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Effect of CdSe nanoparticle addition on nanostructuring of PS-*b*-P4VP copolymer via solvent vapor exposure

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Abastract

The surface morphology of poly(styrene-*b*-4 vinyl pyridine) (PS-*b*-P4VP) diblock copolymer thin films after solvent vapor annealing has been studied. Morphological features can be switched upon exposure to vapors of a solvent selective for one of the blocks. Self-assembled nanostructures such as hexagonal or striped morphologies were obtained varying vapor exposure time. In addition, the effect of the pres- ence of CdSe nanoparticles located in the P4VP block on obtained nanostructures was analyzed. Atomic force microscopy (AFM) was used for morphological characterization of the block copolymer and the nanocomposites. AFM images showed that nanostructuring was different depending on the amount of CdSe nanoparticles, due to the decrease in P4VP chain mobility.

1. Introduction

Self-assembly of block copolymers (BC) has received increasing interest due to the rich variety of nanostructures that can be gen- erated depending on the nature of the blocks, molecular weight and composition, and the processing characteristics [1–3]. These kinds of materials could open a way to generate different nano- structures with applications in fields such as medicine [4,5] and electronics [6]. For many applications where regular periodic ar- rays are required, it will be necessary to generate long-range align- ment of nanostructures in block copolymers films [7–10]. Different techniques and parameters for film preparation, such as applica- tion of electric fields [11] and mechanical strain [12,13], controlled solvent evaporation [14,15], variation in film thickness [16,17], or chemical tailoring of film/substrate interface [18,19], could allow the manipulation of nanostructures. The preparation of BC thin films under various solvent evaporation conditions turns out to be a good way to manipulate the microstructures.

The incorporation and distribution of nanoparticles (NP) and other nanoscale fillers within BC to obtain nanostructured nano- composites have evolved into an area of considerable research [20,21]. One of the mayor issues in developing nanoparticle/poly- mer composites is how to stabilize the hybrid blend against mac- rophase separation or agglomeration of the nanoparticles. Different strategies such as grafting of polymers on the surface of nanoparticles [22,23], electrophoretic deposition [24] or hydrogen bonding among the nanoparticles and host matrix [25,26] have been used to avoid agglomeration of nanoparticles. Hydrogen bonding has been widely used for supramolecular assembly of small molecules as nanoparticles and polymers because of its molecularly specific and highly directional characteristic.

In this work, after following the nanostructuration of a poly(sty- rene-*b*-4-vinyl pyridine) (PS-P4VP) block copolymer by exposure to dioxane vapors the effect of mercaptoethanol capped CdSe nanoparticles on it has been analyzed. A good dispersion of nano- particles in the P4VP domains of the copolymer has been obtained, avoiding agglomeration by the hydrogen bonding between the nitrogen (N) atom of vinylpyridine and the hydroxyl group of mercaptoethanol.

2. Experimental section

2.1. Materials

2-Mercaptoethanol (ME), cadmium sulfate hydrate ($3CdSO_4$-$8H_2O$), selenium metal powder (Se), sodium sulfite (Na_2SO_3) and N,N-dimethylformamide (DMF) were purchased from Panreac and used without further purification. ME capped CdSe nanoparti- cles were prepared as in previous works [27]. Poly(styrene-*b*-4-vinyl pyridine) (PS-P4VP) block copolymer was purchased from Polymer Source with number average molecular masses (*M*n) of 22,500 and 29,000 g/mol for poly(styrene) (PS) and poly(4-vinyl pyridine) (P4VP) blocks, respectively and a polydispersity index (*M*w/*M*n) of 1.2 for both blocks.

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2.2. Thin film preparation

1 wt% PS-P4VP solutions in DMF were deposited onto a silicon wafer by spin-coating. Nanocomposites were prepared adding 1, 2 and 5 wt% of ME–CdSe nanoparticles with respect to the block copolymer, preparing the films in the same way than those of the neat block copolymer. Samples were then exposed for different times to saturated dioxane vapors in a closed vessel kept at room temperature.

2.3. Characterization

FTIR spectra were carried out in a Nicolet Nexus spectrometer. Spectra were taken with 2 cm^{-1} resolution in a wavenumber range from 4000 to 400 cm^{-1}. Block copolymer solutions and block copolymer/CdSe nanoparticle solutions were placed on KBr pellets and left to dry under vacuum.

Atomic force microscopy (AFM) was performed in tapping mode (TM) using a Dimension 3100 NanoScope IV (Veeco). Etched singlebeam cantilever (110–140 lm length) silicon nitride probes were used, having a tip nominal radius of 10 nm. Scan rates ranged from 0.7 to 1.2 Hz s^{-1}. Measurements were performed with 512 scan lines and a target amplitude of around 0.9 V. In order to obtain repeatable results of the nanocomposites morphology, different re- gions of the specimens were scanned.

