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

Pinar Akcora [a], Robert M. Briber [b], Peter Kofinas [a],*

[a] *Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742-2111, USA*
[b] *Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA*

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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.

Keywords: Diblock copolymer; Iodine staining; Iron oxide nanoparticles

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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* Corresponding author. Tel.: +1 301 405 7335; fax: +1 301 405 0523.
E-mail address: kofinas@umd.edu (P. Kofinas).
URL: www.glue.umd.edu/kofinas.

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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 ($Cd(CH_3)_2$) 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) benzylidine 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

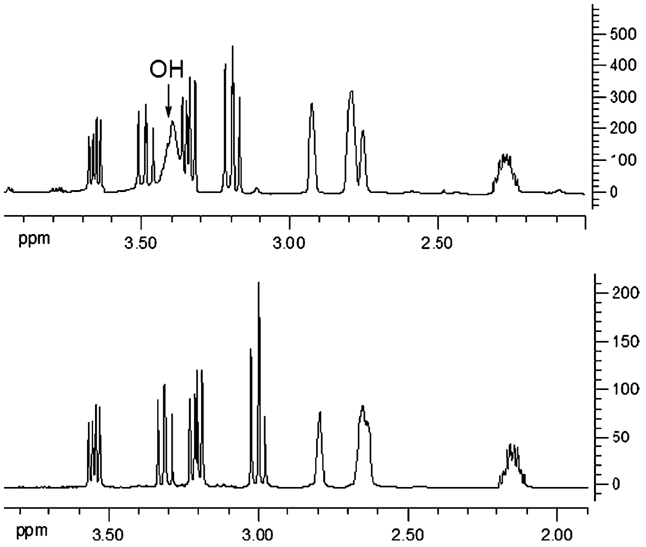

Fig. 1. ^1H NMR spectra of NORMeOH and NORMeOH–TMS.

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

It has been shown in an earlier study that iodine staining works also for polyvinylpyridine domains by selective absorption [18]. We have tried staining the blends of homopolymers to verify the selective staining of iodine in either NORMEOH or NORCOOH domains. The analysis of the images was unclear to deduce any result.

In this study, the norbornene methanol/norbornene dicarboxylic acid copolymer morphology was examined after staining with iodine vapor. Samples for TEM analysis were prepared by ultramicrotoming the solution cast undoped and metal oxide solution doped films. Films were embedded in epoxy resin and thin sections (approximately 40 nm) were microtomed using a Leica EM UC6 microtome at room temperature with a diamond knife. The microtomed sections were placed on microscope slides and allowed to stain in a dessicator containing aqueous iodine solution. The samples were stained by exposure to iodine vapor for 6 h. Staining was achieved by the differential physical sorption of iodine into one of the blocks. The iodine affinity for either methanol or carboxylic acid groups is unexplored. The morphologies of the undoped and doped copolymers were examined using TEM (Hitachi H-600, operated at 100 keV).

4. Results and discussion

The volume fraction of the norbornene methanol group was found to be 0.5 from UV–vis measurements. The block copolymer composition was determined using Perkin–Elmer Lambda 25 UV–vis spectroscopy. A calibration curve was obtained by measuring the absorbance as a function of the volume fraction of NORMEOH homopolymer in a series of NORMEOH and NORCOOH homopolymer blends. A sweep run was performed between wavelengths 210–310 Å. As the norbornene methanol fraction increased in the mixture, the intensity of the peak between 225 and 250 Å increased. The pure norbornene methanol homopolymer showed a peak maximum at 239 Å. The absorbance values at 239 Å were monitored for samples with varying norbornene methanol amount. A calibration curve was formed by plotting the absorbance values at 239 Å as a function of norbornene methanol volume fraction (Fig. 2). The polydispersity indeces (PDI) of the first block (NORMEOH) and the diblock copolymer were determined as 1.07 and 1.12, respectively, by gel permeation chromatography (GPC) using a Waters 2410 RI detector, a Waters 515 pump and a Rheodyne 7125i injector with a 200 μl loop. The mobile phase was THF with a 1 ml/min flow rate. Waters styragel mixed bed columns were used for these measurements.

Two metal loading methods (thin film surface versus bulk solution doping) were employed to examine the effect of the metal doping process on the resultant nanoparticle dispersion. In thin film surface doping, iron oxide particles were associated to the carboxylic groups of a thin film (approximately 40 nm thick) that was prepared by microtoming. The microtomed block copolymer sections were soaked in 0.007 M NaOH solution for 16 h, rinsed with water and then immersed in 5 mM aqueous $FeCl_3$ solution for 5 min [8]. In thin film doping, the density of the particles can be increased by immersing the film in iron salt solution at longer times. The effective doping of iron oxide particles within the polymer template was observed for short doping times (5 min). In this method, Fe^{+3} ions exchange directly with the Na^{+1} ions associated to the COOH group leading to a faster iron ion uptake within the thin film. Soaking the copolymer in NaOH does not affect the methanol groups. The proton on the methanol group do not exchange with Na. The NORMEOH homopolymer was mixed with iron salt and then immersed in NaOH. It was observed that spherical nanoparticles were not created in the NORMEOH matrix. This result conjectures that iron oxide particles were preferentially coordinated with the COOH units and this coordination is enhanced with the Na^+ exhange.

