

Preparation and morphology control of amphiphilic block copolymer thin films using mixed solvent vapors



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ABSTRACT

A well-defined amphiphilic diblock copolymer, poly[*N,N*-(dimethylamino)ethyl methacrylate]-block-polystyrene (PDMAEMA-*b*-PS), was synthesized using activators regenerated by electron transfer atom transfer radical polymerization. The formation and transition of morphologies in PDMAEMA-*b*-PS thin films annealed under the vapors of water, tetrahydrofuran, and their binary mixed solvents were first investigated by using atomic force microscopy and scanning electron microscopy. By changing the composition of the annealing solvent, morphological evolution with increasing vapor preferential affinity was observed. A vertical nanocylinder structure forms in the PDMAEMA-*b*-PS thin film when it is annealed under a mixed solvent vapor with $\Delta\chi \sim -0.975$ having a strong preferential affinity for the minority PDMAEMA block at ambient temperature. The self-assembly of PDMAEMA-*b*-PS thin films provides a new convenient way to fabricate stimuli-responsive substrates with potential applications in adhesion control, wetting, and binding or release of functional molecules at surfaces.

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1. Introduction

Block copolymers (BCPs) have attracted considerable attention for their ability to self-assemble into a variety of periodic structures with a characteristic length scale of tens of nanometers [1–3]. Block copolymer thin films are particularly interesting because of their ability to form predetermined periodic structures with a high degree of ordering via self-assembly for emerging nanotechnologies, including organic optoelectronics [4,5], porous membranes [6,7], magnetic storage media [8], and plasmonic nanophotonics [9]. Compared to bulk systems, surface energetics and confinement effects strongly influence the self-assembled morphologies in thin films [10,11]. Thus, many strategies for substrate surface modification [12,13] and controlled annealing conditions [14,15] have been used to control the morphology and nanostructure orientation of BCP thin films.

Recently, stimuli-responsive BCP films, which undergo phase transitions in response to an external stimulus, have been extensively researched in adhesion control, wetting, and binding or release of functional molecules [16–18]. Poly[*N,N*-(dimethylamino)ethyl methacrylate] (PDMAEMA) is both pH- and

temperature-responsive and has been vigorously investigated and targeted as nucleic acid carriers [19,20] and gene delivery systems of transfection agents [21,22]. The pH- and temperature-sensitive behaviors of BCPs containing PDMAEMA and polystyrene (PS) have been studied in aqueous solutions [23–25]. However, there is no systematic report on the self-assembly of PDMAEMA-*b*-PS in thin films, which should offer interesting properties because PS is hydrophobic, and PDMAEMA is hydrophilic and multiply stimuli-responsive.

Generally, the order in thin films of block copolymers can be induced by thermal annealing or solvent annealing [26–28]. However, crosslinking reactions can take place in PDMAEMA samples during heating. There are two primary explanations. Firstly, free radicals can be generated when the amine functionality in the polymer interacts with a free-radical initiator. Secondly, the peroxidic impurities can react with tertiary amino groups of polymers [29]. Therefore, solvent annealing provides an attractive alternative to thermal annealing for controlling the morphologies of PDMAEMA-*b*-PS thin films.

Solvent annealing has been applied more and more widely in recent years [30,31]. However, the mechanism of this approach still remains unclear because the relevant experimental parameters governing the resultant BCP morphologies, such as the nature of the solvent, the relative solvent vapor pressure, and the annealing time, are usually complex and difficult to control. Among these factors, the nature of the solvent is of crucial importance [31], which

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influences the degree of swelling of each block and thus has a significant impact on the self-assembled morphologies in thin films [32,33]. BCP thin films annealed under different solvents result in different morphologies and orientations [32–34].

In this work, we synthesized a series of asymmetric PDMAEMA-*b*-PS block copolymers with different molecular weights (MWs) through the activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) method. The morphologies and morphological transitions of the PDMAEMA-*b*-PS diblock copolymer thin films annealed under the vapors of H₂O, tetrahydrofuran (THF), or their binary mixed solvents were systematically investigated for the first time utilizing atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Tris[2-(dimethylamino)ethyl]amine (Me₆TREN, Sigma-Adrich, 98%) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Sigma-Adrich, 98%) were used as received. Styrene and *N,N*-(dimethylamino)ethyl methacrylate (DMAEMA, Beijing Chemical Reagents Co., A.R.) were passed through a column filled with basic alumina and distilled under reduced pressure. Anisole was purified by washing with sodium hydroxide to remove residual phenol, followed by washing with water, and then it was dried with anhydrous calcium chloride and finally distilled. *N,N*-Dimethylformamide (DMF), chlorobenzene, and THF (Beijing Chemical Reagents Co., A.R.) were used after distilled. CuCl₂ (Beijing Chemical Reagents Co., A.R.) and tin(II) 2-ethylhexanoate (Sn(EH)₂, Sigma-Adrich, 98%) were used as received. 2,2,6,6-Tetramethylpiperidinoxy (TEMPO) was purchased from Acros Organics and used as received. CuBr (Beijing Chemical Reagents Co., A.R.) was purified by washing with acetic acid, followed by washing with methanol, and then it was dried for use.

