

## Structure of Thin ABC Triblock Copolymer Films Developed by Solvent Treatment

Kenji Fukunaga

UBE Industries, Ltd. Goi-minamikaigan 8-1, Ichihara, Chiba 290-0045, Japan

Fax: 81-436-22-3348, e-mail: 28658u@ube-ind.co.jp

Structure of thin ABC triblock copolymer film developed by solvent treatment is investigated by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM). Combination of the surface and the interior microscopy demonstrates how the self-assembly of the film proceeds in the solvent treatment. At beginning of the treatment, furthermore, repelling of defects from free surface is observed.

Key words: thin film, block copolymer, micro domain, self-assembly; microscopy

### 1. INTRODUCTION

There is a growing interest in block copolymers mainly due to their potential to self-assemble into highly ordered structures of mesoscopic scale [1]. In those materials, two or more block chains are covalently bonded together, and incompatibility between the constituent blocks gives a variety of micro phase separated morphologies after an appropriate thermal equilibration. Annealing above the glass transition temperature in vacuum is a simple way to achieve a thermodynamic equilibrium, however, many complex block copolymer systems have rather low thermal degradation temperature which does not suffice to adequate annealing within a reasonable time. Moreover, complex metastable structures may form during the sample preparation, which in turn constitute severe kinetic barriers for the chain transport necessary to achieve the thermal equilibrium. Therefore, drying from or swelling in neutral solvents has become a prominent alternative route for "equilibration" of block copolymers [2,3]. Although the solvent treatment is widely used, the details of this treatment are left rather unclear.

In the present work, the micro domain morphology in thin ABC triblock copolymer films developed by solvent vapor swelling and subsequent is investigated drying procedure. High molecular weight triblock copolymers are typical examples of polymeric systems where vacuum annealing is not a feasible route to equilibrate the system. Here, surface-induced micro phase development and domain alignment is demonstrated, this is similar to the situation known from symmetric diblock copolymer in thin films.

### 2. EXPERIMENTAL

Poly(styrene-*b*-2vinylpyridine-*b*-*tert*-butylmethacrylate) triblock copolymer (volume fractions  $\phi_{PS} = 0.18$ ,  $\phi_{P2VP} = 0.39$ , and  $\phi_{PBMA} = 0.43$ ) with molecular weight of 293 000 synthesized by sequential anionic polymerization was studied in this work [4]. Bulk pieces of the triblock copolymer were shown to exhibit a lamellar morphology after slow drying from tetrahydrofuran (THF) solution. THF is almost non-preferential to the constituent blocks. Thin triblock copolymer films were deposited onto a silicon wafer covered with native oxide layer ( $SiO_x$ ) by dip-coating from THF solution (polymer concentration 6 g/l). After drying, the samples were subjected to solvent

treatment [5]. The samples were exposed to the saturated THF vapor in a closed vessel kept at room temperature. After 1 min, the sample was swollen up to ca. 113 % of the initial thickness (therefore, the polymer concentration in the film was decreased to ca. 88 %) [6]. After certain duration of the treatment, the samples were removed to the atmosphere, where the THF was immediately evaporated from the sample. The surface topography of the samples was investigated by both reflection optical microscopy (OM) and atomic force microscopy (AFM). The AFM images were captured on a Nanoscope III (Digital Instruments) microscope operated in tapping-mode. As well as the surface structure, the interior structure of the samples was investigated by transmission electron microscopy (TEM). For the sake of ultramicrotoming, the thin film of the triblock copolymer has to be removed from the rigid Si wafer. Strong affinity of polar P2VP block to  $SiO_x$  surface holds back the film removal [5], therefore, the sample was contacted with aqueous solution of KOH for a few seconds. Subsequently, some portions of the thin film were floated off in distilled water. The floating thin films on water were corrected on polyimide sheet and embedded in UV curing acrylic matrix. The embedded film was stained by  $RuO_4$  to harden the triblock copolymer, and thereafter ultra-microtomed. The cross sections were further stained by  $OsO_4$  and observed on JEM-200CX (JEOL) microscope.

