Evolution of Microphase-Separated Structures upon High Temperature Annealing in Block Copolymer Thin Films Studied by Transmission Electron Microtomography

Ken-ich Niihara¹, Yukihiro Nishikawa¹, Toshio Nishi² and Hiroshi Jinnai^{1,*}

¹Department of Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto 606-8585, Japan Fax: 81-75-724-7800, e-mail: hjinnai@kit.ac.jp

²Department of Organic and Polymeric Materials, School of Science and Engineering, Tokyo Institute of Technology, 2-12-1,

Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

*: To whom correspondence should be addressed

Abstract: Evolution of microphase-separated structures of poly(styrene-*block*-isoprene) (SI) block copolymer thin films upon high temperature annealing were studied by transmission electron microtomography (TEMT). The thin films were prepared by spin coating from SI benzene solution. The as-spun films were annealed at 120°C for certain period of annealing time, and the three-dimensional (3D) structures in the annealed thin films were observed by TEMT. It was found that the as-spun film had complicated structure, each phase of which was continuous in the 3D space. It looked much alike the bicontinuous structure found during the spinodal decomposition of polymer blends. Upon annealing the thin films, the bicontinuous-like structure gradually transformed into a "column-like" structure in which cylindrical polyisoprene (PI) phases bridge the upper and lower PI wetting layers. The size of the columns had lower and upper limits that were governed, respectively, by the hydrodynamics and block chain conformation.

Key words: Block copolymer thin films, Transmission electron microtomography, Microphase-separated structure, Young-Laplace equation

1. INTRODUCTION

Block copolymers exhibit periodic nanostructures due to immiscibility between the dissimilar (A and B) sequences in mesoscopic dimensions. The presence of external interfaces can significantly influence the resulting microdomain morphologies, especially in thin films, as the component with the lowest interfacial energy may accumulate at the respective interface, thereby aligning the microdomains [1]. In symmetric diblock copolymers, if the lamellar spacing is not commensurate with the thickness of the film, either holes or islands are formed and nucleated on the film surface in order to adjust the local film thickness to the preferred quantized value ("thickness quantization") [1,2].

Although a considerable number of studies have been carried out on thermally equilibrium thin films of block copolymers [3-5], less is known about the process of self-assembly in thin block copolymer films. Moreover, not much information about the formation of the quantized holes (or islands) is available.

In the present work, we explore the evolution of the microphase-separated structure in thin films upon annealing at a temperature above glass transition temperature. The nano-structures at various annealing times were examined by transmission electron microtomography (TEMT) [6] in order to obtain structural information not only lateral but also depth directions of the thin film. Final equilibrated morphology of the block copolymer thin film was

clarified with TEMT and the structure mechanism of self-assembly will be discussed.

2. EXPERIMENT

2.1. Materials

Poly(styrene-block-isoprene) block copolymer (SI) was purchased from Polymer Source, Inc. The weight average molecular weight (M_n) of PS and PI blocks were 135,000 and 131,000, respectively. Volume fraction of PI in the SI copolymer is 0.49. The molecular weight distribution, M_w/M_n , for the diblock copolymer is 1.10.

2.2. Sample preparation

Copolymer films (ca. 120 nm thick) were prepared by spin coating from 2.0wt% benzene solution of the copolymers onto a mica substrate. The mica was cleaved, and then coated with carbon by vacuum deposition. The copolymer films on the substrates were further annealed at 120°C for 404, 1440, and 5134 minutes under vacuum. The annealed sections were floated off the mica substrates and were picked up onto Cu mesh grid. Transmission electron microscopy (TEM) observations have been carried out with these grids (see Fig. 1 later). In cases that cross-section(s) of the thin films were examined, the floated-off thin films described above were picked up onto epoxy block, instead of Cu mesh grid, and subsequently ultramicrotomed at room temperature ("cross-sectional sections"). The cross-sectional sections were put on the Cu mesh grid for TEMT investigations. All the sections were stained with OsO_4 vapor for 1 hour to enhance the contrast under TEM and TEMT.

