Thickness dependent Optical Characteristics of 1D Block Copolymers

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ABSTRACT

Block copolymers (BCPs) have been investigated for fabricating functional nanomaterials due to their properties of self-assembly. We prepared polystyrene-b-poly(2-vinylpyridine) (PS-b-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer have 57 kg/mol-b-57kg/mol. The lamellar stacks are obtained by exposing the spin coated film under chloroform. The P2VP blocks were then quaternized and crosslinked to various extents using 5wt% of iodomethane. The quarternized films with thickness varied from 0.43 ㎛ (446 nm absorption maximum) to 0.25 ㎛ (478 nm absorption maximum). The band shift as well as scattering around 400 nm clearly suggests that the each layer thickness changed accompanying with the roughness of the layer interfaces.

Keywords: Block Copolymer, Photonic Crystals, BCP, Poly(styrene-block-2-pyridine)

1 INTRODUCTION

Applications of nano-materials to the electric and electronic devices have been attempted. Block copolymers (BCPs) are fascinating materials to make uniform and regular shapes with periodicity in three dimensional spaces. [1-3]. In photonic crystals, which are also known as photonic band gap materials, electromagnetic waves with certain energy that matches the bandgap are prohibited to propagate through the photonic crystal [4]. Photonic crystal materials have been proposed as various applications such as controlling and processing light, active component of display, sensory or telecommunication devices [5-8]. The generation and manipulation of light requires the construction and engineering of active and passive light-interactive structures. Photonic crystals have been emerging as vital structures in manipulating light.

Many different methods of tuning of photonic band gap by changing the refractive index and/or the periodicity of the photonic crystal structure have been demonstrated [9-13]. Block copolymer also have drawn increasing attention as platforms of creating various photonic band gap structures. For instance, Effective way of fabricating photonic crystal structures demonstrated that self-assembly of block copolymers can be provide 1D, 2D and 3D photonic band gap materials from lamellae, hexagonally packed cylinders and double gyroids respectively [14-17]. The well-ordered photonic crystal lamellar films are also called photonic gels [18]. During the fabrication of photonic gels, sometimes poor ordered films are discovered. They cannot show clear color at swelling state like other photonic gels. It can be a problem of development of photonic gel for various applications.

Currently, there is the study of band gap tuning method by BCP's thickness. The band gap can be changed by ionic strength and size of cation. They found that lager cations

and strong ionic strength induce the shift of photonic band gap to the shorter wavelength [19-20].

This study shows that the total film thicknesses change the absorbance band by affecting the thickness of layers consisting of PS-b-P2VP photonic crystals

2 EXPERIMENTAL DETAILS

2.1 Fabrication of photonic gel

We prepared polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer have 57 kg/mol-b-57 kg/mol. To fabricate the photonic gel, well-oriented lamellar film were prepared by spin-coating (MIDAS Model spin1200D) from a 5 % PS-b-P2VP solution in propylene glycol monomethyl ether acetate. We also were fabricated by spin-coating at 5 kinds of speed (700, 800, 900, 1000 and 1100 RPM). The spin-coating films were annealed in chloroform vapor at 50 ℃ for 48 hours. Quaternization was performed with 5 wt% of iodomethane, which solubilized in n-hexane.

The quaternized photonic gel films were dried and saved for measurements. PS-b-P2VP was purchased from Polymer Source (Doval) and iodomethane chemicals were purchased from Aldrich.

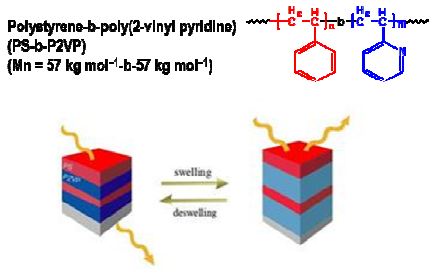


Figure 1 : Structure of PS-P2VP block copolymer

2.2 Measurements

The photonic band gaps were measured with the diode array type spectrophotometer (Agilent Model 8435) The spectra of lamellar films were taken at dried state and swollen state by exposing to the ethanol.

3 RESULTS AND DISCUSSION

Generally, PS-b-P2VP films do not show any significant visible absorption and stay transparent in the visible region when they were stored in dry conditions. Spreading distilled water or ethanol on the surface of the films induced immediate visible color on the film with reflection and interference of visible light. The swelling occurred with any solvents which were smaller than pentanol. Large and high molecular weight solvents did not penetrate into the films.