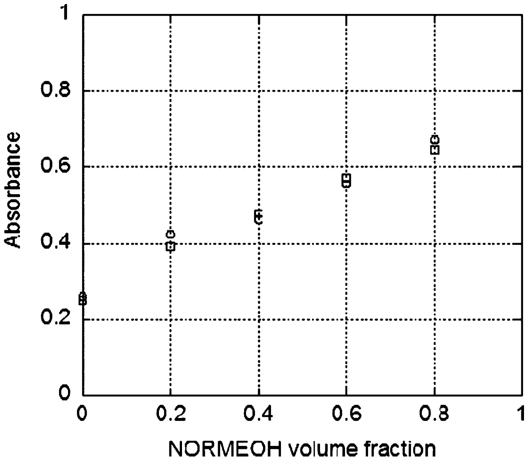

Fig. 2. Calibration curve showing the absorbance change as a function of volume fraction of NORMEOH homopolymer in NORMEOH/NORCOOH mixtures.

The bulk solution doping procedure was followed as stated in literature [2,10]. The block copolymer solution (5 wt%) was mixed with a $FeCl_3$ solution in tetrahydofuran under argon for 12 h. The polymer–metal solution was cast in solvent saturated atmosphere to form bulk films containing 8 wt% Fe_2O_3. These films were soaked in 2 M NaOH solutions to produce Fe_2O_3 particles for 24 h. A final water wash removes any unbound metal and sodium salts. It is known that the bulk solution doping method followed by oxidation produces well dispersed but disordered γ-Fe_2O_3 nanoparticles within block copolymer matrices [11]. Iron oxide doped block copolymer films were embedded in epoxy resin and then microtomed into 40 nm thick sections.

The TEM of the undoped norbornene methanol/norbornene dicarboxylic acid diblock copolymer, which was ultramicrotomed and then stained with iodine displayed a lamellar microstructure as shown in Fig. 3. Lines with varying thicknesses are attributed to the staining of one of the blocks and the formation of segregated silane groups, which were used for the protection of the carboxylic acid and methanol groups of the block copolymer. A domain spacing of 50 nm (measured between the two dark lines in Fig. 3) was obtained. The fast Fourier transform (FFT) image of the corresponding electron

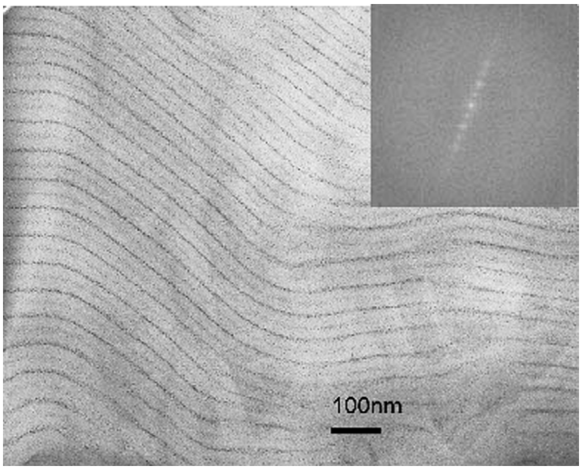

Fig. 3. Electron micrograph of NORMEOH/NORCOOH diblock copolymer, stained with iodine vapor. The insert picture shows the FFT of the image.

micrograph shows the diffraction pattern of the lamellar domains, as displayed in the insert of Fig. 3. This lamellar morphology was also observed at various microtome sections of the polymer.

The thin film surface doping method was employed to microtomed sections of the block copolymer. The ordering of the iron oxide nanoparticles followed the underlying lamellar morphology of the pure copolymer as indicated by the TEM micrograph of Fig. 4. The size of the particles was uniform with an average particle size of 6 nm in diameter. The γ-Fe_2O_3 nanoparticles were lined up along one of the individual lamellar domains and the distance calculated between two adjacent nanoparticle arrays was between 70 and 90 nm. The average particle size was found as 8 nm, however, as seen in Fig. 5, the nanoparticles agglomerated and formed interconnected aggregates of iron oxide nanoparticles, which were not templated by the underlying block copolymer structure.

