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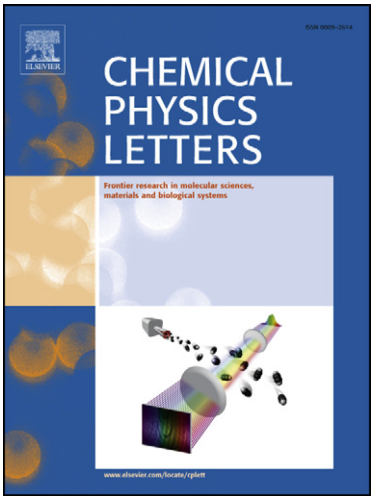

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Toroid Formation in Polystyrene-*block*-Poly(4-vinyl pyridine) Diblock Copolymers: Combined Substrate and Solvent Control

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Abstract

A polystyrene-*block*-poly(4-vinyl pyridine) diblock copolymer (PS-*b*-P4VP) has been used to create nanosized toroid-like structures on nitrided silicon oxide and gold substrates *via* simple solvent annealing of spun cast films. The significance of the role of polymer-substrate interactions in defining the morphology of the self-assembled block copolymer structure is discussed.

1. Introduction

Nanopatterning of polymer thin films has been extensively studied in recent years because of potential applications in microelectronics [1], cell growth [2], nanotechnology [3] etc. Block copolymers (BCPs) can undergo self-assembly in both the solid state and in solution to form a rich variety of morphologies, e.g. spheres, cylinders, lamellae and toroids of various sizes (typically 5 – 50 nm) [4,5]. Control of both the film thickness [6] and interfacial interactions (i.e. at the polymer-substrate and polymer-air interfaces [7]) is critical in obtaining the desired film structure. Polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) is an amphiphilic non-ionic BCP that forms self-organised structures in a thin film format *via* solution phase micelle formation. Typically, in non-aqeuous organic media, the less soluble block (P4VP) forms core domains that are surrounded by a highly swollen corona of the more soluble block (PS). Depending upon the BCP-solvent interactions micelles of various shapes (typically spheres or cylinders) are possible and these can assemble into different ordered arrangements [8,9], for example cubic or hexagonaly. Stamm *et al.* [10] have reported that depending on experimental conditions PS-*b*-PVP with 2-(4'hydroxybenzeneazo) benzoic acid (HABA) self-assembly results in hexagonally packed PVP cylinders orientated either perpendicular or parallel to the surface. The orientation of the cylinders can be readily controlled or reversed upon exposure to appropriate solvents. The PS-*b*-P4VP film was subsequently used to template the fabrication of arrays of ordered nanodots and nanowires. The preparation of block copolymer thin films under various solvent evaporation conditions has also proven to be an efficient way of manipulating the microstructures. *Han et al* [11] have shown that thickness confinement and solvent-induced reconstruction of the film are responsible for the PS-*b*-PMMA morphology and surface chemistry development.

In recent years, the formation of more complex arrangments than simple cubic or cylindrical arrays has become the subject of considerable interest because of their potential in facilitating more complex patterns for use as nanolithographic etch masks. Besides changing the polymer composition, the self-assembled structures can also be influenced by changing the solvent [12,13] and/or by using binary solvent mixtures [14,15]. Schubert *et al.* investigated the solvent responsive of block and gradient copoly(2-oxazoline)s in binary water-ethanol mixtures to address the effect of monomer distribution [16]. Toroidal structures have been demonstrated *via* self-assembly of a number of systems [17,18] including the PS-*b*-P4VP system which is reported to form toroids in strongly acidic conditions [19]. However, formal control of toroid formation remains elusive and the role of interfacial interactions in providing the conditions needed for toroid formation have yet to be explored in depth.

2. Experimental

Two PS-*b*-P4VP (Polymer Source Inc.) diblock copolymers were used in this work. with number average molecular weights (Mn) of Mn^{ps} = 20,000 g mol^{-1}, Mn^{p4vp} = 19,000 g mol^{-1} and Mn^{ps} = 57,500 g mol^{-1}, Mn^{p4vp} = 18,500 g mol^{-1} reffered to as PS-*b*-P4VP1 and PS-*b*-P4VP2 respectively. Thin films were prepared by spin-coating (speed = 3200 rpm) using a Speciality Coating Systems G3P-8 spin-coater, from a toluene solution at a concentration of 0.3wt%. These films were then solvent annealed at 25°C for 24 h. Substrates used were silicon (100) wafers with a thermally grown oxide overlayer (SiO_2), similar silicon substrates terminated with a 300 nm nitrided silica layer (SiO_xN_y) and further substrates coated with a gold layer (30 nm gold and a 5 nm chromium interfacial layer to enhance gold adhesion). Substrates were ultrasonically cleaned in ethanol, toluene and acetone prior to use. Topographic and phase images of film surfaces were recorded simultaneously by AFM (DME DS-50 dual scope) in tapping mode.

