

TEM characterization of diblock copolymer templated iron oxide nanoparticles: Bulk solution and thin film surface doping approach

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Abstract

The morphology of a novel diblock copolymer, poly(norbornene methanol)-*b*-poly(norbornene dicarboxylic acid), was investigated before and after metal oxide doping by transmission electron microscopy (TEM) using a novel iodine vapor staining method to image the undoped polymer. A lamellar morphology was observed by TEM after staining the undoped diblock copolymer with iodine vapor. Thin film surface doping resulted in a confinement of the iron oxide nanoparticles within the lamellar domains. Spherical nanoparticle aggregates were observed through a bulk solution doping method. It was observed that the particles were templated by the underlying lamellar structure of the copolymer when the thin film surface doping method was used.

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1. Introduction

Diblock copolymers have been used as templates in the synthesis of inorganic nanoparticles for potential magnetic storage, electro-optical, catalytical and biological applications [1–6]. The block copolymers template the arrangement of metal oxide nanoparticles within the polymer matrix. There are two general methods for the formation of such block copolymer metal oxide nanocomposites: in the ‘bulk solution doping’ method, a mixture of metal salts are associated to block copolymer chains in solution. Upon solvent evaporation, the resulting nanoparticles are dispersed within the block copolymer matrix. In the ‘thin film surface doping’ method, nanoparticles are templated within an pre-existing microphase separated block copolymer thin film by submerging the film in a metal salt aqueous solution. Nanoparticle aggregation is prevented by reducing their mobility within solid copolymer films. The coordination of the particles to the functional sites, and the sizes of the resulting nanoparticles and aggregates are

controlled by soaking the polymer film in metal salt solution for varying time periods.

Solution and thin film metal oxide doping methods have been applied in the past to various norbornene based block copolymer systems [2,7–10]. However, the metal oxide ordering obtained using different doping methods have not been correlated to the same undoped norbornene based diblock copolymer system, because of difficulties in obtaining the required contrast for transmission electron microscopy (TEM). The comparison of the undoped copolymer structures obtained from the two metal doping methods is important for the elucidation of the templating role of the block copolymer matrix. Particle–particle interactions may influence the dispersion of the metal oxide nanoparticles, and these interactions vary in bulk solution doping versus the thin film surface doping methods. In the bulk solution doping method for iron oxide, the microphase separation of the copolymer occurs concurrently with the presence of chelated iron ions and with the nucleation and growth of iron oxide nanoparticles. Some portion of the iron ions can be oxidized during the stirring of polymer–Fe salt solutions over time. The influence of the resultant nanoparticles (6–10 wt% Fe) on the block copolymer microphase separation has been reported in a previous study where the change in the morphology obtained prior and after metal incorporation was observed by small-angle neutron scattering [11]. Other studies have examined the effect of particle concentration on particle dispersion and polymer

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morphology. It has been reported that a diblock copolymer containing 3 vol% nanoparticles facilitated the particle growth and influenced the final morphology of the polymer nanoparticle composite [12]. Particle mobility and interactions during solution phase doping are dominant factors influencing the block copolymer microphase separation and the final morphology of the solid cast copolymers.

The morphology of norbornene based diblock copolymers containing coordinated metal ions to functional groups present on one of the polymer blocks have been imaged using TEM in two previous studies: a norbornene dicarboxylic acid-*b*-acetylene diblock copolymer, stained with diethyl zinc vapor [13] and norbornene methanol-*b*-carbazole functionalized norbornene stained with dimethyl cadmium ($\text{Cd}(\text{CH}_3)_2$) vapor [14]. After vapor staining, these block copolymers were microtomed into thin sections for TEM characterization.

This paper reports on the synthesis of a novel diblock copolymer, poly(norbornene methanol)-*b*-poly(norbornene dicarboxylic acid). The diblock copolymer displayed a lamellar morphology and the ordering of iron oxide nanoparticles within the copolymer template was examined with TEM when the bulk solution and thin film surface doping methods were employed. The undoped polymer morphology was visualized using an iodine vapor staining method. This novel staining method allowed the comparison of the undoped polymer to the bulk solution doped and thin film surface doped morphologies for the same norbornene-based block copolymer system. It was shown that the iron oxide nanoparticles were confined and ordered within the lamellar domains of the block copolymer when the thin film doping was applied, while TEM images of solution doped samples showed aggregation of spherical iron oxide nanoparticles. This result reveals that diblock copolymers can be good templates for nanoparticle arrays when thin films are submerged in dilute iron salt solutions. Our experiments address the effect of polymer template and of the doping method on producing ordered metal oxide nanoparticles in thin and bulk films.

