius of 4.9 ± 0.9 nm.

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1. Introduction

Materials based on cobalt oxides have attracted a great interest in view of their technological and fundamental scientific importance [1–3]. Kobayashi et al. [1] have reported that in the presence of CO and H_2 , thin films of Co_3O_4 show reversible

changes in the Vis-near IR absorption band. This phenomenon can be applied in the fabrication of solid-state gas sensors. Thin films of Co_3O_4 have been reported to change color from brown to light yellow when Li^+ ions are inserted [2]. The reversible changes of optical properties of Co_3O_4 under an external stimulus can be used to fabricate electrochromic devices (ECD) [3]. Such a broad perspective of utilization has increased the importance of synthesizing cobalt oxide nanocomposites.

In this paper, we report the morphology and magnetic properties of polymer-cobalt oxide

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nanocomposites synthesized by ring opening metathesis polymerization (ROMP) of norbornene (NOR) and 5-norbornene-2,3-di-tert-aminocobalt (Co[bTAN]). Unlike the previously reported methods of formation metal oxide nanoparticle using block copolymer templates [4–7], where the metal salt is introduced after the polymer synthesis, here metal was associated with the polymer chain during polymer synthesis. In this method, no further doping is required after polymer synthesis, which removes the uncertainty involved during the ion exchange between metal salts and functional groups in the polymer backbone. This is the first report of room temperature synthesis of cobalt oxide nanoparticles, uniformly dispersed within a polymer matrix.

2. Experimental

Pyridine (99.8% anhydrous), dimethyl fumarate, toluene sulfonyl chloride, lithium aluminum hydride (LiAlH_4), benzophenone, tert-butylamine and cobalt chloride were purchased from Aldrich. NOR, sodium sulfate (Na_2SO_4) and calcium hydride (CaH) was purchased from Fisher Scientific. Butyllithium (2.5 M in hexane) was purchased from Acros Organics. Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine] ruthenium (IV) dichloride (Grubbs's second generation catalyst) was purchased from Strem Chemicals. The Grubbs's catalyst, LiAlH_4 and CoCl_2 were stored inside a nitrogen filled MBraun100 glovebox. Anhydrous tetrahydrofuran (THF), diethyl ether, benzene, ethyl vinyl ether, dimethylformamide, pentane and methanol were purchased from Aldrich. These solvents were used without any further purification for the reactions that were performed outside the glovebox. For the reaction performed inside the glovebox, THF, benzene and diethyl ether were distilled over sodium benzophenone ketyl under argon and stored in the glovebox. Pentane was washed with a mixture of 5% nitric acid and sulfuric acid, stored over calcium chloride and then distilled over sodium benzophenone ketyl under argon.

ROMP of NOR and Co(bTAN) was used to synthesize diblock copolymers of $[\text{Co}(\text{bTAN})]_{20}/[\text{NOR}]_{200}$. Co(bTAN) was prepared according to literature procedures [8]. A 0.33 molar solution of Co(bTAN) was prepared by dissolving 0.17 g of Co(bTAN) in 1 mL benzene and the polymerization was initiated by adding 1/20 M equivalent of the Grubbs's catalyst solution. Norbornene (0.1 g, 200 M equivalent) was dissolved in 100 μL benzene and added to the living polymerization after 48 h. The reaction mixture was stirred for 24 h. The polymerization was terminated by adding 10 μL ethyl vinyl ether to the reaction mixture. The polymer was recovered by precipitation from pentane and was dried under vacuum for 24 h. The polymer was then dissolved in benzene, and solid films were formed by static casting. The films were then treated with H_2O_2 for 24 h, in order to oxidize the block copolymer nanocomposite and form cobalt oxide nanoparticles inside the self-assembled nanodomains of the block copolymer. The nanocomposite films were flexible and light blue in color.

Gel Permeation Chromatography (GPC) was performed with a Wyatt Technology Mini-DAWN light scattering detector, Waters 2410 RI detector, Waters 515 pump and a Rheodyne 7725i 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

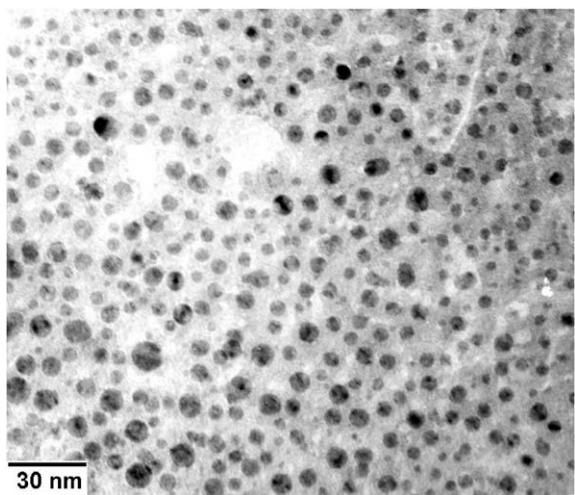


Fig. 1. Transmission electron micrograph of the polymer-cobalt oxide nanocomposite.