3. Results and Discussion

Spin coating onto all substrates from toluene solutions produces nanopatterned thin films having a typical structure as shown in figure 1. This has been reported previously [20] as a micellar-type structure (as opposed to that formed by microphase separation) where spherical micelles, formed in solution prior to film formation, form a partially ordered hexagonal arrangement at the substrate upon spin coating. Evidence for this type of arrangement is provided by the variation in height between the nanofeatures (30 - 50 nm – figures 1(A) and (C) compared to a few nm expected for microphase separation). This variation in height agrees well with the average thickness of 40 nm as measured by ellipsometry and indicates that the film is only one micellar-layer thick. The spacing between features is *ca.* 48 nm but the pattern formed is not as regular as those formed by nanophase separation [20]. Small angle x-ray scattering (SAXS) studies (figure 1(C)) do not indicate good ordering but weak scattering in the regions where features might be expected from a hexagonally packed arrangement are observed in figure 1(C). The observation of scattering confirms the spacing of *ca.* 48 nm and the micellar nature of the system (since the observation of x-ray scattering requires more electron density contrast than provided by microphase separation of the polymers). A representation of the formation process is shown schematically in figure 2. The polar hydrophilic P4VP groups are sequestered in the micelle core and hydrophobic PS groups form the micelle corona (figure 2(A)). On the substrate surface these form hemispheres (figure 2(B)) because of the favorable interaction (wetting) of the corona with the substrate.

Other authors [21,22] have shown that inversion of the BCP micelle formed in non-polar solvents such as toluene can occur under very strong acidic conditions and novel toroid-like structures form. Here we demonstrate that micelle inversion and formation of toroid structures can occur under mild hydrophilic solvent atmospheres such as methanol and ethanol. For toroid formation it is necessary to reduce the hydrophobicity of the surface and we only observed formation on the gold coated and nitrided substrates. Typical data are shown in figure 3. A concentration of 0.3 wt % polymer in solution produces densely packed toroids with highly regular dimensions on the SiO_xN_y (figure 3(A) and (B)) and gold-coated substrates (figure 3(C)). The inner diameter of the toroid is *ca.* 18.5 nm with an outer diameter of *ca.* 49 nm indicating that the micelle size is largely unchanged upon inversion. A height profile across the diameter of the toroids is shown in figure 3(D) indicates the toroids are around 30 - 40 nm in height. It also suggests that the centre of the toroid is void.

The micelle form including a void at the centre is shown schematically in figure 2(C). A resultant toroid structure is proposed in figure 2(D). It is suggested that the expected spherical shape of the micelle in solution is ‘flattened’ by interaction with the surface. Figure 2(E) displays a simple schematic of the toroids at the surface. It should be noted that in order to form toroids under these mild conditions it is necessary to use a hydrophilic solvent and substrate combination.

4. Conclusions

The importance of the solvent annealing method can also not be overstated. Simple spin-coating combined with vacuum or air annealing does not yield these structures. This is extremely important if these BCP systems are to provide a practical method of forming highly regular nanopatterns for creation of ultra low dimension circuitry. The toroids may also be of importance because the centre of the shape may allow creation of very small isolated features since this is much less than the repeat distances in the normal hexagonal structures formed upon microphase separation. The presence of the vapour during solvent annealing clearly stabilizes micellar structures allowing these non-equiilibrium morphologies to form. These results underline emerging evidence that the method of solvent annealing of BCP films provides greater control of nanostructure than can be achieved by more direct thermal methods.