2. Materials

5-Norbornene-2-methanol (mixture of *endo/exo*) and 2-norbornene-5,6,*endo,exo*-dicarboxylic acid, ethyl vinyl ether, dichloromethane (CH_2Cl_2), deuterated fumaric-2,3- D_2 acid (98 at.% D), bis(tricyclohexyl phosphine) benzylidene ruthenium(IV) dichloride (first generation Grubbs' catalyst) and aqueous iodine solution (0.1 M) (I_2) were purchased from Aldrich. CH_2Cl_2 was distilled over calcium hydride under argon. All solvents, monomers and catalyst required for polymer synthesis were stored inside an MBraun LabMaster100 glovebox.

3. Experimental

Methanol and carboxylic acid groups were protected by capping with trimethylsilane. 5-Trimethylsilyloxymethyl norbornene was synthesized as follows: 5-norbornene-2-methanol (8.25 g, 0.0664 mol) and pyridine (5.25 g, 0.0664 mol) were

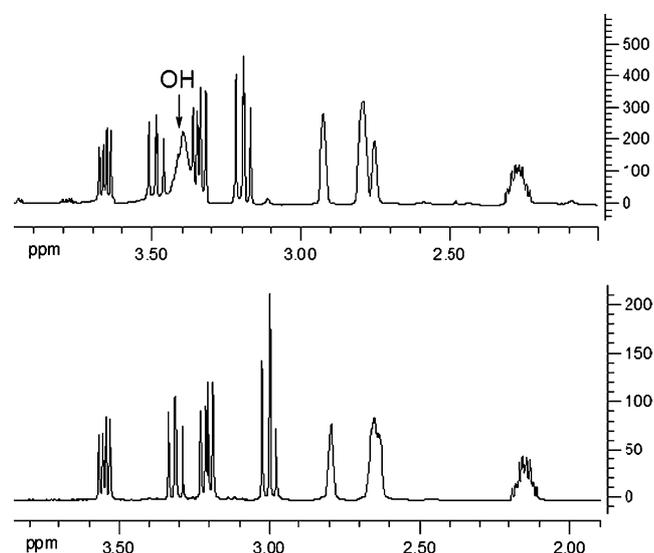


Fig. 1. ^1H NMR spectra of NORMeOH and NORMeOH-TMS.

stirred in 150 ml ether under argon. Trimethylsilylchloride (7.21 g, 0.064 mol) was added slowly to the stirring solution. The solution was stirred under argon for 24 h and filtered through celite. A second filtration was done through celite by washing with pentane. The liquid product was obtained after stripping the solvent and vacuum distilling it under 11.5 psi at 180°C . The distilled product was a clear, slightly viscous liquid and was kept in an argon filled glove box. As seen in Fig. 1, two doublets of methylene protons, which were identified at 3.24 and 3.38 ppm disappeared after the methanol groups were capped with trimethylsilane.

2-Norbornene-5,6 dicarboxylic acid bis(trimethylsilyl) ester was synthesized as reported in literature [13]. The norbornene methanol (NORMEOH)–norbornene dicarboxylic acid (NORCOOH) diblock was synthesized using the first generation Grubbs' catalyst in CH_2Cl_2 by initiating the polymerization of the norbornene methanol trimethylsilane monomer. Polymerization of 5-trimethylsilyloxymethyl norbornene took 24 h and 2-norbornene-5,6,dicarboxylic acid bis(trimethylsilyl) ester was added and stirred for another 24 h. The reaction was terminated with ethyl vinyl ether and the diluted polymer solution was stirred with alumina to remove the catalyst. The methanol and carboxylic acid groups were hydrolyzed by adding 0.5 ml acetic acid to remove the trimethylsilyl protecting groups through rigorous stirring in air, and then films of diblock copolymers were slowly static cast for 5 days under a CH_2Cl_2 saturated atmosphere in a dessicator.

Morphological characterization of diblock copolymers by TEM has been reported for various systems where one of the blocks was stained with ruthenium or osmium tetroxide [15–17]. These staining agents are used to stain unsaturated carbon–carbon bonds and have been applied to polymers such as polybutadiene. Staining with osmium tetroxide was tested but it did not work on the NORMEOH/NORCOOH block copolymer. We then attempted iodine staining, which was successful. The physical absorption of I_2 can selectively stain one of the blocks of the NORMEOH/NORCOOH system.

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