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Effective Reflective Indices of Polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) Lamellar Films

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Block copolymers have drawn increasing attention for fabricating functional nanomaterials due to their properties of self-assembly. Especially, photonic crystals hold promise for multiple optical applications. We prepared 1D photonic crystals with polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer of 57 kg/mol-b-57 kg/mol. The lamellar stacks, which are alternating layers of hydrophilic and hydrophobic moiety of PS-b-P2VP, are obtained by exposing the spin coated film under chloroform vapor. The band gaps of the lamellar films interestingly varied after immersion into the quaternizing solvents containing 5 wt% of iodomethane solubilized in n-hexane. To study of spectral characteristics, UV-visible absorption spectra were measured as a function of the incidence angle (in 10° steps) at swollen films with distilled water and ethanol. The UV-visible maximum absorption spectra shifted by Bragg's law. From transmission spectra, effective refractive index of the photonic crystal was calculated based on the modified Bragg-Snell law.

Keywords Bragg-Snell law; photonic crystals; Uv-visible absorption spectra

1. Introduction

Photonic crystals are periodic optical structures that are formed to affect the motion of photons, which is similar as the periodicity of semiconductor crystals affects the motion of electrons [1]. 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 [2,3]. Photonic band gap materials have drawn increasing attention due to their unique potential use in various applications such as controlling and processing light, active component of display, sensors and telecommunication devices [4–8].

Effective way of fabricating 1D photonic crystal from lamella structure has been demonstrated using self-assembly of block copolymers [9–11]. The well-ordered photonic crystal lamellar films are also called photonic gels, which have photonic band gap. The photonic band gap generally exhibits bright colors, which can be

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tunable and controlled by external stimulus, such as electric field and dielectric modulations. The microstructures of photonic crystals are very diverse. The refractive index difference between two layers determines the light path and interferences. In the study, we attempt to find the effective refractive index through the Bragg-Snell law when the photonic gel films were swollen by distilled water. To study of spectral characteristics, UV-visible absorption and transmission spectra were measured as a function of the incidence angle (in 10° steps).

2. Experimental Section

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 [12]. The spin-coated films were annealed in saturated chloroform vapor at 50°C for 24 hours. After the annealing, we identified that the well-oriented lamellar film were swelling by ethanol and shows significant light. Quarternization was performed with 5 wt% of iodomethane which solubilized in n-hexane. Iodomethane were reacted with pyridine groups in PS-b-P2VP at 50°C for 72 hours as shown Figure 1. Figure 2 shows processes of fabrication for photonic gel films. The quarternized photonic gel films were dried and saved for measurements. PS-b-P2VP was purchased from Polymer Source (Doval) and iodomethane was purchased from Aldrich. These chemicals were used as it was without further purifications.

2.2. *Measurement*

The photonic band gaps were measured with the diode array type spectrophotometer (Agilent Model 8435). The spectra of lamellar films were taken at swollen state by exposing to the distilled water and ethanol, respectively. The UV-visible absorption and transmission spectra were measured in the range of 300–800 nm and the spectra were recorded at different incidence angles θ (in 10° steps) from 0° to 60° through fabricated kit. The prevent drying of films during measurement of film spectra, the films were covered with cover glass after swollen with the aqueous solutions.

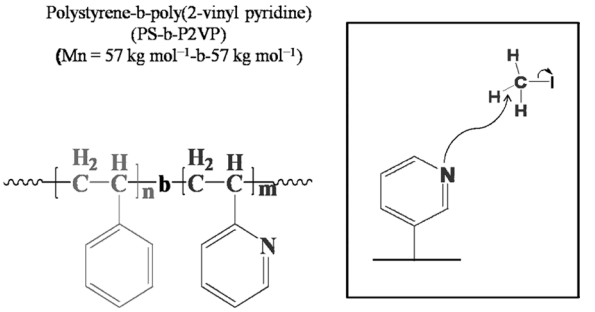


Figure 1. Structure of PS-P2VP Block copolymer and quaternization mechanism.

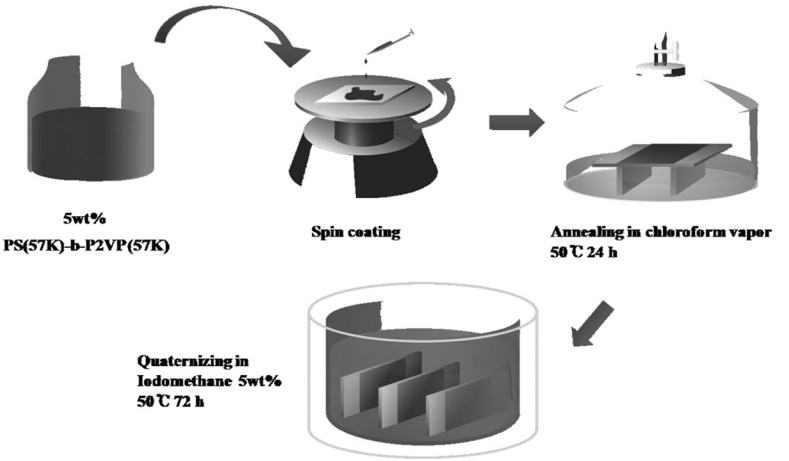


Figure 2. Preparation of photonic gel films.

