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Morphologies of an Amphiphilic Diblock Copolymer of Poly (Ethylene Oxide)-*b*-Polystyrene and Its Blends with Poly (2,6-Dimethyl-1,4-Oxide)

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Summary

Systems containing block copolymers are of great interest due to the ability of copolymers to self-assemble into a variety of structured, ordered, or partially ordered morphologies. A fascinating morphology of two-dimensional arrays of hexagonal-like holes was observed for the first time in the diblock copolymer of poly (ethylene oxide)-b-polystyrene (PEO-*b*-PS) by transmission electron microscopy (TEM). The blends of PEO-*b*-PS with poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) were obtained by solution blending, and the morphologies of PEO nano-dispersed particles in PPO/PS matrix were observed by atomic force microscopy (AFM) and TEM. Using the film forming technique on water/air interface, the core-shell morphology with PEO as shells was obtained in PEO-*b*-PS/PPO blends. Thus, three different morphologies were obtained by controlling preparation conditions. Especially, PEO-*b*-PS self-organized into the hexagonal-like holes patterns was first found to our knowledge.

Introduction

To design ordered nanostructures and microstructures with well-defined size and shapes attracts much interest due to their important applications in areas such as membranes, optical communications, electrical and ionic conductors, nanotemplating, and nanolithography [1-6]. The fabrication of these nanostructured materials in most cases involves self-assembling of molecules through covalent or noncovalent forces. Systems containing block copolymers are of great interest due to their specific multi-phase morphology with interesting or useful self-assembly behavior. Block copolymers alone can undergo microphase separation and form microdomains with interesting structures such as lamella, bicontinuous, cylinders, and spheres [7-10].

Also, block copolymers, often as compatibilizers, are added or generated in situ during blending of immiscible polymers. They tend to segregate to the interface where they promote the formation of small droplets by reducing interfacial tension and suppressing coalescence events. However, it is difficult to further decrease the size of droplets to nano-level by common compatibilization methods. The recent report [11] suggested that block copolymers could be harnessed in a much more powerful way to construct blends down to molecular scale, that is, a few tens of nanometers, if block copolymers were at higher concentrations in the blend than those used for compatibilization. Studies of such blends are mainly focused on binary blends of a copolymer with a homopolymer like A-*b*-B/A system [12-14], showing that block copolymer/homopolymer can indeed form interesting nanostructures, but only in a relatively narrow window of molecular parameters, composition, temperature and so on. The mixing patterns in homopolymer/diblock copolymer systems are conveniently summarized in three categories based on the ratio ($N_{h,A}/N_{b,A}$), where $N_{h,A}$ and $N_{b,A}$ refer to the degrees of polymerization of A homopolymer and A block, respectively [15]. When $N_{h,A}/N_{b,A} < 1$, homopolymer swells the corresponding block, a situation often referred to as a “wet brush”. Increasing the homopolymer molecular weight to $N_{h,A}/N_{b,A} \approx 1$ leads to expulsion of the homopolymer from the brush interior and localization of the homopolymer at the central portion of the microdomain; this is known as the “dry brush limit”. When $N_{h,A}/N_{b,A} \geq 1$, the homopolymer is rejected from the block copolymer altogether, a condition known as macrophase separation. Thus, various morphologies can be designed by adjusting the molecular weights, but microphases in nano-size are obtained only when short-chained homopolymers are used. Considering the more complex blends A-*b*-B/C system, where C is a homopolymer different from either block A or block B and only miscible with block A, it is found the effect of the homopolymer molecular weight on its solubilization was small or nonexistent, which is ascribed to the favorable interactions between the C homopolymer and the A block. The existence of such attractive interactions could suppress macrophase separation when long-chained homopolymers is used [16-17].

Herein, with the aim to construct nano-structured blend using self-assembly behavior of the block copolymer, we synthesized the amphiphilic diblock copolymer of PEO-*b*-PS and blended it with the homopolymer of PPO. First, we observed the morphology of the block copolymer synthesized and found it self-assembling into a new structure. Then, the morphologies of the block copolymer self-assembled in the blends were investigated.