### 3. RESULTS

As prepared film exhibits a homogeneous color in the OM images. It indicates that the film has macroscopically uniform thickness. Corresponding to this, in wide-scan AFM images, the film surface appears flat and featureless. However, as shown in Fig. 1, AFM images of high magnification reveal that small corrugations with short-range order present at the surface. The height of the corrugations is some 3 nm, and the characteristic length of the short-range order is found to ca. 70 nm by power spectrum density of this image. It suggests that the film has a lateral structure, which is more or less distorted from regular structure, near the film surface.

By contrast to the as-prepared film, the sample passed the solvent treatment for 1 min exhibits macroscopically a stepped surface in AFM images (Fig. 2). In the THF

vapor, areas of well-defined thickness are immediately developed on the film. It is found that the step height  $d$  is constant within the experimental error and amounts to 40 nm from cross sections of AFM image taken at different positions of the sample. Noting that the bulk pieces of the polymer exhibit lamellar morphology, this situation resembles the well-known surface induced alignment, which has been observed on thermally equilibrated thin films of symmetric diblock copolymers [7]. The preferential attraction of the respective blocks to the boundary surfaces generally leads to an in-plane alignment of the lamellae. It strikes one odd in the case of the particular triblock copolymer studied in this work, since the P2VP middle block is expected to preferentially adsorb onto the  $\text{SiO}_x$  substrate. As reported before, this puzzling situation is explained by development of thin adsorbed layer, micro-phase separated copolymer "brush" [5].

By the AFM, one cannot obtain direct information with respect to the sample interior. Therefore, to confirm the expectations deduced by AFM, the interior structure of the sample was further examined by cross sectional TEM. In Fig. 3, the polyimide sheet and the curing matrix are seen upper and lower side of the triblock copolymer film, respectively. Therefore, in the THF vapor treatment, the upper boundary of the film has been faced to THF vapor, whereas the lower boundary has been adjacent to  $\text{SiO}_x$  substrate. There are some possibilities of damaging the sample in preparation of the cross sections, especially in the process of contacting with aqueous KOH solution and of embedding in the curing agent. To check artifacts induced by these processes, in advance of the TEM preparation procedure, some samples were stained by  $\text{RuO}_4$  to fix the structure. However, the pre-staining procedure does not produce any additional features in the TEM images. Consequently, it can be concluded that the TEM preparation procedure does not significantly modify the sample structure. There is another possibility that some layers of the thin film are left on the original  $\text{SiO}_x$  substrate. Therefore, after peeling of the thin film, surface of the  $\text{SiO}_x$  substrate was checked by AFM. It confirms whole layers of the film present in the cross sections. Under the staining condition of this work, PS, P2VP, and PtBMA domains appear white, black, and gray, respectively, in TEM images. As seen in Fig. 3, as-prepared film shows a "sponge" like morphology [8, 9]. This distorted structure exhibits a short-range order. The spacing of white domains in the image is measured to some 70 nm. This characteristic length is very similar with the characteristic wavelength found for the surface corrugations observed in the AFM. Therefore, it seems to be supposed that the surface corrugations are somehow related to the micro domain morphology of the interior. However, the TEM image (Fig. 3) shows that the surface of the film is covered with a single lamellar layer, which has the thickness of some 40 nm. Hasegawa and Hashimoto demonstrated that the free surface of PS-PI diblock copolymer film is always covered by the lower critical surface tension component [10]. In the PS-P2VP-PtBMA triblock copolymer, PtBMA end block is supposed attracted to the free surface [5]. Therefore, PtBMA micro domain covers the film surface and this leads the formation of wetting layer of the lamellar micro domains of the triblock copolymer. If the height image of

the AFM reflects the respective micro domain morphology, the micro domains may affect the surface topography through undulation of the homogeneous wetting layer.

As expected by the AFM results, the TEM observation has revealed that the THF vapor treatment immediately develops the aligned lamellar morphology. In Fig. 4, the sample after the vapor treatment for 5 sec exhibits development of lamellar micro domains, which align to in-plane direction of the thin film. We must draw attention to that the most lamellae are developed as aligned to the film surface. Moreover, this development is seen only in upper part of the film, whereas the lower part remains the distorted structure of the as-prepared film. This situation resembles well-known surface directed phase separation in binary blends [11]. A preferential surface, which attracts one of two species of a binary blend, leads the composition oscillations toward the film center after a quenching through its demixing critical point. The topmost layer, i.e. the wetting layer described before, reflects such kind of effect. It is demonstrated in Figs. 4-5 that the aligned phase grows toward the opposite boundary (substrate) with treatment time. Within 1 min, the aligned lamellar domains govern the whole interior of the film.