and 10^6 \AA columns. The morphology of the polymer nanocomposites was studied using a HITACHI H-600 transmission electron microscope (TEM) operated at 100 keV (Fig. 1). A Beckman DU 7400 UV–Vis spectrophotometer was used to obtain the UV–Vis spectra of the polymer–cobalt oxide nanocomposite films. FTIR spectra of the polymer–cobalt oxide nanocomposite films was obtained using a Nicolet Series II Magna-IR 550 FTIR spectrometer. The magnetic properties of the block copolymer samples were measured using a Walker Scientific VH-4H vibrating sample magnetometer (VSM).

3. Results and discussion

The molecular weight of the polymer was determined with GPC. GPC results indicated that the block copolymer has a molecular weight of 21,270 with a polydispersity index of 1.53. The TEM image shows that the nanoparticles are uniformly dispersed within the polymer matrix. The molecular weight distribution of the block copolymer matrix, and the size distribution of the templated nanoparticles are shown in Fig. 2. The average nanoparticle radius was found to be $4.9 \pm 0.9 \text{ nm}$, and the average spacing between the nanoparticles was $8.3 \pm 1.8 \text{ nm}$. The volume fraction of the nanoparticles was $\sim 8.7\%$.

The polymer–cobalt oxide nanocomposite was very susceptible to electron beam damage and degraded during electron diffraction measurements in the microscope. As a result, the crystal structure of the samples could not be analyzed with electron diffraction. X-ray diffraction also could not be used to characterize the polymer–cobalt oxide nanocomposite because, due to the large weight fraction of the amorphous polymer matrix ($\sim 90\%$), the amorphous contribution dominated the scattering spectrum, and it was not possible to clearly discern the metal oxide contribution in the overall scattering of the nanocomposite. We therefore used FTIR and UV–Vis spectrophotometry to characterize the polymer–cobalt oxide nanocomposite. The UV–Vis spectra indicates that the polymer nanocomposites have an absorption edge at 300 nm and, are

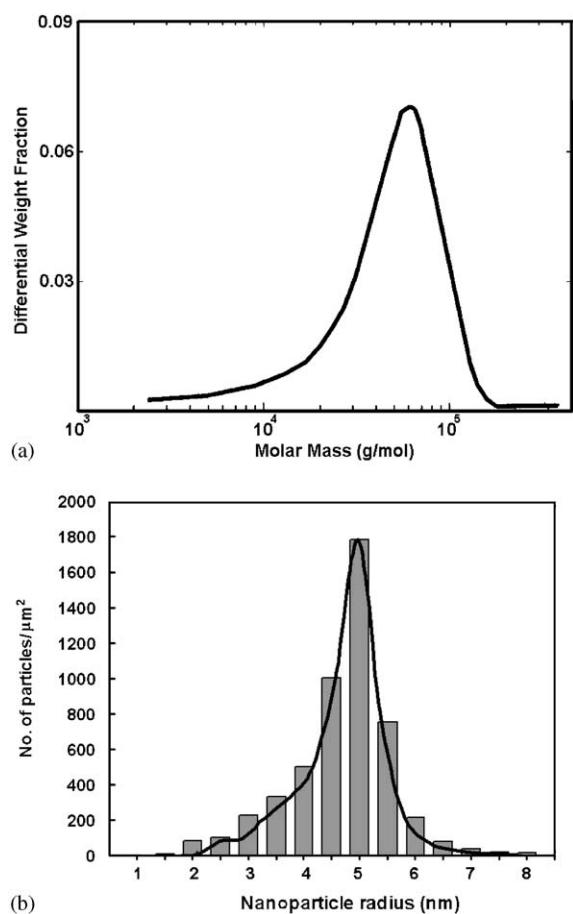


Fig. 2. (a) Molecular weight distribution of block copolymer, (b) particle-size distribution of Co_3O_4 nanoparticles.

transparent in the visible range. Beyond 300 nm, three major peaks were observed in the UV–Vis spectra (Fig. 3). The peak at 487 nm (typical for Co^{II} in octahedral coordination), and a broad absorption doublet at 583 nm and 602 nm (typical for Co^{III} in tetrahedral coordination) indicate the formation of Co_3O_4 [9]. FTIR spectra of the polymer film showed two peaks at 665 and 703 cm^{-1} , which are attributed to the presence of cobalt oxide in the polymer nanocomposite (Fig. 4). These two peaks closely match the reported values of the optical vibration modes of Co_3O_4 [10]. However, it is very difficult to differentiate between the UV–Vis and FTIR spectra of pure Co_3O_4 and that of Co_3O_4 with CoO impurities.