Experimental

Materials

Poly (ethylene glycol) monomethyl ether (MPEG; Mn = 5000 g mol^{-1}) from Fluka was dried at 30°C in vacuum overnight before use. Styrene (Shanghai Chemical Reagent Co., > 99%) was stored over calcium hydride and then vacuum distilled before use. Copper bromide (CuBr, Shanghai Chemical Reagent Co., > 98.5%) was washed with aqueous 10 wt% acetic acid and acetone until colorless, and then dried in vacuum. Methylene dichloride (CH_2Cl_2) was shaken with portions of concentrated H_2SO_4 until the acid layer remained colorless, then washed with water, aqueous 5 wt% $NaHCO_4$ and with water again, and finally distilled from CaH_2. 2-bromopropionyl bromide (BPB, Aldrich, > 97%), triethylamine (TEA, Shanghai Chemical Reagent Co., > 99%), 4-(dimethylamino) pyridine (DMAP, Shanghai Chemical Reagent Co., > 99%), and other reagents were used as received without further purification.

Preparation of PEO-b-PS diblock copolymer

PEO-*b*-PS diblock copolymer was synthesized via atom transfer radical polymerization (ATRP) according to a literature procedure with partial improvement [18]. A 250 mL three-necked bottle was charged with 0.7 mL of TEA and 10 mL of CH_2Cl_2 containing 0.92 g of DMAP. After cooling to 0°C, 1.3 mL of BPB in 10 mL of CH_2Cl_2 was added. Then 50 mL of dried CH_2Cl_2 containing 2.5 mmol of MPEG was added dropwise over 1 h, keeping at 25°C under N_2 for 18 h. The mixture was filtered, and most of solvent was evaporated. The residue was dissolved in THF and precipitated in cold diethyl ether. It was then filtered, washed with ether, and dried in vacuum to give MPEG macroinitiator as a white solid (60%). A flask was charged with 0.25 mmol of PEG macroinitiator, 0.072 g of CuBr, 0.234 g of bipy and 9 mL of styrene. The system was degassed and nitrogen filled three times. The flask was then sealed up and kept in an oil bath of 110°C for 24 h. The crude product was dissolved in CH_2Cl_2 (50 mL), passed through an alumina column, and precipitated in hexane (200 mL). The formed solid was washed with cyclohexane and ethanol for 2 days, respectively, then dried under vacuum, dissolved in CH_2Cl_2 again, and precipitated in a large amount of hexane.

Preparation of the PEO-b-PS/PPO blends

The blends of PEO-*b*-PS and PPO were prepared by solution blending with $CHCl_3$ as solvent. The sample was cast from 5 wt% solution, and evaporated slowly at room temperature. Residue solvent was further removed under vacuum at 50°C.

Characterization

The composition of block copolymers was determined by the ratio of ^{1}H NMR signal intensity of the phenyl peak region (6.4-7.3 ppm) to that of the MPEG region (3.4-3.8 ppm), using a Brucker AV400 spectrometer and $CDCl_3$ as solvent. Integration of the aromatic and aliphatic peak region gave 56 wt% PS, so M_n of PS was 6300 g mol^{-1}.
The TEM experiments were performed on a Hitachi H-800 transmission electron microscope. The samples were prepared as follows: a drop of polymer solution of 0.1 wt% or 1 wt% in $CHCl_3$ was directly cast onto a carbon coated copper grid, and air-dried at room temperature with relative humidity about 70%. The film forming technique on water/air interface was carried out as this: a drop of sample solution in $CHCl_3$ was cast onto a surface of water, and the drop spread out on the surface, and then the thin film of the sample were formed on the surface, dried for TEM observation.
The AFM experiments were carried out with a Nanoscope IV operated in the tapping mode at room temperature. A drop of solution of 0.1 wt% sample in $CHCl_3$ was cast on a freshly cleaved mica, slowly evaporated at room temperature, annealed at 50°C for 2 h in vacuum and then cooled to room temperature.