In the TEM images presented here, it is hard to see the laterally phase separated "brush" layer adjacent to the substrate. Thickness of the "brush" layer is supposed to some 4 nm that is too thin to identify the micro domain structure on the conventional TEM. In Fig. 5, however, the layer faced to the substrate exhibits row of bright dots in the dark stripe, which seems to be a sign of an in-plane phase separation. Although the bare "brush" thickness is found to some 4 nm, this feature is located some 10 nm above the substrate. It indicates that, under the lamellar layers, the "brush" layer is swollen by the triblock copolymer. This may lead the in-plane structure beyond the bare "brush" thickness.

In Fig. 5, one can see that the thin film is composed of grains of the aligned lamellar micro domains. At the grain boundary (indicated by broken line), it is found that the lamellae take an edge dislocation like a smectic-A liquid crystal film [12]. One of the edge dislocations is seen in the figure (indicated by arrow). On the dislocation, thickness of the triblock copolymer film is varying. The cross sectional TEM image manifests that the thickness difference across the dislocation is commensurate to the lamella period. The lamella period (40 nm in Fig. 5) meets the step height measured by the AFM. Therefore, the step observed in the AFM images is supposed to a signature of the dislocation. Here, it should be also noted that the edge dislocations seem to be rather accumulated in the vicinity of the substrate.

#### 4. DISCUSSION

As-prepared film of the triblock copolymer exhibits a distorted phase. Despite only scanty information on this phase, it is obvious that this phase has no long-range order like the aligned phase immediately developed by the solvent vapor treatment. In this study, same solvent (THF) is used in both the film preparation and the vapor treatment. It is expected that the sample have been more or less exposed to THF vapor in the preparation. However, this process does not develop an aligned lamellar phase at

all (except for the wetting layer). We have to inquire, to some extent, into the difference between the solution desorption process (in the preparation) and the solvent absorption process (in the solvent vapor treatment). Heat expenditure due to the solvent evaporation may account for the difference of these two processes. In the film preparation, rather large amount of the solvent (more than 99 wt% in the present case) is evaporated from the sample. Therefore, the sample has deeply quenched on drying due to the latent heat loss (vaporization entropy of THF is 33 kJ/mol at room temperature). In this case, kinetic barriers for the chain transport are severely enhanced. Contrary, in the vapor treatment, the solvent is condensed on the sample, and this leads a heating of the sample. In this case, the sample is contacted with the solvent at the moderate temperature. At the end of the treatment, "annealed" structure is frozen with the solvent evaporation. This expectation has been confirmed experimentally [6]. The sample is quenched at least 10°C on drying in the dip-coating process, whereas the sample is slightly heated in the solvent vapor treatment. In the latter case, the temperature increases some 2°C in the first 5 sec followed by gradual decrease to room temperature over 500 sec. We may say that the solvent vapor treatment is feasible to "equilibrate" the system in short time.

We shall now look into defects in the thin triblock copolymer film. In the system studied here, the steps are appeared on the surface after the solvent vapor treatment, and they are found associated with the edge-dislocations. As seen in Fig. 4, grains of the aligned lamellar phase, which are developed from the free surface, grow faster in the in-plane direction than in the out-of-plane direction. It is contrast to the bulk case [13] and indicates that the grain growth is directed by the free surface. Noting that the sample is contacted with THF at the free surface, it may be associated with diffusion of the THF molecules into the film. Here, if the film thickness is incommensurate with the lamella period, the polymer system may feel frustration near the substrate. For thin films of PS-PMMA diblock copolymer, it has demonstrated that reduced specific interactions with the substrate allow the frustration to be relaxed by perpendicular ordering of the lamellar micro domains to the substrate [14]. In the present case, there is a strong affinity between the P2VP middle block and the substrate. The fact that the substrate prefers the middle block makes the situation rather complex than the diblock copolymer case. However, this specific interaction is significantly screened by the adsorption layer of the triblock copolymer. Therefore, the lamellae aligned to the perpendicular direction are supposed to be allowed when the frustration presents. In fact, under the certain experimental condition, the perpendicular lamellae are observed on the thin film of the same ABC triblock copolymer [5]. If the discontinuity between the parallel lamellae and the perpendicular lamellae is relaxed by either bending of or bifurcation of the lamellae to adjust each other near the substrate, this may lead the edge-dislocation type of defect. Thus, the asymmetric development of the aligned lamellar phase develops the asymmetric distribution of the edge-dislocations. Once the edge-dislocation is created in the thin film, chain deformation due to the dislocation is "smoothed-out" toward the free surface [15]. Consequently, step is