3. Result and Discussion

3.1. *UV-Vis. Absorption Characteristics*

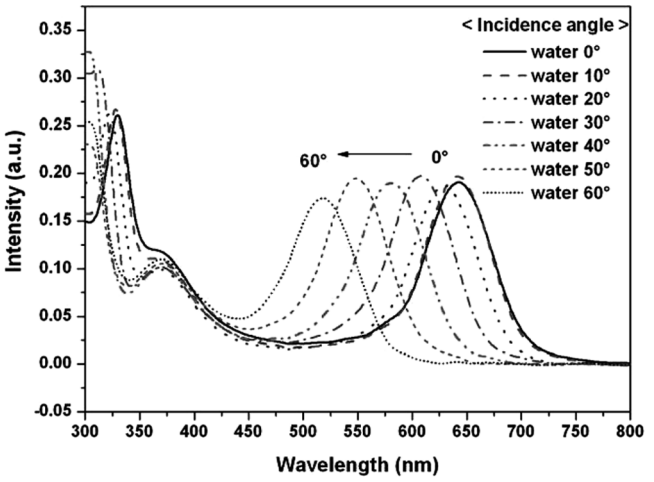
The PS-b-P2VP films do not show any significant visible absorption and stay transparent in visible region at dry state. Spreading distilled water and ethanol on the surface of the films induced immediate visible color on the film with reflection and interference of visible light. The absorption maxima the films swollen with water and ethanol located at 648 nm and 512 nm, respectively. The absorption peak wavelength show hypsochromic shift as increase the incidence angle visible light. These visible absorption peaks indicate formation of photonic gel having photonic band gap by lamellar structure. As shown in Figure 3, the absorption maximum of the PS-P2VP films shifted gradually to the shorter wavelength as increasing incidence angles up to 518 nm for the films swollen with water and 418 nm for the films swollen by ethanol. The amount of hypsochromic shift was 124 nm and 94 nm with incidence angle. For the films swollen by ethanol, the light scattering increase dramatically at higher incidence angle. The absorption bands are mixed with light scattering, which can be created by less discrete interface. The absorption maximum at 60° of incidence angle swollen by ethanol was not measured because it mixed with second peak as shown in Table 1.

3.2. *Transmittance Characteristics*

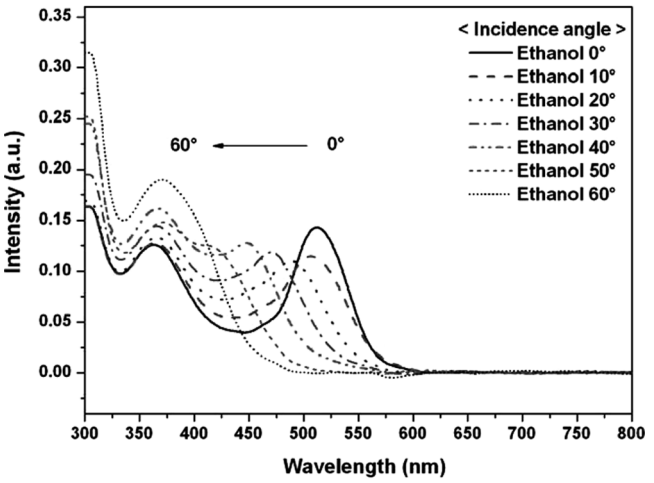
Figure 4 shows broad transmission band in the range of 400 nm to 610 nm. The transmission band position shift to shorter wavelength and the band width becomes narrower and the transmittance becomes reduced as increase the incidence angle. The position of the maximum transmission wavelength shifts to shorter wavelengths with incidence angle, obeying the Bragg-Snell law:

$$\lambda = 2D\sqrt{n_{eff}^2 - \sin 2\theta} \tag{1}$$

where D is the interplanar spacing and n_{eff} is the effective refractive index of photonic gel films. Figure 5(b) shows the plot of λ^2 versus $\sin^2\theta$ (where λ is the wavelength of



(a)



(b)

Figure 3. UV-vis. absorption spectra of PS-P2VP photonic gel swollen by (a) water (b) ethanol.