Results and discussion

Morphologies of PEO-b-PS diblock copolymer

Figure 1 displays TEM morphologies of PEO-*b*-PS diblock copolymer self-organized on the carbon coated copper grids without any special stains. Therefore, the contrast observed is due to diffraction and phase contract in the sample. A morphology of two-dimensional arrays of hexagonal-like holes was distinctly observed to the sample cast onto the carbon coated copper grid from 0.1 wt% $CHCl_3$ solution and air-dried at room temperature (25°C) with relative humidity of about 70%, which to our knowledge is first found in PEO-*b*-PS diblock copolymer. When increasing the concentration to 1 wt%, the hexagonal-like holes morphology was still observed, but the size of holes nearly expanded ten times.

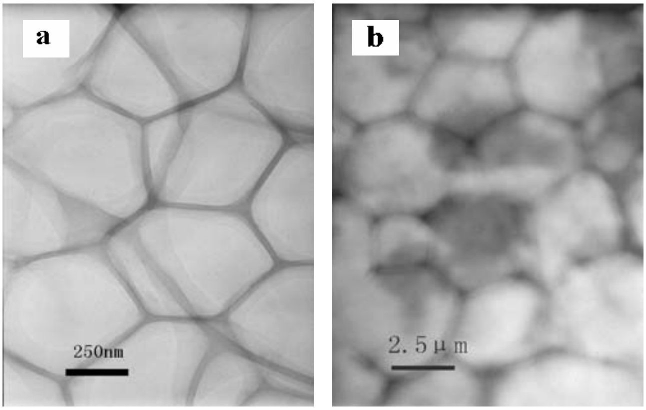

Figure 1. TEM micrographs of PEO-*b*-PS diblock copolymer cast from 0.1 wt% (a) and 1 wt% (b) $CHCl_3$ solution onto the carbon coated copper grids

Other groups have also reported hexagonal patterns. Jenehke *et al.* [19-20] reported on the self-assembly behavior of rod-coil diblock copolymers of poly(phenylquinoline) and polystyrene in a selective solvent. They thought the formation mechanism is that the coil segment self-assembled into hollow spherical micelles with diameters of a few micrometers, and subsequently self-organized into a two-dimensional hexagonal superlattice prior to film casting and evaporation of the solvent. From their findings, solvent was a critical parameter to obtain ordered superstructures. However, Deimede *et al.* [21] demonstrated in a volatile nonselective solvent a two-dimensional ordered hexagonal structure was also formed by triblock coil-rod-coil copolymers. While, in our case, it should be pointed out that the structure of hexagonal-like holes was observed in a coil-coil diblock copolymer in a nonselective solvent, not a rod-coil block copolymer. Other researchers also found such morphologies in linear PS or linear carboxylate-terminated PS in volatile solvent [22-23]. These suggested that such morphologies formed are mostly related to the film forming process and are less influenced by molecular architecture. Recent studies [24-26] have revealed the formation mechanism of such honeycomb structures. The rapid evaporation of the volatile organic solvent resulted in the cooling of the surface of polymer solution, which made the small water droplets absorbed on the surface condensate. On the one hand, the polymer prevented the coalescence of the water droplets via adsorption at the solvent-water interface. On the other hand, upon evaporation of the organic solvent, the polymer could vitrify the pattern created by the condensation of the water droplets. Bunz [27] has summarized the correlative published literatures and ascribed the formation mechanism of such hexagonal patterns including rod-coil copolymers to Breath Figure Arrays (BFA) method applied for the generation of micro- or nano-scale materials. Thus, we thought the morphology of two-dimensional arrays of hexagonal-like holes reported here was formed due to the rapid evaporation of solvent and the condensation of small water drops on the solution surface, i.e. mostly dependent on the film forming process. As thus, the humidity was a key factor to affect the final patterns. To confirm our assumption, we repeated our TEM measurement in a dry atmosphere, and a disordered morphology was formed. The effects of humidity and other factors would be performed in our future studies.

Morphologies of PEO-b-PS/PPO blends

PPO was chosen as a homopolymer to be blended with PEO-*b*-PS diblock copolymer in consideration of the case that PPO and PS were the paradigm of a miscible polymer pair over the entire composition range, at least at atmospheric pressure [28]. Figure 2 presents the AFM micrographs of PEO-*b*-PS/PPO blends with different PPO contents. It can be seen that the amount of PEO particles dispersed in the matrix is deceased with the increase of PPO contents, while the size of PEO particles maintains constant about 10-20 nm. Thus from the AFM observation, it can be concluded that the nanoblends of PEO-*b*-PS/PPO with PEO as dispersed phase can be obtained by the blending of PEO-*b*-PS copolymer and PPO homopolymer, even though the homopolymer chains are long and their structure is different from either block. Figure 3 shows the TEM observation of the PEO-*b*-PS/PPO blends. It can be seen that dark PEO nano-particles are dispersed in the light PS/PPO matrix, which is consistent with AFM observation.

