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Solvent vapor induced morphology transition in thin film of cylinder forming diblock copolymer

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ABSTRACT

The morphology formation and transition of thin film of a cylinder-forming polystyrene–*block*–poly(methyl methacrylate) (PS–*b*–PMMA) diblock copolymer annealed under 1,1,2-trichloroethane (Tri-CE), toluene (Tol), and their binary mixed solvent vapors is investigated by using optical microscopy (OM) and transmission electronic microscopy (TEM). By modulating the annealing solvent vapor pressure and the preferential affinities, a detailed morphology evolution with increasing the vapor pressure and a series of morphologies depending on the preferential affinities have been observed. A phase diagram by plotting the morphologies as a function of the annealing solvent vapor pressure and its preferential affinity is subsequently constructed.

1. Introduction

Block copolymers, which consisting of two different polymer molecules linked end-to-end by a covalent bond, have become the subject of considerable attention for their ability to self-assemble into complex periodic structures with a characteristic length scale of tens of nanometers [1–7]. The key in the use of block copolymers is the control over the orientation and lateral ordering of the morphologies in thin films [8].

Generally, the order in thin films of block copolymers is usually induced by the way of thermal annealing and solvent annealing. For thermal annealing, there usually only exists a small window between the T_g and the degradation temperature of the involved blocks which are usually susceptible to thermal degradation [9]. For these systems, solvent annealing provides an attractive alternative to thermal annealing. Since sufficient mobility of the block chains is easily induced at room temperature without the danger of degradation in solvent annealing [10–14], the approach of solvent annealing has been used more and more widely in recent years [15–20]. However, the details of solvent annealing remain rather unclear since the relevant experimental parameters governing the resultant block copolymer morphologies (nature of the solvent, the relative solvent vapor pressure, the annealing time, etc.) are usually complex and difficult to control. Among these factors, the nature of the solvent [11,17,21–23] and the relative solvent vapor pressure [9,10,13,17,24–26] are crucial. The nature of the solvent influences the degree of the swelling of each block and accordingly has severe effects on the resulting block copolymer morphologies [17,22,23]. It has been shown that block copolymer thin films annealed under different selective solvents and nonselective solvents result in different morphologies and orientations [11,17,22,23]. On the other hand, once a solvent is selected, the solvent vapor pressure is the key factor to control the resultant morphologies. A lot of methods have been used in reported works to control the solvent vapor pressures, such as the use of the flow of N_2 [10,13,24,25], vary the amount of solvent in reservoir [17], close the lid of dish more or less tightly [9], and change the ratio between the surface area of the solvent and the empty volume of the annealing chamber [26]. More recently, Lu et al. [27,28] reported a novel controlled solvent vapor pressure annealing (C-SVA) method which can control the solvent vapor pressure easily and precisely, and have created homogeneous and reproducible fullerene nanorods in thin films successfully.

In the present work, the morphology transition of a cylinder-forming PS–*b*–PMMA diblock copolymer thin films annealed under Tri-CE, Tol, and their binary mixed solvent vapors with different vapor pressures by the way of C-SVA is systematically investigated. In our previous work [29], the morphology transition of a similar PS–*b*–PMMA diblock copolymer at different block copolymer concentration cast from 1,1,2,2-tetrachloroethane has been studied. With the solution becoming concentrated, disordered spheres, inverted spheres, inverted cylinders, inverted hexagonally perforated lamella, lamella and finally normal cylinder in turn have been obtained by freeze-drying method. However, because of the

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limitations of the freeze-drying method, the copolymer concentration increases rapidly as the amount of solvent decreases, especially at relative higher concentrations, it is difficult to trap the morphology of the diblock copolymer in detail. Here, the C-SVA is an effective method in which the solvent vapor pressure can be controlled precisely and stably (from saturated pressure (P_0) to close to zero) [27,28], the morphology transition at higher block copolymer concentration can right be easily implemented. Meanwhile, both Tri-CE and toluene has similar volatility and opposite preferential affinity for the PS and PMMA blocks, which makes it is easy to modulate the preferential affinity of the binary mixed solvent vapors simply by changing the mixed volume fraction of two solvents, Tri-CE and toluene. By precisely controlling solvent vapor pressure and solvent vapor preferential affinity, the evolution of morphologies of solvent vapor annealed PS–*b*–PMMA thin films has been understood in detail, which will offer a good reference in modulating the morphology of block copolymer thin films.