2.3. Transmission Electron Microtomography

TEM and TEMT experiments were performed with JEM-2200FS (JEOL, Co. Ltd., Japan) operated at 200 KV. The digital data of the transmitted images were collected with a slow-scan CCD camera (Gatan USC1000, Gatan Inc., USA). Note that only the transmitted and elastically scattered electrons (electron energy loss of 0 ± 15 eV) were selected by an energy filter installed in JEM2200FS (Omega filter, JEOL Ltd., Japan) in order to obtain achromatic projections. Prior to TEMT observations, the gold particles of 5 nm diameter were placed on the ultrathin sections using the gold colloidal solution (GCN005, BBInternational Ltd, UK). The gold particles were used as fiducial markers for the alignment of the tilt series of the TEM images. A series of TEM images with 1024 x 1024 pixels were acquired at tilt angles ranging from -60° to +60° in 1° increments. Subsequently, the tilt series of the TEM images (121 images) were aligned by fiducial marker method [7] and then reconstructed on the basis of the filtered-back-projection method [8].

2.4. Atomic Force Microscopy (AFM)

The thin film annealed for 5134 min was subjected to AFM observation in order to examine the surface structure on the free surface. The height image of the thin film with mica substrate was obtained by Nanoscope III (Digital Instrument, Inc., US) operated with tapping mode.

3. RESULTS

3.1. TEM observations of SI block copolymer during annealing

The microphase-separated structure in a bulk state of the SI block copolymer was typical lamellae as displayed in Fig. 1. The lamellar domaind spacing was estimated to be 110 nm form this image. Thus, in this study, the thickness



Fig.1 TEM micrograph of a ultrathin section of the bulk sample, stained with OsO_4 . Dark phase corresponds to PI phase. Bar represents 400nm.



Fig.2 TEM micrographs of the thin films stained with OsO_4 after annealing at 120°C for (a) 0min, (b) 404min, (c) 1440min, and (d) 5134min. Bicontinuous-like microdomains are dominant in (a)-(c), and island-like structures of PI phase grow with annealing time [(c)-(d)]. Eventually, only island-like structure remains (d). Bar in each micrograph represents 400nm.

of the SI thin films was comparable with the domain spacing. Figure 2 shows TEM images of the SI block copolymer thin films as a function of annealing time, t. The microphase-separated structure right after the spin coating (as-spun film) is shown in Fig. 2(a), in which both dark phase (PI microdomain) and bright phase (PS microdomain) exhibited continuous domains with certain periodicity (ca. 80 nm). The morphology was analogous with the bicontinuous structure found in the spinodal decomposition (SD) of polymer blends [9]. The structure gradually changed from such continuous-type to islands-in-sea type morphologies with increasing t. The volume fraction of PI microdomain, ϕ_{PI} , at each t, roughly estimated from the TEM micrographs, decreased from 0.51 (t=0, as-spun film) to 0.20 (t = 5134 min.). According to the intrinsic volume fraction of the diblock copolymer, ϕ_{Pl} should be around 0.5. The decrease of ϕ_{PI} indicated formation of PI wetting layer at surfaces (the mica substrate and/or free surface) because the wetting layer(s) perpendicular to the optic axis of the microscope would not appear under TEM's geometry. In order to clarify those ambiguities, 3D structure at each annealing time was examined by TEMT.

3.2. TEMT observations of SI block copolymer during annealing

Figure 3(a) shows 3D image of the as-spun film in which the PI microdomain was continuous not only in lateral direction (direction parallel to the film surface, x - y plane) but also in depth direction (x - z and x - z planes), demonstrating that the microphase-separated structure right after the spin coating was



Fig.3 3D reconstructions of the thin films after annealing at 120°C for (a) 0min (b) 404min (c) 1440min (d) 5134min. White phase corresponds to PI phase. x - ycorresponds to lateral direction of the thin film. zdirection corresponds to depth direction of the thin film. White bars represent 200 nm.

"bicontinuous". ϕ_{PI} evaluated from the 3D reconstruction shown in Fig. 3(a) was 0.48, in excellent agreement with the known composition of the copolymer, i.e. 0.49. These results indicated no wetting layer was formed in the as-spun film.

We here note that the y-axis corresponds to the tilt-axis in the TEMT experiments. In the conventional TEMT experiments, electron beam was directed along z-axis and, if the wetting layer lies perpendicular to the z-axis, the wetting layer would not appear in the 3D reconstruction [10]. In order to make sure that the wetting layer will be reconstructed in TEMT experiments, the cross-sectional sections were tilted in the microscope instead of tilting the thin film, which we hereafter call "Cross-sectional TEMT" as opposed to the conventional TEMT.