By changing film forming condition, a new morphology was observed in the PEO-*b*-PS/PPO blend. Figure 4 displays the images of PEO-*b*-PS/PPO blends prepared from film forming technique on water/air interface (described in experimental part). It can be seen clearly from Figure 4 that the core-shell structure is formed, with PPO/PS as core and PEO as shell. Because water is the selective solvent for PEO-*b*-PS, while chloroform is non-selective solvent for PEO-*b*-PS, during the film forming process, the blend droplets in chloroform solution were flat on the water surface with PEO hydrophilic segment oriented towards water phase. With the evaporation of chloroform solvent, PS/PPO shrank to core with PEO segments around them as shell.

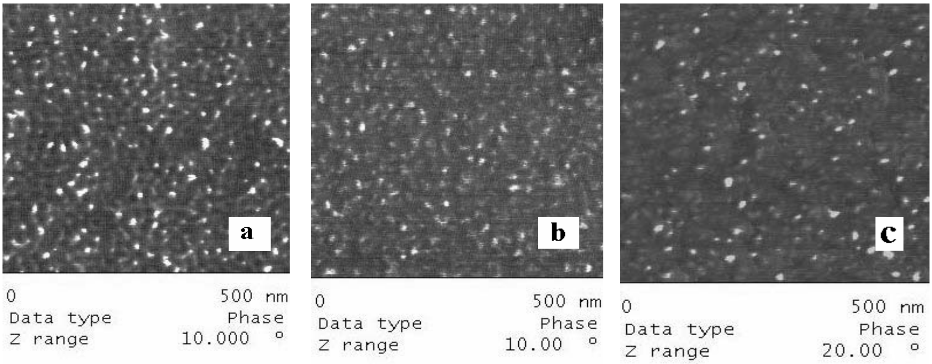

Figure 2. AFM images of PEO-*b*-PS/PPO blends cast from $CHCl_3$ (a) $f_{PEO} = 0.28$; (b) $f_{PEO} = 0.20$; (c) $f_{PEO} = 0.12$

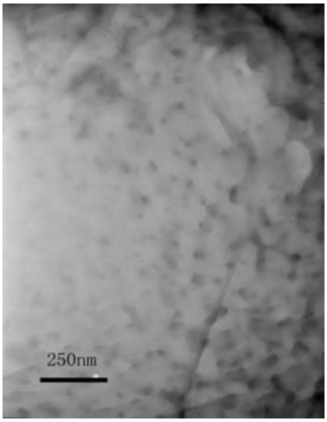

Figure 3. TEM images of PEO-*b*-PS/PPO blends cast from $CHCl_3$, $f_{PEO} = 0.28$, direct observation after solve casting at room temperature

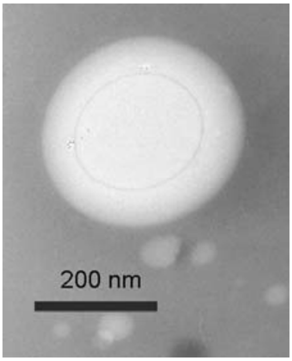

Figure 4. TEM observation of PEO-*b*-PS/PPO blends, $f_{PEO} = 0.20$, the samples were prepared from 0.1 wt% chloroform solution and cast onto water surface

Conclusions

By controlling preparation conditions, three different morphologies were successfully prepared in PEO-*b*-PS block copolymer and PEO-*b*-PS/PPO blend. A new morphology of two-dimensional arrays of hexagonal-like holes was first observed in the diblock copolymer of PEO-*b*-PS. The nano-structured blends of PEO-*b*-PS and PPO were also obtained by solution blending, with PEO nano-sized particles dispersed in PPO/PS matrix. Using the film forming technique on water/air interface, the morphology of core-shell structure with PEO as shells was obtained.

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