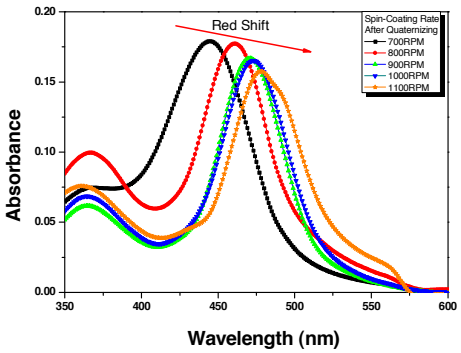


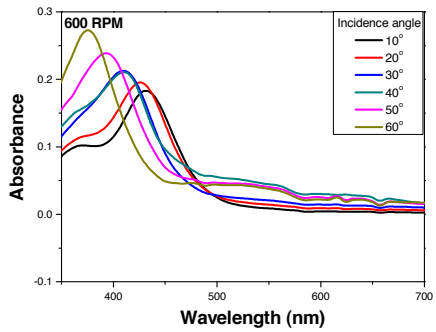
Figure 2. Visible absorption spectra of PS-P2VP photonic gel with variation of film thickness.

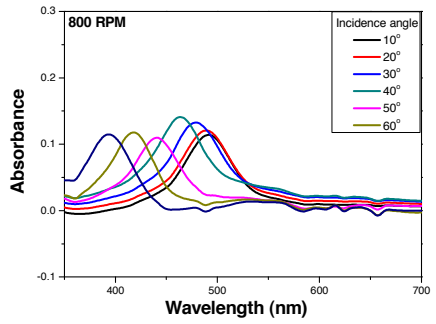
The phase separation of BCP can be very sensitive to the film thickness. The films thickness was obtained after quarternization of the films formed with varying the spin rate. The film thickness measured by alpha step clearly increased at low spin rate. When the rate was 700 rpm, thickness was 0.43 ㎛, which became 0.25 ㎛ for highest

speed spin coating. The absorption maximum shifted from 446 nm for thicker film to 478nm for the film made with the maximum spin speed. The band shift as well as scattering around 400 nm clearly suggests that the each layer thickness also changed accompanying with the roughness of the layer interfaces.

Speed (rpm)	*Thickness (㎛)*	*Abs. Max (nm)*	*FWHM*
700	**0.435**	**445**	**72**
800	**0.405**	**461**	**48**
900	**0.350**	**471**	**51**
1000	**0.295**	**473**	**53**
1100	**0.250**	**478**	**57**

Table 1. Spin coater spin rate, film thickness and absorption maximum obtained with PS-b-P2VP photonic gels.





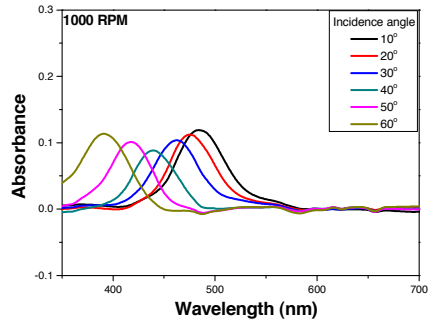


Figure 3. Visible absorption spectra of PS-P2VP photonic gel with variations of films incidence angle (600, 800, 1000RPM)

Figure 3 shows variations of films incidence angle. It has a bigger reflectance which has low RPM. This cause the increase of an absorbance because the amount of penetration is small. Bandwidth of the reflectance was not considerably changed in spite of thickness variation.

4 CONCLUSION

The significant reflection band shift may due to the decrease of interlayer thickness.

The phase separation process of BCP was very sensitive to the film thickness. The quarternized films thickness varied from 0.43 ㎛ to 0.25 ㎛ for highest speed spin coating. The absorption maximum shifted from 446 nm for thicker film to 478 nm for thin film, Figure 4 and Table 1. The band shift as well as scattering around 400 nm clearly suggests that the each layer thickness also changed accompanying with the roughness of the layer interfaces.

The reflectance rapidly increases with incidence angle, due to the tight light path for the transmission of thicker films.

ACKNOWLEDGEMENT

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