For nanocomposite pyrolysis the TGA/SDTA851 (Mettler Tole- do) thermogravimetric analyzer was used under nitrogen atmo- sphere at a heating rate of 30 ºC/min from room temperature to 600 ºC.

3. Results and discussion

In the first step, after a bibliographic revision [28], different sol- vents (neutral, PS selective solvent and P4VP selective one) were studied for nanostructuring the block copolymer. As best results were obtained with dioxane, it was chosen as solvent for nano- structuring block copolymer and nanocomposites. Dioxane is a selective solvent for PS. The effect of exposure time of PS-P4VP films to saturated dioxane vapors was analyzed by AFM. Fig. 1 shows AFM images of PS-P4VP thin films before and after dioxane vapor treatment. As shown in Fig. 1a for the film before any treat- ment, a soft microphase separation is observed but without the formation of any ordered microstructure. Two different scale colors can be distinguished: PS blocks appear brighter than P4VP self- assembled domains [29].

In order to improve microphase separation, the film was ex- posed to saturated dioxane atmosphere for different times. Fig. 1b shows a well defined hexagonal morphology for the PS- P4VP film, obtained after 24 h of exposure to saturated dioxane. Longer exposure time caused a change in the morphology, as it can be observed in Fig. 1c. Prolonged exposure (48 h) led to a to- tally striped morphology, showing a lamellar structure normal to the substrate. The same structure was obtained after longer expo- sure times.

This change in the microstructure can be attributed to the nat- ure of dioxane, which is a good solvent for PS that does not solve the P4VP block. This fact provokes the migration of P4VP from the free surface to the substrate. At the same time, due to its affin- ity, solvent vapor molecules have a strong tendency to attract PS block, pulling it toward the film surface. These chain migrations could provoke the formation of hexagonal microstructure after 24 h of exposure and a totally striped morphology for 48 h expo- sure time.

To study the effect of nanoparticles on the nanostructuring process, different amounts of colloidal dissolutions of CdSe nanoparticles stabilized with mercaptoethanol were added to PS- P4VP block copolymer solution.

1, 2 and 5 wt% of CdSe nanoparticles were added to block copolymer solutions. CdSe nanoparticles were synthesized in an aqueous environment using mercaptoethanol as stabilizing agent to obtain a hydroxyl group on the surface of nanoparticles that takes part in the later functionalization process. Nanoparticle size was characterized by UV–vis, X-ray powder diffraction (XRD) and transmission electron microscopy (TEM), obtaining a 2–4 nm diameter size and the presence of the hydroxyl group on the sur- face of CdSe nanoparticles was confirmed by FTIR measurements reported in a previous work [27]. Fig. 2 shows AFM phase images of the nanocomposites exposed to 48 h to saturated dioxane atmo- sphere. As it can be seen none of the nanocomposites reached the same nanostructure of the neat block copolymer. Fig. 2a shows the structuring of the nanocomposite with 1 wt% of CdSe nanoparti- cles. Although a totally striped morphology is almost obtained, some cylinders located perpendicular to the substrate can be seen. For 2 wt% of nanoparticles (Fig. 2b), the number of cylinders lo- cated perpendicular to the substrate increased. It seems that a mixed morphology containing a striped morphology and a hexag- onal structure is obtained. Finally, for 5 wt% of CdSe nanoparticles a worm like structuring was obtained, as shown in Fig. 2c.

These results suggest that the presence of nanoparticles could affect the mobility of the P4VP block and, consequently, the struc- turing of the nanocomposite. As the size of the nanoparticles is very small the interface area where the interactions between nano- particles surface and P4VP occurred is very extensive. These inter- face interactions affect in the structuring of the block copolymer. For 1 wt% of nanoparticles, the chain mobility seems to be still good enough to obtain almost the same nanostructuring than the neat block copolymer. When the amount of nanoparticles in- creased to 2 wt%, it seems that chains have not enough mobility to reach the totally stripped morphology and a mixed stripped/ hexagonal morphology is obtained. Finally, for the case of 5 wt% of CdSe nanoparticles, the impossibility to reach the lamellar or cylindrical structure could be due to the very low mobility of the P4VP block. In fact, as the interface area between nanoparticles and polymer grows the mobility of P4VP chains decreased due to a bigger number of hydrogen bonds, affecting the structuration.

To confirm the presence of nanoparticles, nanocomposites were pyrolyzed. Fig. 3 shows AFM images of pyrolyzed samples corre- sponding to neat block copolymer and the nanocomposite with 5 wt% of nanoparticles. While for the pyrolyzed neat block copoly- mer film a flat surface sample is obtained (Fig. 3a), for the nano- composite sample the nondegraded CdSe nanoparticles can be seen (Fig. 3b).