Figures 3(b), 3(c) and 3(d) show 3D reconstructions at three different t, from which it was observed that lateral continuity of the bicontinuous microdomains gradually lost while perpendicular continuity persisted throughout the annealing [see also Figs. 2]. Eventually, the microphase-separated structure was transformed into "column-like" structure in which cylindrical PI phases bridge the upper and lower PI wetting layers [Fig. 3(d)]. Note that ϕ_{PI} took constant values around 0.5 regardless of t. A quite similar trend was observed in a phase separation process (SD) of a polymer blend in a confined space [11]. In the case of polymer blend, the structural transformation occurred when the domain periodicity, Λ_m , matched thickness of the sample, D. Thus, the domain periodicities of the SI thin films both in the lateral and in perpendicular to the film surface, denoted Λ_{ml}

and $\Lambda_{m,p}$ respectively, were evaluated from the 3D reconstructions. $\Lambda_{m,l}$ was estimated either from a peak position of the structure factor or from a chord length [12] at maximum frequency in its histogram. The structure factor, S(q), was obtained from the 3D image by 3D Fourier transformation. S(q) was then averaged in the $q_x - q_y$ plane, where q_x and q_y denote respectively the x and y axes in Fourier space [9,13].

 $\Lambda_{m,p}$ was estimated from a concentration variation of PI along the depth direction (z direction), $\phi_{PI,z}$. As displayed in Fig. 4(a), $\phi_{PI,z}$ fluctuated as a function of z and $\Lambda_{m,p}$ was defined as the wavelength of $\phi_{PI,z}$.

In Fig. 4(b), both $\Lambda_{m,l}$ and $\Lambda_{m,p}$ are plotted against t in a semi-logarithmical way. $\Lambda_{m,p}$ gradually increased with t until it reached the film thickness (indicated by a gray horizontal bar) of the specimen, while $\Lambda_{m,l}$ was almost time-independent in the beginning at ca. 80 nm and then rapidly increased with t. According to



Fig.4 (a) Area fraction of PI, $\Phi_{PI, Z}$, in X - yslice of the 3D volume obtained by TEMT plotted against the distance from the substrate. $\Lambda_{m,p}$ is domain spacing of the thin film in the perpendicular direction to the substrate. (b) Domain spacing of perpendicular, $\Lambda_{m,p}$, and lateral, $\Lambda_{m,l}$, direction plotted against the annealing time. (c) Interface area per unit volume, S/V, measured from 3D volume obtained by TEMT plotted against the annealing time.

the previous study concerning the confined polymer blend, the structural transformation occurred when a scaled thickness, D/Λ_{ml} , approached unity [11]. From Fig. 4(b), this condition was met at $t \approx 1800$ min, above and helow which the microphase-separated morphologies of the SI thin films were surely column-like and bicontinuous structures, respectively. In this regard, the block copolymer thin film showed quite similar structure evolution as the polymer blend thin film. Note that, although the annealing process of the SI thin film studied here is a process in which the trapped non-equilibrium morphology due to the spin coating gradually relaxes to the equilibrium structure, it is intriguing that the process has some similarity to the typical non-linear and non-equilibrium phenomena such as the SD in polymer blend systems.

Another important structural parameter, interface area per unit volume, S/V, was plotted against t in Fig. 4(c). S/V decreased with t until 1800 min and stayed afterwards. It is likely that the structural transformation was driven by the decrease of S/V, as observed in the phase-separating polymer blends [11].

4. DISCUSSION

4.1. Transformation from bicontinuous to column-like morphology

now consider Let us how the microphase-separated structure transforms from the initial bicontinuous structure (free from surface effects) to the configuration strongly influenced by the preferential wetting of the surfaces by one component of the block copolymer (PI, in this case). It is very likely that the hydrodynamics due to the capillary instability [14] plays a crucial role in the annealing process under the influence of wetting. The wettability is important mainly in the very initial stage to



Fig.5 (a) A schematic illustration of growing and disappearing columns. D and a are, respectively, a film thickness and a radius of a column-like PI microdomain. (b) Histogram of the columns diameter (2a) at 5134 min. The upper limit and the lower limit of diameter were 132 nm and 496 nm, respectively.

establish the initial configuration where the surface is covered by the wetting layer ($t \sim 404$ min), to which the bicontinuous tubes are connected. This initial configuration establishes the anisotropic pressure gradient from the bicontinuous tubes to the wetting layer. The interconnectivity of the bicontinuous morphology allows the hydrodynamic pumping of fluid into the wetting layers. Thus, the more wettable phase (PI phase) is transported into the wetting PI layer in a very efficient manner. Eventually, tubes start to bridge the two wetting layers and form disk-like columns.