2. Experimental

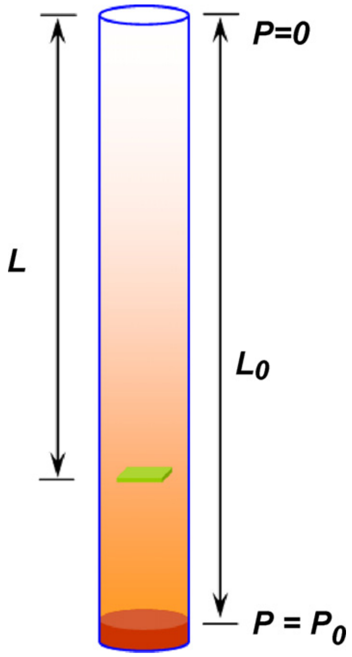
2.1. Materials

An asymmetric diblock copolymer used in this work PS_{1411}–*b*–$PMMA_{540}$ (the numbers in subscript refer to the number-average degree of polymerization of each block) with polydispersity index 1.10 was purchased from Polymer Source Inc. and used as received. In bulk state, the block copolymer adopts hexagonally packed PMMA cylinders with a center-to-center distance (the period L_0) about 65 nm embedded in a PS matrix [30].

2.2. Sample preparation

Block copolymer films were prepared by dissolving the sample in 1,1,2-trichloroethane (Tri-CE) to yield 10 mg/ml solution and spin-coating the solution onto carbon-coated mica at 2000 rpm for 30 s. The thickness of the films is approximately 70 nm as measured by transmission electronic microscopy (TEM) cross-sectional observation.

For the experiment of controlled solvent vapor pressure annealing (C-SVA), the fresh spin-coated films were suspended at different height in a long glass tube (6 cm in diameter and 160 cm in height) containing Tri-CE, Tol, and their binary mixtures at the bottom respectively, as shown in Scheme 1. The characteristics of the annealing solvents are listed in Table 1, and the calculated polymer–solvent interaction parameters (χ) for different pairs of polymers and solvents at room temperature are shown in Table 2. Upon achieving an equilibrium state through the diffusion of solvent vapor within the tube, a gradient distribution of solvent vapor pressure along the tube is constructed, from saturated pressure (P_0) at the bottom to close to zero at the top. Note that the performance should be done carefully so as to avoid interrupting too much to the vapor diffusion equilibrium in the tube. After being exposed to the solvent vapor for 24 h, the films were removed from the glass tube as quickly as possible and air-dried at room temperature to make the residual solvent in the film volatize instantaneously and accordingly to preserve the morphology formed during the annealing process in the film. The period 24 h of the film exposure to solvent vapor is sufficient to make the film form a morphology matching a certain circumstance of the solvent vapor. And the morphology did not change with further prolonging the annealing time within the time scale of experiment ~48 h.



Scheme 1. Schematic diagram of experimental setup used for C-SVA. L_0 is the effective length given by distance from the up edge of the setup to the surface of the annealing solvent at the bottom of the tube. The actual value of L_0 in this work is 160 cm so as to achieve a stable and highly resolved gradient of solvent vapor pressures P. L is the distance from the up edge of the setup to the specimen position. Solvent vapor pressure is given by $P = (L/L_0)P_0$.
This scheme is from Ref. [27].

Table 2
Polymer–solvent interaction parameters (χ) calculated from different pairs of polymers and solvents.

	PS	PMMA
Tri-CE	0.448	0.385
Tol	0.344	0.374

Calculated from $\chi_{P\text{–}S} = V_S(\delta_S - \delta_P)^2/RT + 0.34$ [31,32], where P represents polymer, S represents solvent, V_S is the molar volume of solvent, R is the gas constant, T is the temperature, and δ_S and δ_P are the solubility parameters of the solvent and polymer respectively.

2.3. Instruments

The morphologies of the films were examined by optical microscopy (OM) and transmission electronic microscopy (TEM). The surface topographies of films were investigated by optical microscopy (OM). OM experiments were carried out by using a Carl Zeiss A1m microscope equipped with a CCD camera. A

Table 1
Characteristics of the solvents.

	Solubility parameter[a] δ (J/cm^3)$^{1/2}$	Molar volume[b] V (cm^3/mol)	Boiling temperature[b] T_b (°C)	Vapor pressure[b] (kPa)
Tri-CE	20.3	92.5	114	4.80 (30 °C)
Tol	18.3	106.3	111	4.00 (26 °C)

[a] Obtained from polymer handbook 4th edition [31].
[b] Obtained from solvents handbook 4th edition [52].