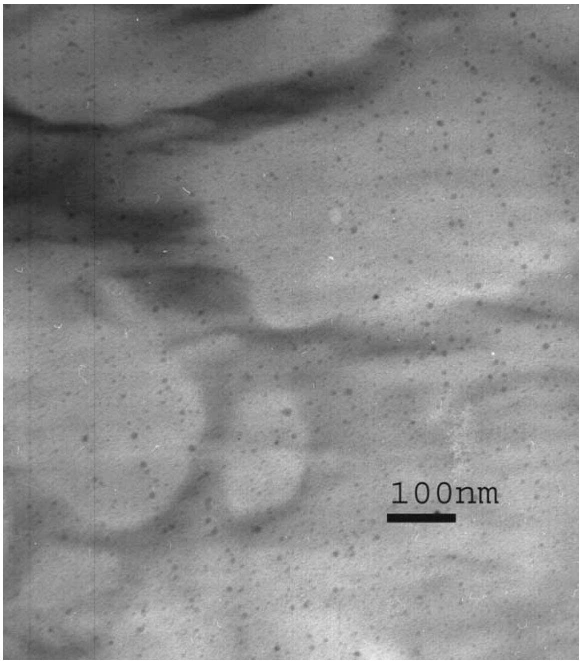

Fig. 4. Electron micrograph of the iron oxide doped NORMEOH/NORCOOH diblock copolymer. The sample was prepared by submerging a thin film in $FeCl_3$ solution (thin film surface doping method).

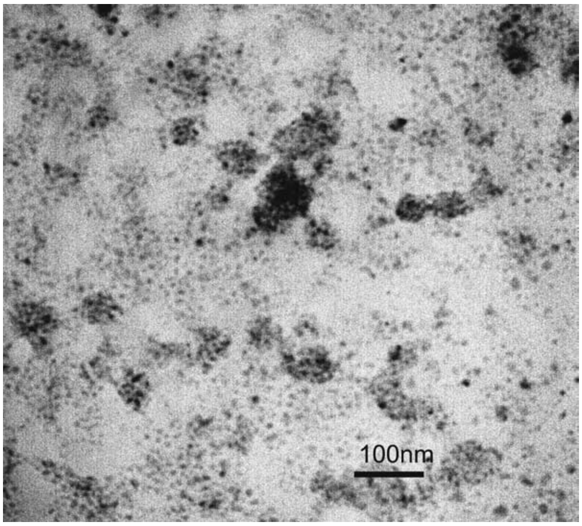

Fig. 5. Electron micrograph of the iron oxide doped NORMEOH/NORCOOH copolymer prepared by bulk solution doping.

There may be several fundamental problems that affect the polymer particle interactions in solution, resulting in disordered nanoparticle aggregates. These problems may arise from competing interactions between solvent, polymer chains and metal particles [19]. The conformation of the polymer chains adhered to the nanoparticles also influences the ordered dispersion of the particles. For example, Hashimoto et al. showed that depending on the molecular weight of a P2VP-*b*-PI copolymer, Pd nanoparticles can be aligned in the middle of P2VP lamellae, near the middle, and also along the interfaces with the PI lamellae [19–21]. The molecular weight and composition of P2VP-*b*-PI block copolymers affect configurations of the copolymer chains adsorbed on the particle. Suppression of microphase separation in the presence of metal particles was observed when a solution doping method was used for this P2VP-*b*-PI system [20]. The particles coordinated and stabilized by the polymer chains, tend to form aggregates due to interparticle interactions. As a result, high Pd particle content suppresses the polymer microphase separation and leads to interconnected aggregates. This experimental result confirmed our own observations on the dispersion of iron oxide particles within NORMEOH-*b*-NORCOOH block copolymers when the bulk solution doping method was used. The microphase separation of the copolymer can be influenced with the introduction of particles in bulk solution doping at high concentrations (>6 wt%). For a similar diblock copolymer system, NOR/*d*-NORCOOH (norbornene/deuterated-norbornene dicarboxylic acid), SANS experiments revealed that the polymer microphase separation was influenced by the presence of the nanoparticles. These results were reported in one of our previous manuscripts published in Ref. [11].

The effect of particle size on the arrangement of metal oxide particles has also been studied by Aussere et al. using neutron reflectivity experiments, who reported that iron oxide particles localize at interfaces and in the center of the domains of PS-*b*-PBMA depending on the particle size [22].

On the other hand, during thin surface doping the metal associates with the pre-existing microphase separated polymer structure. The lamellar structure of the undoped poly(norbornene methanol)-*b*-poly(norbornene dicarboxylic acid) diblock copolymer of this study guided the confinement of iron oxide nanoparticles within one of the microphase separated lamellae, when the thin film surface doping technique was employed.

5. Conclusions

We have synthesized novel norbornene methanol/norbornene dicarboxylic acid diblock copolymer system exhibiting a lamellar morphology. Block copolymer doped with iron ions using a bulk solution doping method formed iron oxide nanoparticle aggregates upon solid film formation. The main difference between the two metal oxide doping methods is that in the thin-film surface doping case, the polymer microphase separation has occurred prior to metal doping. The pre-existing lamellar microstructure guides the preferential binding and confinement of γ-Fe_2O_3 within the carboxylic acid containing polymer block. The metals interacting with the polymer chains in solution influence the microphase separation of the resulting solid sample upon solvent evaporation in the bulk solution doping method. The film cast using bulk solution doping (which contains 8 wt% iron oxide) presents aggregates of the spherical nanoparticles due to increased particle interactions. Consequently, interparticle and polymer-particle interactions influence the templating mechanism and ordering of the nanoparticles within the block copolymer matrix.

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