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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 $[Co(bTAN)]_{20}/[NOR]_{200}$. 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

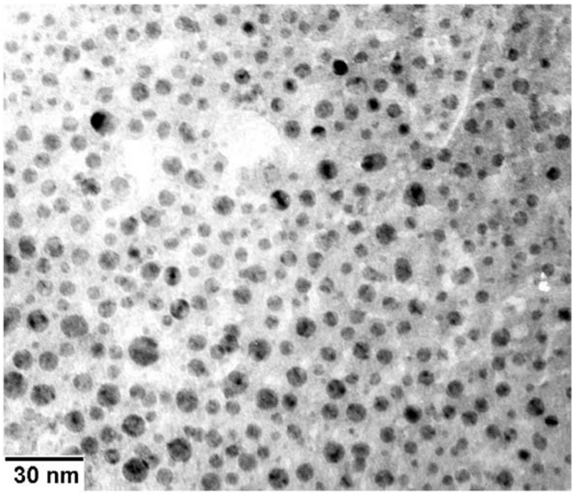

Fig. 1. Transmission electron micrograph of the polymer-cobalt oxide nanocomposite.

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