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Synthesis and characterization of microphase separated primary amine functionalized polystyrene-b-poly(2-vinylpyridine)

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ABSTRACT

Microphase separated block copolymers containing primary amine functionalities would have applications in sensors, templates, anti-microbial surfaces and cell scaffolds. Primary amines allow for a variety of different click chemistries that facilitate these applications. In this investigation microphase separated polystyrene-b-poly(2-vinylpyridine) films were quaternized with a primary amine functionality utilizing the less common trimethylsilyl protecting group and a substitution reaction. The glass transition of the 2-vinylpyridine block was suppressed after functionalization. The newly introduced amine functionalities are susceptible to cross-linking through the use of glutaraldehyde, demonstrating the availability of the amines for further chemical modification. The trimethylsilyl protecting group allowed for the reliable quaternization of PS-b-P2VP with a primary amine, without disrupting the film or its morphology.

1. Introduction

Block copolymers (BCPs) are macromolecules composed of sequences or blocks of chemically distinct repeat units. The covalent bond between constituent blocks allows for microphase separation into spherical, cylindrical, bi-continuous, and lamellar morphologies. The morphology and domain sizes of these self-assembled periodic nanostructures can generally be controlled by adjusting the length of each block and the total molecular mass [1]. Nanostructured BCPs have been developed for applications such as electronics [2], templates [3–7], and cell scaffolds [8,9]. Many of these applications could be enriched by the introduction of block copolymers containing polar or ionic blocks. BCPs of this nature could introduce interesting surface chemistries as well as allow for additional chemical modifications.

BCPs are generally synthesized using living polymerization techniques in order to achieve the low polydispersity required for microphase separation [10]. This makes the synthesis of BCPs consisting of polar and acidic monomers difficult as they can disrupt the polymerization process. Particularly, protic groups such as amines can induce chain transfer and termination events [11]. Additionally, polymers containing a high fraction of ionized units do not microphase separate due to the aggregation of the charged sites [12]. For these reasons it is difficult to synthesize monodisperse BCPs containing amine functionalities, while retaining the microphase separated microstructure. Amine containing BCPs permit the use of epoxide, carbodiimide, aldehyde, and N-hydroxysuccinimide chemistries, which opens the door for a variety of chemical and biological functionalizations such as free thiols, antibodies, oligonucleotides, peptides and enzymes. This would have applications in biosensors, anti-microbial surfaces and cell scaffolds. Poly(imidazoliums) have been reported as an effective means to produce primary amine functionalized polymers, by use of a post synthesis modification [13]. Specifically the imidazoliums are alkylated using a variety of brominated compounds to produce cationic polymers [14–17]. This method is effective, but has not been reported for BCP nanostructures. In the following study we took advantage of the nucleophilic nature of 2-vinylpyridine as a means to introduce a primary amine functionality to the block copolymer polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP) without disrupting its lamellar microphase separation.

PS-b-P2VP is a commonly studied BCP that easily microphase separates into different nanostructures, which have been exploited for applications such as antimicrobial surfaces [18–20], nanoparticle templates [21,22], as well as photonic crystals [23]. The nucleophilic nature of P2VP has been taken advantage of in previous studies, but only in the attachment of alkyl chains for quaternization and crosslinking purposes. This nucleophilic reaction is thought to proceed as a Sn2 reaction [24,25]. Modifying nanostructured PS-b-P2VP is a delicate process to ensure the survival of the aforementioned nanostructure. The solvent utilized cannot delaminate the surface or disrupt the desired nanostructure.

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Covalently attaching a primary amine would require a compound containing a leaving group or electrophile and the primary amine. Reactions between the amino group and electrophile can lead to cyclization and polymerization of the reactant, necessitating the use of protected amines. Many protecting groups for amines, such as di-tert-butyl dicarbonate (Boc) can solubilize PS-b-P2VP, dewetting the surface or destroying the nanostructured morphology. Alternatively, the utilization of trimethylsilyl(TMS) protecting groups was examined in this investigation. TMS is commonly used in the protection of alcohols [26] but has had some use with primary amines [27]. The electron-poor nature of TMS groups prevents reactants from solubilizing PS-b-P2VP, while easily being removed with a proton source to yield a primary amine functionality. Utilizing this process would allow for the fabrication of primary amine containing block copolymer nanostructures.

2. Materials and methods

2.1. Materials

All materials purchased were used as received unless otherwise indicated. Polystyrene-b-poly(2-vinylpyridine) was purchased from Polymer Source. 3-Bromo-N,N-bis(trimethylsilyl)propan-1-amine was purchased from Synthonix and stored under argon gas. Glutaraldehyde, acetonitrile and acetic acid were purchased from Sigma. Ultra stick APTES functionalized glass slides were purchased from Ted Pella. Spurr's resin was purchased from Electron Microscopy Sciences.