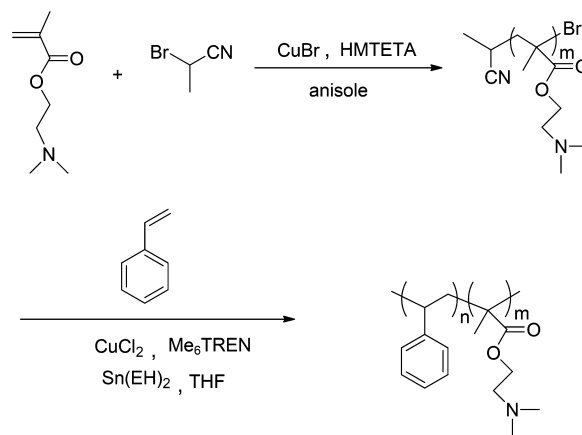
2.2. Synthesis of the macroinitiator

2-bromopropionitrile-terminated PDMAEMA (PDMAEMA-Br)

The monomer DMAEMA (3.00 mL, 18.0 mmol), 2-bromopropionitrile (4.87 μL, 56.4 μmol), CuBr (8.08 mg, 56.4 μmol), HMTETA (46.0 μL, 169 μmol), and anisole (5.0 mL) were charged into a polymerization tube. After being stirred and degassed by three freeze–pump–thaw cycles, the tube was sealed under vacuum and subsequently immersed into an oil bath thermostated at 50 °C for 5 h. It was then quenched in liquid nitrogen and taken out to ambient condition. The solution was passed through a neutral alumina column to remove copper salt. Finally, the polymer was precipitated out in a large volume of petroleum ether and dried in vacuum overnight with a yield of 83%. Fig. S.1a in supporting information is the representative ¹H NMR spectrum of PDMAEMA-Br in CDCl₃. Peaks at 2.28 ppm are assigned to the resonance signals of protons of the methyl group in PDMAEMA. Peaks at 2.55 and 4.05 ppm are assigned to the protons of —OCH₂CH₂N< of PDMAEMA-Br.

2.3. Synthesis of PDMAEMA-*b*-PS through ARGET ATRP

The copolymerizations of DMAEMA with styrene have been studied using reversible addition fragmentation chain transfer (RAFT) polymerization [35] and ATRP method [36] in literatures. To the best of our knowledge, there is no report on the copolymerization of DMAEMA with styrene using ARGET ATRP techniques. ARGET ATRP, a new initiation process for a controlled/“living” radical polymerization, has been developed by Matyjaszewski



Scheme 1. Synthetic route of PDMAEMA-*b*-PS diblock copolymers.

et al. [37,38]. This method allows an ATRP process to be conducted with a very active copper catalyst at a significantly low concentration (several ppm) in excess of an appropriate reducing agent. In a typical experiment for polymerization (Scheme 1), styrene (3.99 mL, 35.0 mmol) and THF (15.0 mL) were charged into a polymerization tube. Then, PDMAEMA-Br (0.735 g, 0.0350 mmol) and a solution of CuCl₂ complex (0.612 mg, 4.56 μmol)/Me₆TREN (1.17 μL, 4.56 μmol) in DMF (0.6 mL) were added. The resulting mixture was degassed by three freeze–pump–thaw cycles. After the mixture was melted, a solution of Sn(EH)₂ (18.5 mg, 45.6 μmol) and Me₆TREN (11.7 μL, 45.6 μmol) in DMF (0.6 mL) was added. The mixture was stirred and degassed by three freeze–pump–thaw cycles, and then the tube was sealed under vacuum and subsequently immersed into an oil bath thermostated at 90 °C. The polymerization was stopped after 12 h by exposing the catalyst to air, diluted with THF, filtered through a neutral alumina column, and precipitated into petroleum ether. The block copolymer was dried under high vacuum; the yield was 3.39 g (78%). Fig. S.1b in supporting information shows a typical ¹H NMR spectrum of PDMAEMA-*b*-PS in CDCl₃. Peaks at 2.55 and 4.05 ppm are assigned to the resonance signals of protons of —OCH₂CH₂N< in the PDMAEMA block. Peaks at 6.4–7.2 ppm are assigned to the aromatic protons of the PS block.

2.4. Synthesis of PDMAEMA-*r*-PS random copolymer through TEMPO-mediated living free radical polymerization

A hydroxyl end-functionalized random copolymer of styrene and DMAEMA, PDMAEMA-*r*-PS, was synthesized in bulk by means of a TEMPO “living” free radical polymerization [39] (Scheme S1 in supporting information). In a typical polymerization, DMAEMA (2.00 mL, 12.0 mmol), styrene (3.00 mL, 30.0 mmol), hydroxyl-functionalized 2,2,6,6-tetramethylpiperidinoxy (14.0 mg, 0.0500 mmol), and chlorobenzene (5.0 mL) were charged into a polymerization tube. After the mixture was stirred and degassed by three freeze–pump–thaw cycles, the tube was sealed under vacuum and subsequently immersed into an oil bath thermostated at 130 °C. The polymerization was stopped after 5 h by exposing to air. The resulting mixture was diluted with chlorobenzene and precipitated into petroleum ether. The random copolymer was dried under high vacuum with a yield of 81%. Fig. S.2 in supporting information is a representative ¹H NMR spectrum of the PDMAEMA-*r*-PS random copolymer.

A PDMAEMA-*r*-PS-grafted substrate was used as a neutral surface for the PDMAEMA and PS blocks. This is a simple technique for controlling the interfacial energies and wetting behaviors of polymers in contact with solid surfaces [40–42].

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