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Figure 1

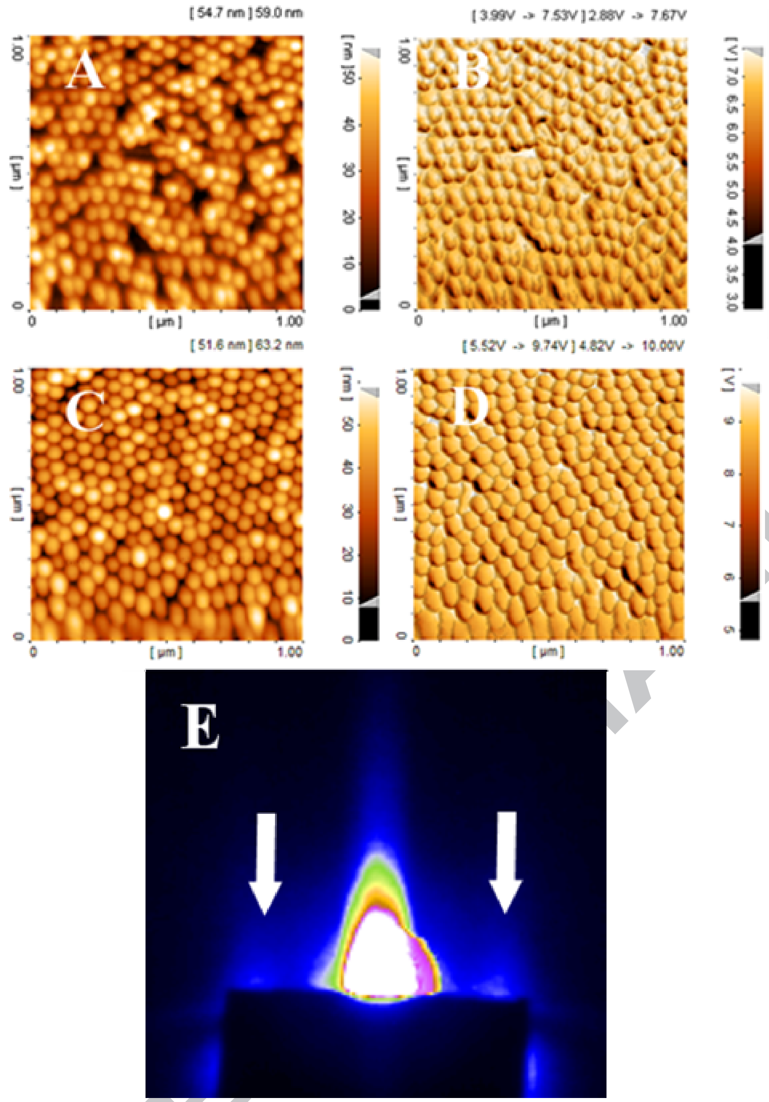

Figure 1: Tapping mode AFM images of as-cast PS-*b*-P4VP1 thin films spin-coated from toluene solutions onto SiO_x ((A) = topographic and (B) = phase image) and $SiO_x N_y$ ((C) = topographic and (D) = phase image) terminated substrates. (E) is a SAXS profile of the films in (A) and (B). The white arrows indicate weak (1,0) scattering.

