

SAXS Analysis of Mesoporous Thin Films

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1 Introduction

Diblock copolymers composed of two polymer chains that present inherent immiscibility can undergo microphase separation in both bulk and thin film, and form different morphologies[1] as shown Figure 1. They depend on the degree of polymerization, volume fractions of blocks and Flory–Huggins interaction parameters. These microphase separated structures have been attracting attention as a template with a size of around 10

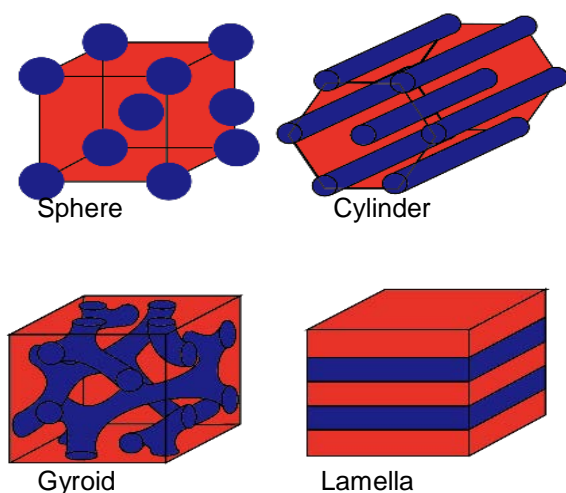
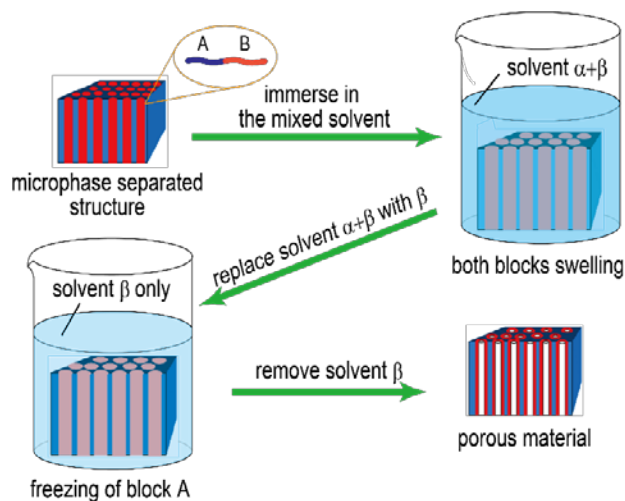


Figure 1. Microphase segregation of diblock copolymer

nm that is difficult to access in the other technique. Especially, fabrication of the porous material using block copolymer has been studied extensively because porous materials have various applications, such as gas separation, catalysts, and separation membranes. There are several methods to obtain porous materials using block copolymer, such as the decompositions of polyisoprene using ozone, of biodegradable block with base, and of polymethylmethacrylate by ultraviolet light[2]. However, it is difficult to apply the advanced functions to the surface by those methods because those block copolymers become simple homopolymers after decomposition.

In this study, we fabricated porous materials nondestructively by using block copolymers as a template and selective swelling with mixed selective solvents. Then I investigated the structure control of the porous materials by controlling the concentration of mixed selective solvents.



Scheme 1. Fabrication method

2 Experiment

Porous materials were fabricated according to the Scheme 1. The solvent α swells block A and B, and β swells block B only. First, the block copolymer films were prepared from a toluene solution on Si wafer by spin-coating method. The films were annealed under vacuum at respective temperature for 20 h in order to induce microphase separated structure. Next, films were immersed in the mixed solvent of α and β at 303 K for 24 h. Subsequently, the mixed solvent was replaced with the solvent β to freeze block A. Then, the solvent β was evaporated under vacuum for 24 h to obtain porous materials. The volumes occupied by the solvent β were converted into pores in this process. With proper selection of a pair of solvents, this method will be applicable to