supposed to be formed on the free surface above the dislocation.

I note that the thin film structure shown in Fig. 5 is a meta-stable structure. After a prolonged treatment with the THF vapor, terrace dewetting accompanied with thickening of the lamellae is observed [6]. This process is supposed associated with anisotropic chain diffusivity with respect to the lamellar interfaces [1]. Furthermore, the solvent evaporation to terminate the treatment is supposed to bring some additional features into the film. The solvent desorption induces both shrinkage of the film [5] and increase in the domain spacing [16]. In the present case, the lamellar domains align parallel to the surface. Therefore, the shrinkage may be suppressed in the normal direction of the surface. However, macroscopic shrinkage in the in-plane direction may be also constrained by the substrate. Competition between the above two effects is supposed to induce non-equilibrium structure in the film. Such feature can be seen in Fig. 5 (indicated by "A").

## 5. CONCLUSION

In this study, thin film structure of the ABC triblock copolymer developed by the solvent treatment is investigated by means of both AFM and TEM. The AFM reveals that the initially flat surface of the film is turned into the stepped surface after the solvent vapor treatment. The TEM reveals that the initially distorted phase in the film is transformed into the lamellar phase that is aligned to the in-plane direction by the treatment. Moreover, the TEM observation demonstrates the surface induced alignment process of the lamellar micro domains. Feasibility of the solvent treatment to "equilibrate" the thin film structure is discussed. Furthermore, it is discussed that the defects in the lamella order are firstly repelled from the free surface in the treatment. Stability of the thin film structure observed here will be reported in the subsequent publication. The detail of the initial distorted structure and the thin adsorption layer ("brush") is remained to future investigations.

## Acknowledgements

The author thanks R. Stadler (deceased) and E. Giebeler for synthesis and bulk characterization of the ABC triblock copolymer. Technical support from K. Itoh (UBE Scientific Analysis Center) for the TEM observation is acknowledged. The author appreciates helpful discussions with H. Elbs, G. Krausch, and especially T. Hashimoto in conducting this study.

## References

- [1] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990)
- [2] G. Kim, M. Libera, *Macromolecules* **31**, 2569 (1998)
- [3] H. Elbs, K. Fukunaga, R. Stadler, R. Magerle, G. Krausch, *Macromolecules* **32**, 1204 (1999)
- [4] E. Giebeler, Dissertation, Universität Mainz, 1997
- [5] K. Fukunaga, H. Elbs, R. Magerle, G. Krausch, *Macromolecules* **33**, 947 (2000)
- [6] K. Fukunaga, T. Hashimoto, to be submitted
- [7] T. P. Russell, G. Coulon, V. R. Deline, D. C. Miller, *Macromolecules* **22**, 4600 (1989)
- [8] T. Hashimoto, S. Koizumi, H. Hasegawa, T. Izumitani, S. T. Hyde, *Macromolecules* **25**, 1433 (1992)

- [9] T. P. Russell, in "Ordering in Macromolecular Systems", ed. A. Teramoto, M. Kobayashi, T. Norisuye, Springer-Verlag, 217 (1994)
- [10] H. Hasegawa, T. Hashimoto, *Macromolecules* **18**, 589 (1985)
- [11] G. Krausch, J. Mlynek, W. Straub, R. Brenn, J. F. Marko, *Europhys. Lett.* **28**, 323 (1994)
- [12] Y. Liu, M. H. Rafailovich, J. Sokolov, S. A. Schwarz, S. Bahal, *Macromolecules* **29**, 899 (1996)
- [13] N. Sakamoto, T. Hashimoto, *Macromolecules* **31**, 3815 (1998)
- [14] G. J. Kellogg, D. G. Walton, A. M. Mayes, P. Lambooy, T. P. Russell, P. D. Gallagher, S. K. Satija, *Phys. Rev. Lett.* **76**, 2503 (1996)
- [15] M. S. Turner, M. Maaloum, D. Ausserré, J.-F. Joanny, M. Kunz, *J. Phys. II France* **4**, 689 (1994)
- [16] M. Shibayama, T. Hashimoto, H. Hasegawa, H. Kawai, *Macromolecules* **16**, 1427 (1983)