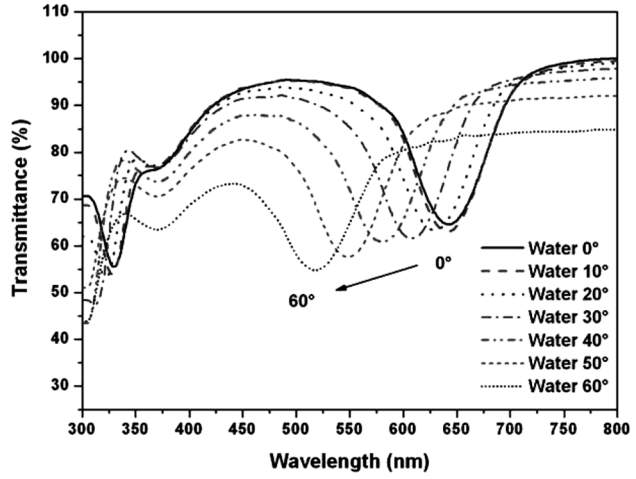
the minimum of transmittance and θ is the angle of incidence) and the linear fit to the experimental data. The latter can be determined from λ^2 versus $\sin^2\theta$ plot because the linear fit to the experimental data has a gradient of $-4D2$ as shown in Figure 5(b). The calculated value of n_{eff} is about 1.38 which is the lower than the polymer's refractive index. ($n_{PS} = 1.59$, $n_{P2VP} = 1.62$). The effective refractive index can be also expressed as

$$n_{eff} = \sqrt{n_{PS}^2 \cdot f_{PS} + n_{P2VP}^2 \cdot f_{P2VP} + n_{water}^2 \cdot f_{water}} \tag{2}$$

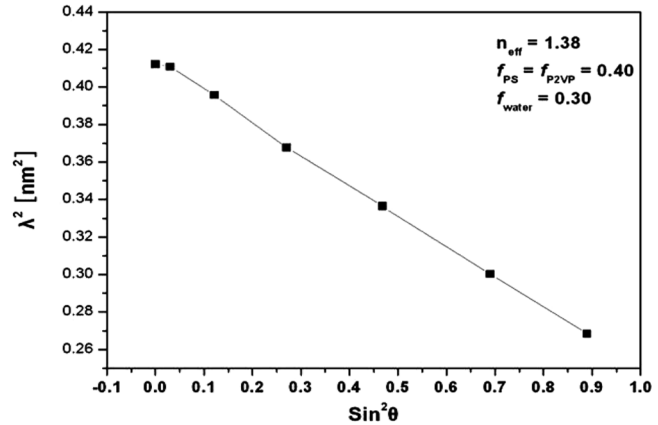
where $n_{PS} = 1.59$, $n_{P2VP} = 1.62$ and $n_{water} = 1.33$ are refractive indices of polymers and water, respectively. The $f_{PS} = f_{P2VP} = (1 - f_{water})/2$ accordingly PS-b-P2VP polymer have 57 kg/mol-b-57 kg/mol are volume fractions occupied in PS-b-P2VP

Table 1. UV-vis. absorption maximum dependent on solution and incidence angle

	Absorption maximum (nm)	
Incidence angle	Water	Ethanol
0°	642	512
10°	641	507
20°	629	489
30°	608	470
40°	580	448
50°	548	418
60°	518	—



(a)



(b)

Figure 4. (a) Transmittance spectra of PS-P2VP photonic gel films swollen by water measured at different angels of incidence θ from 0° to 60° with a step of 10° (b) Plot of λ^2 versus $\sin^2\theta$.

photonic gel films, respectively. In the case of $n_{eff} = 1.38$, Eq. (2) gives $f_{PS} = f_{P2VP} = 0.30$ and $f_{water} = 0.40$. These results indicate that 40% of the water soaks through the P2VP layer and it makes low effective refractive index. The calculated n_{eff} is lower than PS-b-P2VP polymer's refractive index and higher than water refractive index. Therefore, we can suggest the effective refractive index the swollen photonic gel films through the transmission spectra and Bragg-Snell law.

4. Conclusions

We prepared polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer of 57 kg/mol-b-57 kg/mol. The lamellar stacks, which is alternating layer of hydrophilic and hydrophobic moiety of PS-b-P2VP, are obtained by exposing the spin coated film under chloroform vapor. The band gaps of the lamellar films interestingly varied after immersion into the quaternizing solvents containing 5 wt% of iodomethane solubilized in n-hexane.

The absorption maxima of PS-b-P2VP films quaternized with iodomethane and 1-iodohexane and swollen by water and ethanol stays at 642 nm and 512 nm, respectively. The visible absorption maximum PS-b-P2VP film shifted to the shorter wavelength as increasing incidence angles. The transmission spectra also shifted to same directions as increasing incidence angle, corresponding to the Bragg-Snell law: We proposed that from the spectral analysis the effective refractive index of the film was 1.38 and about 40% of water was swollen into the film.

Acknowledgments

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