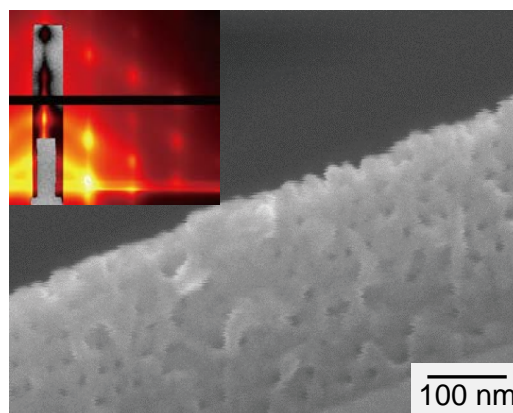


Figure 2. GI-SAXS pattern and SEM image of cross-section of PS-P2VP film after porous treatment in methanol

many different type of block copolymers. In order to verify the versatility, poly(styrene-*b*-2-vinylpyridine) (PS-P2VP) and poly(styrene-*b*-isoprene) (PS-PI) with very different amphiphilicity were used. The solvent α was tetrahydrofuran (THF), β was methanol, and annealing temperature was 423 K for PS-P2VP. In the case of PS-PI, α was toluene, β was hexane, and annealing temperature was 393 K. In either case, block A is always PS, for which methanol and hexane are typical poor solvents. The structures of porous materials were observed by field-emission scanning electron microscope (FE-SEM) and grazing incidence small-angle X-ray scattering (GI-SAXS) at Photon Factory BL-6A.

3 Results and Discussion

Figure 2 shows the GI-SAXS pattern and SEM image of cross-section of PS-P2VP film after porous treatment in methanol. The volume fraction of P2VP domain is 0.247, so the morphology in the equilibrium state is cylindrical. The GI-SAXS pattern indicates that the cylindrical pores are well arranged parallel to the substrate because the hexagonal spots are observed, and the scattering intensity of porous films became stronger than that of the annealed sample. The structure that GI-SAXS indicated was also confirmed from the cross-sectional SEM image of the porous film. From these results, it is confirmed that the introduction of pores to block copolymer was succeeded by this method.

Figure 3 shows the SEM images of the surface and cross-section of PS-PI films after porous treatment in hexane. The volume fraction of PI domain is 0.203, so the morphology in the equilibrium state is spherical. From the surface image, a sufficient introduction of pores was observed without the addition of toluene because hexane plasticized not only PI but PS. So the additional selection of appropriate solvent is required to perform more precise structure control. From the cross-sectional image, the pores extended to the back from the surface were observed. This means that it is possible to make the pores in the entire sample by this method.

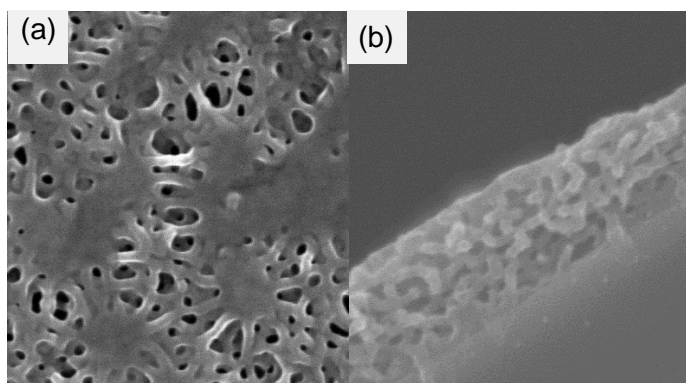


Figure 3. SEM images of the surface (a) and cross-section (b) of PS-PI films after porous treatment in hexane

4. Conclusion

We revealed that it is possible to introduce the pores into block copolymer by using mixed selective solvents.

This method is applicable to fabricating membranes with pores open on the surface.

To prove the universality of this method I introduced pores into PS-PI which has very different polarity. For further understanding this method, it is necessary to understand the affinity between the polymer and solvent more quantitatively. I'll introduce the solubility parameters[3] and predict the swelling behaviors in order to choose an appropriate pair of solvents for this method.

References

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