Though nanoparticles are not visible in the images of Fig. 2, their presence has been confirmed by pyrolyzing the composites. As no agglomerations shown in Fig. 2, nanoparticles seem to be good dispersed in the block copolymer. In fact, they are expected to be located and dispersed in the P4VP block, due to hydrogen bonding between hydroxyl groups of nanoparticles surface and the nitrogen (N) atom of vinylpyridine. Hydrogen bonding has been widely used for supramolecular assembly of small molecules and polymers because of its molecularly specific and highly direc- tional characteristics [30]. Because of the strong enthalpic attrac- tion of H-bonds, macrophase separation of nanoparticles is suppressed favoring microphase separation [31].

Hydrogen bonding interactions between pyridine groups on PS- P4VP and hydroxyl groups on CdSe–ME nanoparticles were con- firmed by FTIR spectroscopy. Fig. 4 shows FTIR spectra of the 950–1050 region, where the absorbance band of hydrogen bonded pyridine at 1003 cm^{-1} increases by the addition of CdSe–ME nanoparticles while the band of free pyridine at 993 cm^{-1} decreases [32,33].

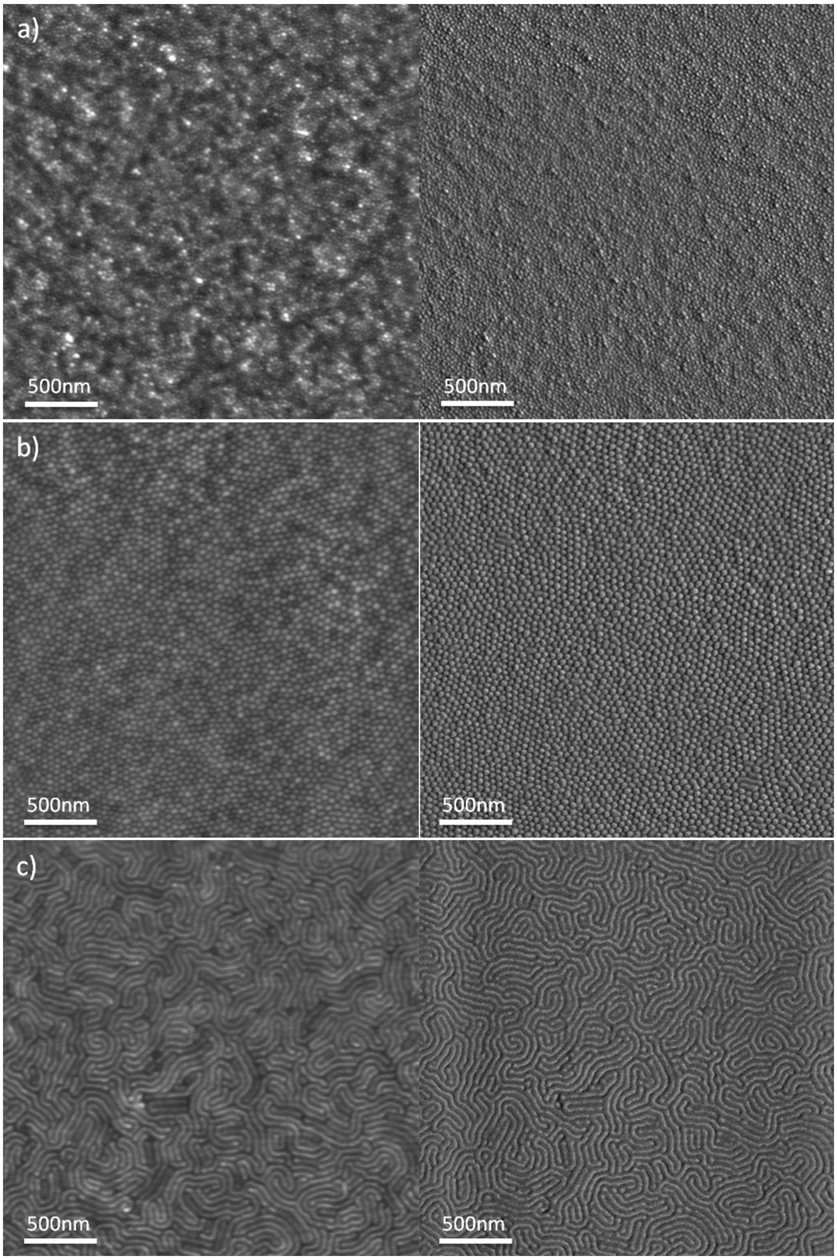

Fig. 1. AFM images (left/right: height/phase) of neat PS-*b*-P4VP thin films (a) before exposure to dioxane saturated atmosphere, (b) after 24 h of exposure and (c) after 48 h of exposure.