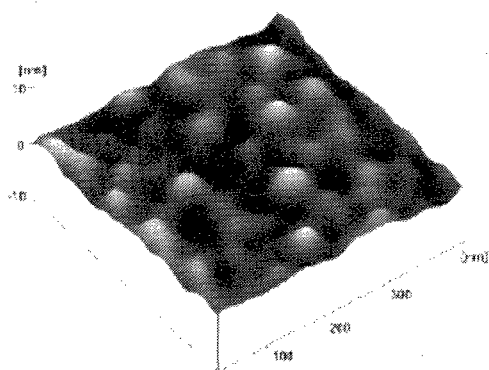


Fig. 1 AFM height image taken for the as-prepared thin film of the triblock copolymer. Scan area size is 400 nm × 400 nm.

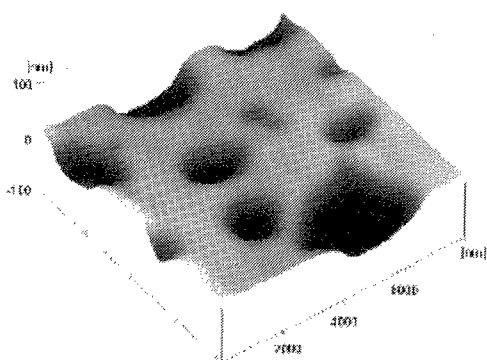


Fig. 2 AFM height image taken for the thin triblock copolymer film subjected to the THF vapor treatment for 1 min.

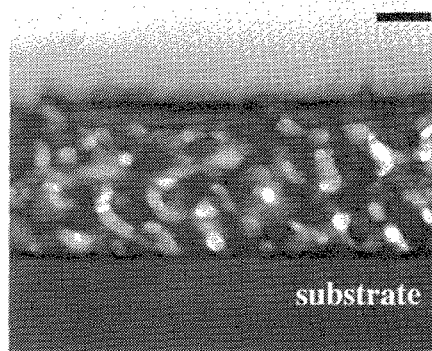


Fig. 3 TEM cross section taken for the as-prepared thin film of the triblock copolymer. Black bar represents 100 nm.

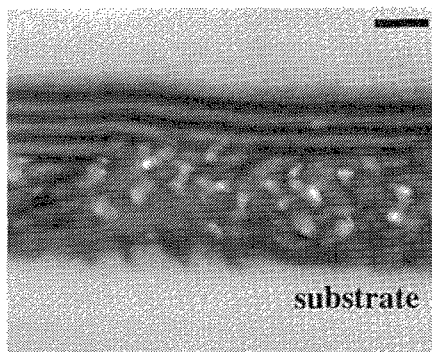


Fig. 4 TEM cross section taken for the thin triblock copolymer film subjected to the THF vapor treatment for 5 sec.

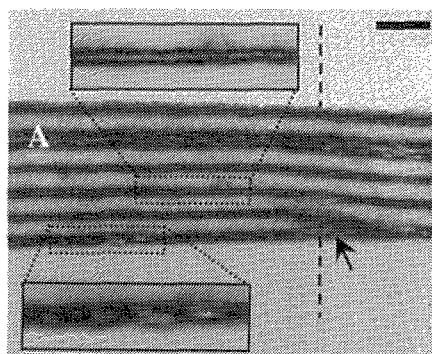


Fig. 5 TEM cross section taken for the thin triblock copolymer film subjected to the THF vapor treatment for 1 min. Dashed areas are zoomed up in respective insets. Broken line and arrow indicates the grain boundary and the dislocation, respectively. A singular lamellar layer is seen around "A" (see text).