2.2. Fabrication of unmodified microphase separated PS-b-P2VP films

A solution of PS-b-P2VP (133 kDa-b-131 kDa) was dissolved in propylene glycol monomethyl ether acetate (PGMEA) at a concentration of 5% w/v. PGMEA was chosen due to its slow rate of evaporation, allowing for the development of uniform films. 300 μL solution was spun-cast onto a 1 "X1" APTES functionalized glass slide at 350 rpm for 120 s until dry. APTES was utilized as it reduces the surface energy of the glass slides, preventing delamination events. The resulting film was then solvent annealed at room temperature inside a glass petri dish containing 2 mL of chloroform for 12 h. This process produces an approximately 1 μm thick PS-b-P2VP film with lamellae parallel to the substrate.

2.3. Functionalizing the BCP film with 2-(Boc-amino)-ethyl bromide

An initial attempt was performed to quaternize the P2VP block with 2-(Boc-amino)-ethyl bromide (BAEB). Breifly, a range of 5–30 mg of BAEB was dissolved in 10 mL of acetonitrile. A PS-b-P2VP film was immersed in the solution and allowed to reflux at 90 °C for 5–18 h.

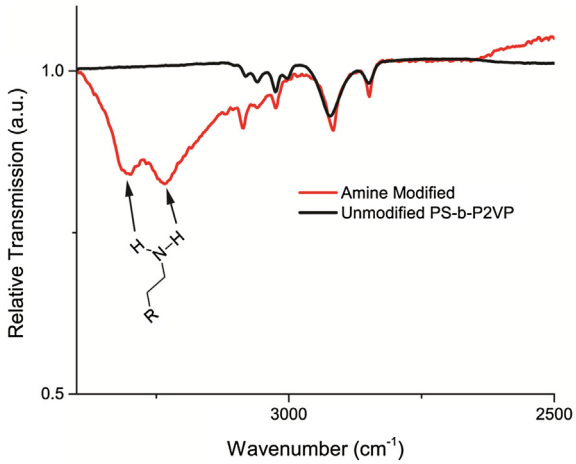


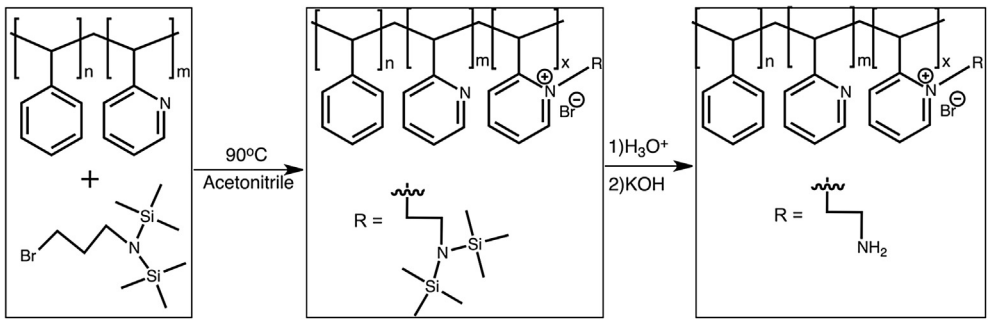
Fig. 1. FTIR of unmodified PS-b-P2VP, demonstrating the characteristic aromatic crown at 2900 cm^{-1}. The spectra of the amine modified PS-b-P2VP displays the double primary amine peak at 3300 and 3200 cm^{-1}.

2.4. Functionalizing the BCP film with BTMSPA

To quaternize the P2VP block with a primary amine, 3-Bromo-N,N-bis(trimethylsilyl)propan-1-amine (BTMSPA) was utilized. The BTMSPA was stored under an argon environment as the trimethylsilyl protecting group is moisture sensitive. A solution of 200 μL BTMSPA in 10 ml of acetonitrile was prepared and blanketed with nitrogen. A PS-b-P2VP film was then immersed in this solution and allowed to reflux at 90 °C for 18 h under a nitrogen environment. The film was then removed and soaked in excess acetonitrile three times. To remove the TMS protecting group, the now modified PS-b-P2VP film was immersed in a 10% v/v solution of aqueous HCl for 7 days.

2.5. Transmission electron microscopy

Amine functionalized (hence referred to as "modified") and unmodified films of PS-b-P2VP were etched from their glass substrates by soaking the films in a 5% v/v solution of hydrogen fluoride. The removed films were rinsed with excess NaOH and distilled water and allowed to dry at room temperature. The films were then embedded in coffins of Spurr's resin. The embedded films were then microtomed using a Leica EM UC6 and placed on nickel TEM grids. The PS-b-P2VP cross-sections were analyzed using a JEM-2100F 200 kV transmission electron microscope.



Scheme 1. Depiction of the quaternization of PS-b-P2VP. The PS-b-P2VP film is immersed in a solution of BTMSPA in acetonitrile and refluxed at 90 °C. The resulting modification contains the trimethylsilyl protecting group on the amine which is subsequently removed using HCl followed by KOH to neutralize the acid.