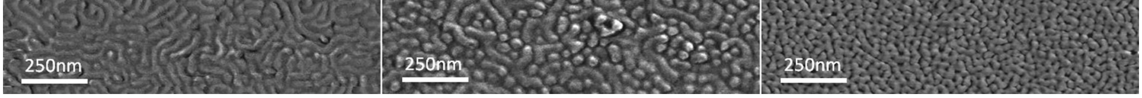

Fig. 2. AFM phase images of CdSe/PS-*b*-P4VP nanocomposites with (a) 1 wt%, (b) 2 wt% and (c) 5 wt% of nanoparticles, after 48 h of exposure to dioxane saturated atmosphere.

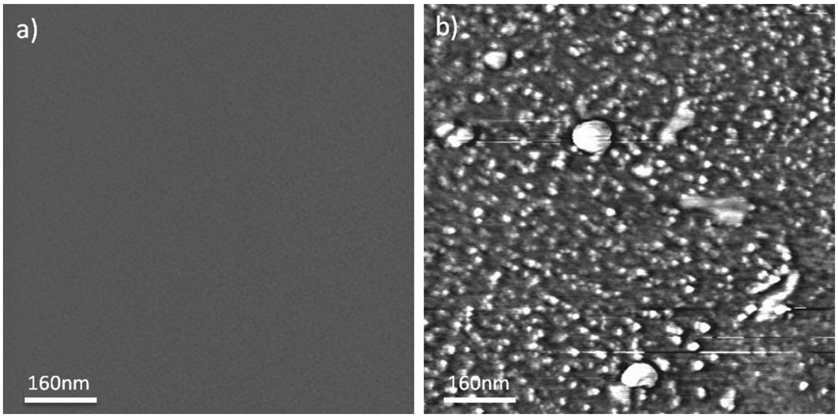

Fig. 3. AFM phase images of (a) neat PS-*b*-P4VP and (b) 5 wt% CdSe/PS-*b*-P4VP nanocomposite films after pyrolisis.

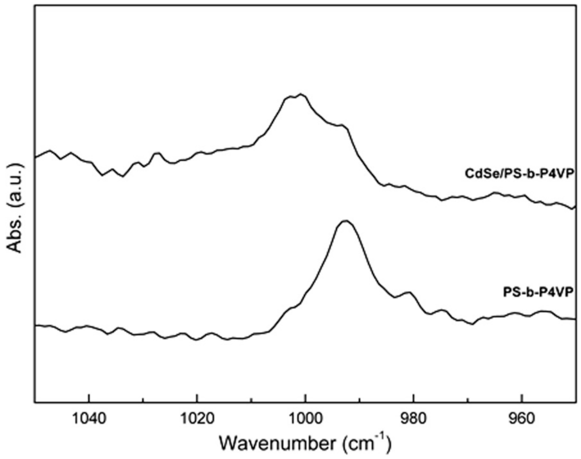

Fig. 4. FTIR spectra of PS-*b*-P4VP and CdSe/PS-*b*-P4VP in the range of 1050– 950 cm^{-1}.

4. Conclusions

In this study, the phase behavior of PS-*b*-P4VP thin films after exposure to a selective solvent (dioxane) vapors and the effect of addition of mercaptoethanol stabilized CdSe nanoparticle colloidal dissolutions on the nanostructuring has been investigated. The sol- vent vapor annealing time appears as a key factor for the evolution of microphase-separated morphologies. Preferential migration of the PS block to the surface due to the affinity with the solvent pro- vokes the obtention of different structures with exposure time. In this case, the dioxane vapor exposure treatment leads to a hexag- onal structure, changing to a totally stripped morphology for long- er exposure times. At higher exposure times the same ordered structure was obtained.

Hydrogen bonding (confirmed by FTIR) could allow the segrega- tion of CdSe nanoparticles inside P4VP domains. The presence of nanoparticles in the P4VP block could decrease its mobility leading to different nanostructures for composites with different nanoparticle amounts. While the addition of 1 wt% of nanoparticles pre- sents a little effect on the nanostructuring, obtaining almost the same morphology than that of the neat copolymer, for 2 wt% load a mixed morphology is obtained probably due to the lower chain mobility. Finally, the addition of 5 wt% of nanoparticles leads to a total change in the obtained structure. So it can be seen that as the interface area between the nanoparticles and polymer grows the hydrogen bonding interaction number grows, decreasing the mobility of P4VP chains. The presence of the nanoparticles was confirmed analyzing pyrolyzed samples by AFM.

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