Figure 2

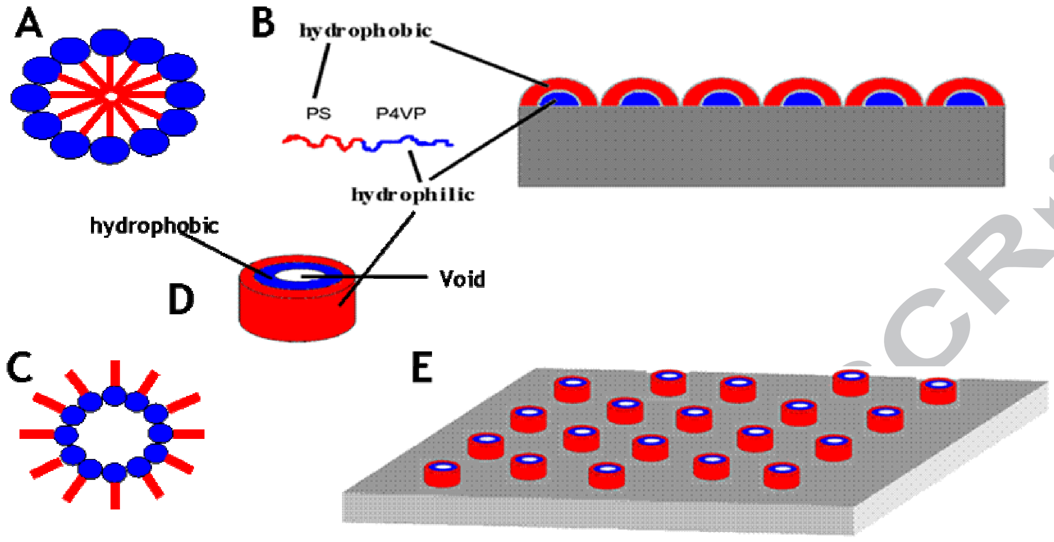

Figure 2: Schematic of film formation in these systems. (A) is the micelle formed in non-polar solvents with the inner 'tails' representing the hydrophobic PS groups and the outer 'heads' representing the more hydrophilic P4VP group. (B) These micelles form hemispheres upon spin coating onto the surface. (C) is the inverse structure where the hydrophobic PS groups form the exterior of the micelle. (D) is a representation of the suggested form of the toroid and (E) their distribution across the surface.

Figure 3

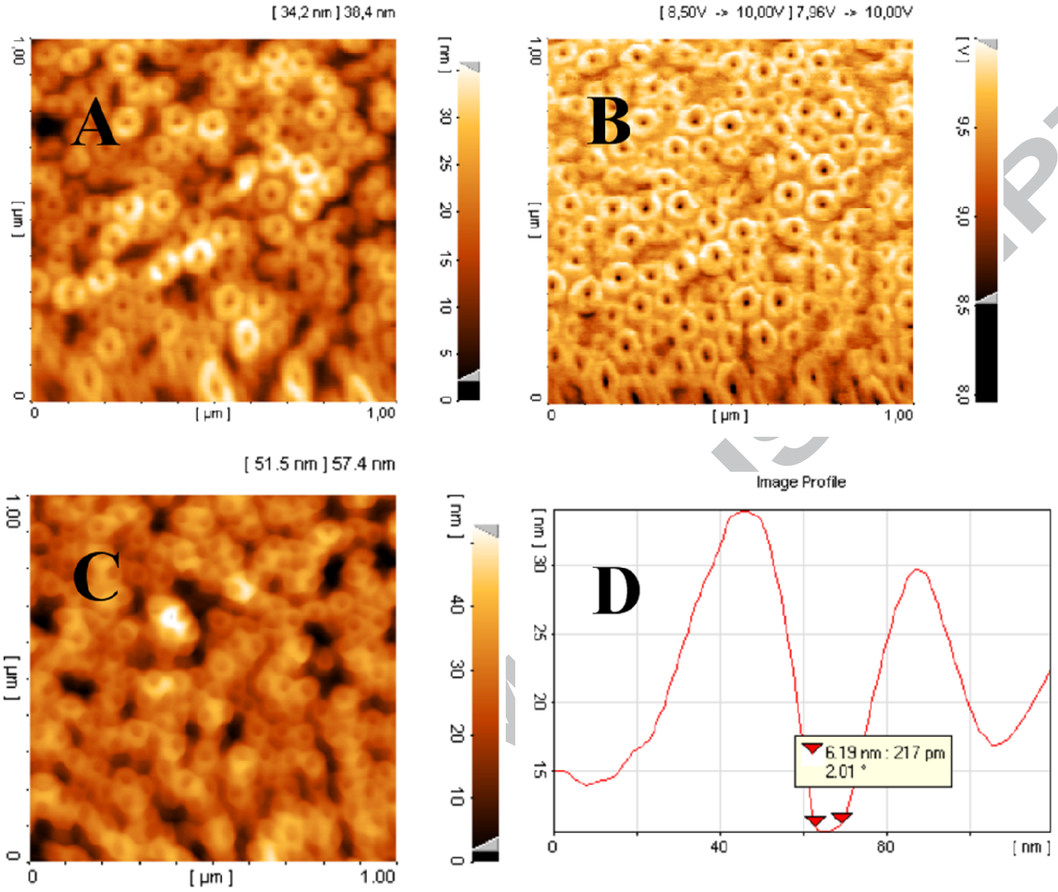

Figure 3: Tapping mode AFM images of toroids formed from PS-*b*-P4VP. (A) and (B) are topographic and phase images of PS-*b*-P4VP2 toroid structures on SiO_xN_y. (C) is a topographic image of PS-*b*-P4VP1 toroid structures on a gold coated substrate. (D) is a height profile across the circumference of an isolated toroid formed as described in (A).

Graphical Abstract

A polystyrene-*block*-poly(4-vinyl pyridine) diblock copolymer (PS-*b*-P4VP) has been used to create nanosized toroid-like structures on substrates *via* simple solvent annealing.