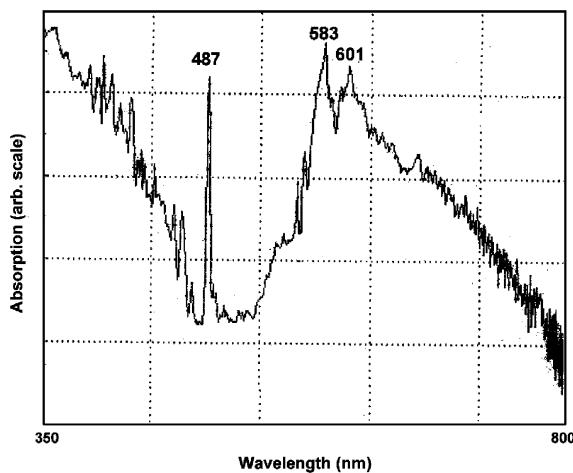


Fig. 3. UV–Vis spectra of polymer-cobalt oxide nanocomposite films.

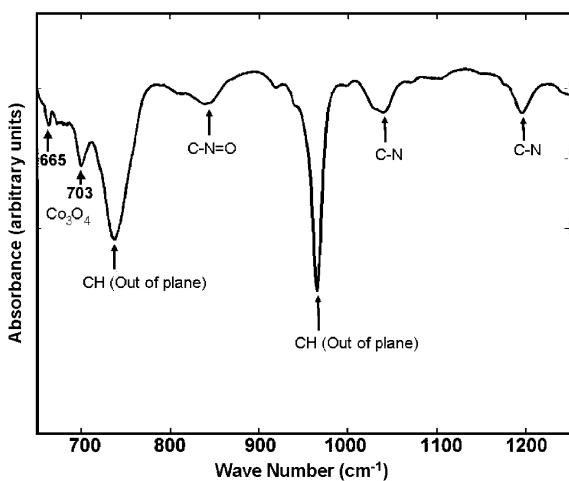


Fig. 4. FTIR spectra of polymer-cobalt oxide nanocomposite films.

Thus the presence of some CoO impurities in the Co_3O_4 nanoparticles cannot be ruled out.

The magnetic properties of the polymer-cobalt oxide nanocomposite is shown in Fig. 5. The measured magnetization was divided by the total mass of the film used. The nanocomposite films were weakly ferrimagnetic at room temperature. At room temperature, the coercivity, H_c , is 200 Oe and the remanence, σ_r , is 0.04 emu/g of nanocomposite. The magnetization, σ , at an applied field of

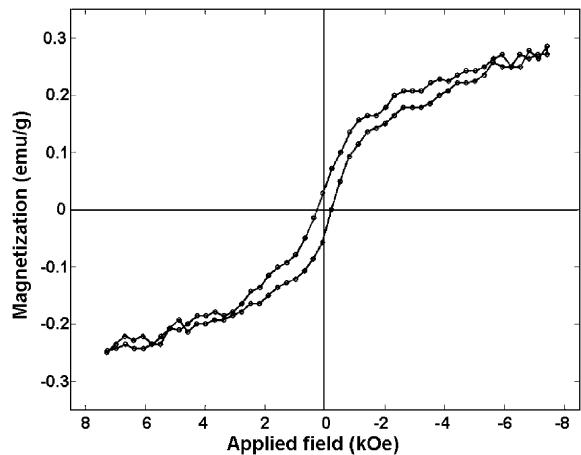


Fig. 5. Magnetic properties of polymer-cobalt oxide nanocomposite films.

8 kOe is 0.28 emu/g of the nanocomposite. $\sigma = 0.28$ emu/g of the nanocomposite corresponds to 3.22 emu/g of Co_3O_4 , since the nanocomposite contains 8.7% Co_3O_4 by weight.

4. Conclusion

Cobalt oxide nanoparticles have been synthesized using an organometallic diblock copolymer of $[\text{Co}(\text{bTAN})]_{20}/[\text{NOR}]_{200}$. The self-assembled nanoscale morphology of the diblock copolymer resulted in uniformly dispersed cobalt oxide nanoparticles within the polymer matrix with an average radius of 4.9 ± 0.9 nm. The polymer-cobalt oxide nanocomposite was weakly ferrimagnetic at room temperature. Both the H_c (200 Oe) and σ_r (0.04 emu/g) were significantly smaller than the values for the bulk Co_3O_4 . These reductions are mainly due to the finite size-effect of the nanoparticles.

Earlier studies [10,11] suggested that a high-temperature ($>325^\circ\text{C}$) processing is necessary to synthesize Co_3O_4 nanoparticles. We succeeded in synthesizing such nanoparticles at room temperature. This indicates the efficacy of organometallic block copolymers as nanoreactors, which can be used to template and synthesized nanoparticles at room temperature.

Acknowledgements

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