As discussed in the following section (Sec. 4.2.), only the columns whose lateral size is larger than the thickness of the section can grow, while all the other small columns just disappear [15].

4.2. Equilibrium structure in SI thin film

The micro-phase separated structure of the SI block copolymer thin film did not significantly change for further annealing (than t=5134 min) and the structural parameters, e.g., S/V and $\Lambda_{m,p}$, have become more or less time-independent [See Fig. 4]. Therefore, it is very likely that the morphology at t=5134 min was an equilibrium one. This equilibrium structure consists of three layers and columns: two PI wetting layers at the substrate and free surface, PS layer in between them, and cylindrical PI phases bridging the upper and lower PI wetting layers [Fig. 3(d)]. It is intriguing that this structure is quite similar to that observed in the phase-separating polymer blends [15].

Let us now consider stability of the columns by the pressure difference between a column and the wetting layer, ΔP , following the similar discussion in phase-separating polymer blends [15]. ΔP is characterized by the following Young-Laplace equation [16]:

$$\Delta P \cong \sigma(\kappa_1 + \kappa_2) \quad . \tag{1}$$

 σ is the interfacial tension between the two phases, κ_1 and κ_2 are the principal curvatures of the interface. ΔP of the column between PS and PI phases can be expressed by the following equation.

$$\Delta P \cong \sigma \left(-2/D + 1/a \right), \tag{2}$$

where the longitudinal curvature of the column is ca. -2/D, and its transverse curvature is 1/a. The sign of ΔP is governed by the sign of -2/D + 1/a, and hence by the balance of D/2 and a. As schematically illustrated in Fig. 5(a), the column bridging the two walls, whose radius a is larger than D/2 ($\Delta P < 0$), starts to thicken over time by absorbing the wetting layers. On the other hand, the column bridging the two walls, whose radius *a* is smaller than D/2 ($\Delta P > 0$), is not formed or disappears. Note that the above discussion is valid in the case of $D \sim \Lambda_{m,l}$. If the thickness of thin-film exceeds $\Lambda_{m,l}$, the microphase-separated structure in the thin film would be different from what we have observed in the present study and hence the discussion using eq. (1) would not be useful. TEMT experiments on thicker film(s) are necessary and are under progress.



Fig.6 Close-up view of y - z cross-section slice of

the column. Dark phase corresponds to PI phase. Black bar represents 100nm. A shallow dent (ca. 10 nm) can be seen at the top of the column.





Fig. 7 (a) Height image of thin film annealed for 5134 min. Bar represents 400nm. (b) Height profile along the line in (a). Triangle markers in (b) correspond to those in (a).



Fig. 8 A schematic illustration of block chain in the column. Solid lines and dotted lines correspond to PI and PS chains, respectively.

Fig. 5(b) shows a histogram of the column diameter evaluated from TEMT and TEM micrographs [Figs. 1(d) and 3(d)]. It was found that the column diameter, 2a, distributed between ca. 130 nm and 500 nm. Concerning the lower limit of the column diameter in the SI copolymer thin film, the system obeys the hydrodynamics, i.e. eq. (2), since the thickness of the film is ca. 120 nm. It is intriguing that the column diameter has not only the lower but also upper limit. We emphasize that this argument concerning the lower limit of the column diameter is *purely* hydrodynamic and thus does not reflect nature of the block copolymer chains. In the case of phase-separating polymer mixtures [11,15], although the column diameter has lower limit due to the hydrodynamics as described above, there would not be such upper limit.

Let us next discuss the upper limit. In Fig. 6, a slice through the reconstruction [Fig. 3(d)] is shown that reveals the PI column and PI wetting layers with great clarity. Note that one of the great advantages of TEMT is that this methodology provides cross-sectional views of 3D objects from any direction: Instead of physically cutting the SI thin film into slices we applied TEMT and obtained truly 3D information on the microphase-separated structure by digital cross-sectioning. Figure 6 shows single y - zslice (1.9 nm thick) in the 3D reconstruction. The upper and bottom sides of the SI thin film were free surface and substrate surface, respectively. It is interesting that the free surface right at the top of the PI column exhibited slight inward curve. A depth of the dent turned out to be ca. 10 nm. The depth of the dents at the free surface was also examined by AFM. Figure 7(a) shows the height image of the thin film. The size of dark islands (PI columns) agreed with the diameter of columns observed by TEMT. The depth of the dark circles was ca. 6 nm, in good agreement with the depth obtained from TEMT.

Since the thin film studied here consisted of block copolymer, we need to consider how to accommodate the block copolymer chains in the thin film. It is commonly known that block copolymers have to place their junctions at the interface. With this restricting condition, the schematic SI block copolymers were displayed in Fig. 8. The dark phase represents PI microdonain in which the PI and PS block chains are drawn as solid and dotted lines, respectively. The contour length of PI block chain is calculated to be ca. 800 nm, and the end-to-end distance, R_0 , of PI and PS blocks are estimated to be 29 and 25 nm, respectively. In addition, the radius of gyration of PI and PS blocks are, respectively, 12 nm and 10 nm. Now, thicknesses of the PI wetting layers at the substrate and free surface were approximately 30 nm, which is comparable to R_0 . Therefore, in the wetting layer, the PI blocks take similar configuration as the Gaussian chains.

In contrast, the block chains in the middle of the thin film, especially the PI blocks, should be considerably elongated as schematically shown by the block copolymers designated as 2 and 3 in Fig. 8. In the column formation upon annealing, there must be a balance between the chain elasticity and the pressure difference described above, from which the column diameter has to be determined. Namely, the hydrodynamics requires the column to become larger but the chain elasticity (entropy) suppresses the column diameter. For example, the block copolymer 3 in Fig. 8 prevents the column growth since the column diameter cannot exceed the contour length of the PI block. This is probably the reason why we observed the upper limit in the column diameter in our SI thin film [Fig. 5(b)]. In addition, although a flat surface is preferred to minimize surface free energy, in order to realize uniform density of the PI segments in the PI microdomain, the free surface of the thin film at the top center of the column has to bend to make the dents [see the block copolymer 2 in Fig. 8].

Acknowledgment

The authors are grateful to NEDO for supporting this study through a Japanese National Project "Nano Structure Polymer Project" by the Ministry of Economy, Trade and Industry. The authors thank Mr. U. Matsuwaki for his help in TEMT experiments.

References

[1] H. Hasegawa, T. Hashimoto, *Macromolecules*, **18**, 589 (1985).

[2] B. L. Carvalho and E. L. Thomas, *Phys. Rev. Lett.*, **73**, 3321 (1994).

[3] G. J. Kellogg, D. G. Walton, A. M. Mayes, P. Lambooy and T. P. Russell, P. D. Gallagher and S. K. Satija, *Phys. Rev. Lett.*, **76**, 2503 (1996).

[4] N. Torikai, Y. Matushita, S. Langridge, D. Bucknall, J. Penfold and M. Takeda, *Physica B*, **283**, 12-16 (2000).

[5] N. Torikai, M. Seki, Y. Matsushita, M. Takeda, K. Soyama, N. Metoki, S. Langridge, D. Bucknall, and J. Penfold, *J. Phys. Soc. Jpn.*, **70**, suppl. A. 344-46 (2001).

[6] H. Jinnai, T. Ikehara, T. Nishi, *Adv. Polym. Sci.*, **170**, 115-167 (2004).

[7] P. K. Luther, M. C. Lawrence, and R. A. Crowther, *Ultramicroscopy*, **24**, 7-18 (1988).

[8] M. Radermacher, "Electron Tomography", Ed. by J. Frank, Plenum, New York, (1992) pp. 91-116.

[9] H. Jinnai, Y. Nishikawa, H. Morimoto, T. Koga, T. Hashimoto, Langmuir, 16, 4380-393 (2000).

[10] J. Frank, "Electron Tomography", Ed. by J. Frank, Plenum, New York, (1992) pp. 1-13.

[11] H. Jinnai, H. Kitagishi, K. Hamano, Y. Nishikawa, M. Takahashi, *Phys. Rev. E*, **67**, 021801 (2003).

[12] O. Kratky, Pure Appl. Chem., 12, 483 (1996).

[13] H. Jinnai, Y. Nishikawa, T. Koga, T. Hashimoto, *Macromolecules*, **28**, 4782-84 (1995).

[14] H. Tanaka, *Phys. Rev. Lett.*, **70**, 53 (1993): *ibid.*, **70**, 2770 (1993).

[15] H. Tanaka, J. Phys.: Condens. Matter, 13, 4637-674 (2001).

[16] A. W. Adamson and A. P. Gast, "Physical chemistry of Surfaces" 6th edition, Wiley Interscience, New York (1997) pp. 4-47.

(Received January 6, 2005; Accepted March 17, 2005)