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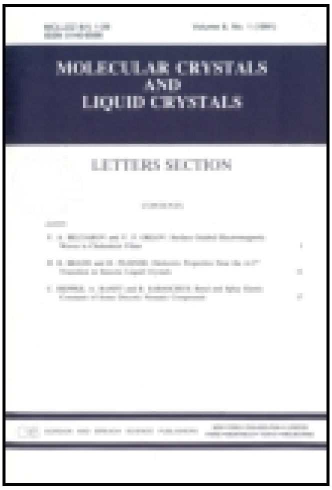

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Effect of Electric Fields on the Hydrogel-Photonic Gel Hybrid Device

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Effect of Electric Fields on the Hydrogel-Photonic Gel Hybrid Device

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Poly(styrene-b-*2-vinyl pyridine) (PS*-b-*P2VP) lamellar film of alternating hydrophobic block-hydrophilic polyelectrolyte block (52 kg/mol*-b-*57 kg/mol) were fabricated on ITO glass for photonic gel films. Poly(acrylamide*-co-*acrylic acid) (PAAm*-co-*PAAc) with potassium salts were synthesized for hydrogel with flat and tetragonal shape. The hydrogel-photonic gel hybrid devices were fabricated with photonic gel layer and hydrogel layer between two electrodes. The reflected wavelength of the cell was changed under electric fields. This experiment showed the effect of electric fields on the hydrogel-photonic gel hybrid devices. The maximum reflectance wavelength of the hybrid device was shifted from 563 nm to 590 nm during electric fields generating time of 25 min. This work shows that reflection color of photonic film can be tuned with hydrogel and electric fields.*

Keywords Photonic crystal; hydrogel; electric fields; photonic band gap

1. Introduction

The periodic structure of photonic crystals results in blocking specific wavelengths such as ultra-violet, visible or near-infrared light, which shows similar behavior to an optical insulator. The motion of photons in photonic crystals with a designated photonic band gap (PBG) is similar to the motion of electrons in semiconductor with an electronic band gap [1–3]. Controlling and processing of light have been attracted for the optical applications [4–8]. In particular, controlling wavelength in the visible region is the main issue in the photonic crystal, leading to application to the active components of display, sensor, or telecommunication devices [9].

Lamellar-forming block copolymer of poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) was used as a photonic active layer [10]. The PS-*b*-P2VP block copolymer has characteristic of self-assembly with faster and easier fabrication method [11]. In addition, the P2VP layers are swollen by a polar solvent, resulting in changing refractive index of photonic gel films [12–16]. However, this type of block copolymer photonic gels has typically shown problems including leakage or fast water evaporation. In this study, we used poly(acrylamide-*co*-acrylic acid) (PAAm-*co*-PAAc) hydrogel with potassium salt to act as reservoir of water and ions for the photonic gel [17]. The hydrogel shows electronic sensitivity, and thus good responsibility to electric fields.

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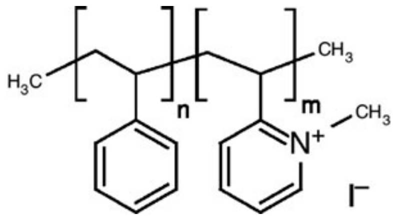

Figure 1. The scheme of PS-*b*-quarternized P2VP block copolymer.

2. Experimental

2.1. Photonic Gel Preparation

Photonic gel films were prepared by 7 wt% poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) ($M_{\mathrm{n,PS}} = 52$ kDa and $M_{\mathrm{n,PS}} = 57$ kDa, Polymer Source) solution in propylene glycol monomethyl ether acetate (PGMEA, Sigma Aldrich). The block copolymer solution was spin-casted on indium tin oxide (ITO) glass (MIDAS Model spin1200D), followed by soft baking on a hot plate at 85°C for 5 minutes. After the baking, the film was annealed under chloroform vapor at 50°C for 24 hours. In order to enhance the rate of swelling in polar solvent, the pyridine group in P2VP block was modified to the pyridinium group by quarternizing process in 5 wt% of iodomethane (Sigma Aldrich) in *n*-hexane at 50°C for 48 hours. Figure 1 shows PS-*b*-P2VP block copolymer after quaternizing process.

2.2. Hydrogel Synthesis

The hydrogel was synthesized by cross-linking acrylamide (AAm) and acrylic acid (AAc) by radical polymerization. Polymerization mixture consisted of monomers (AAm and AAc, 1:1 molar ratio), cross-linker (*N*,*N*-methylenebisacerylamide, MBAAm) and initiators (ammonium persulfate (APS) and *N*,*N*,*N*,*N*- tetramethylethylenediamine (TEMED)) in DI water. The concentration of the precursors was 20 wt% in water, and 0.01 wt% of initiators was added to the mixture.

The reaction mixture was purged with nitrogen gas for 10 minutes to remove oxygen that may interrupt the radical polymerization. After the purging, the mixture was loaded in the sealed containers and heated to 60°C for 12 hours in the constant temperature oven. The sample was then cooled at room temperature and removed the unreacted reactants by DI water several times. After the cleaning process, the hydrogel was submerged in a potassium hydroxide solution to replace hydrogen of hydroxyl group to potassium ion (see Figure 2). The hydrogel was cut in flat and tetragonal shapes by sharp knife with the thickness of about 1 mm.

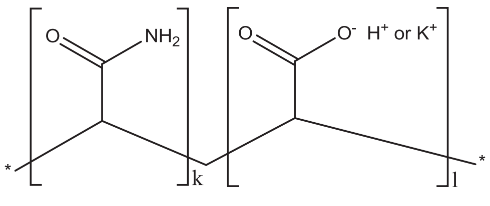

Figure 2. The scheme of synthesized PAAm-*co*-PAAc with partial potassium salt hydrogel.

2.3. Manufacturing Hydrogel-Photonic Gel Hybrid Device

Figure 3 shows a schematic structure of hydrogel-photonic gel hybrid device. To generate electric fields in the device, two ITO glasses were prepared for electrodes. The hydrogel was placed on top of ITO glass, and combined with the PS-*b*-P2VP block copolymer film on ITO glass. The cell was typically fabricated with a gap of 1.1 mm with a spacer, and sealed using UV sealant.

2.4. Measurement

Reflectance of photonic gel was measured using the UV-visible-spectrophotometer (Agilent/HP 8453). The electric fields were generated in the hybrid device by power supply (OPD-305, ODA) with applied voltage of 2 V. The spectra and photograph from the device were taken with annealing time from 0 minute to 25 minute with five minutes interval.

3. Results and Discussion

In our previous results, the PS-*b*-P2VP block copolymer photonic gels were swollen by polar protic solvents, and showed visible color that was dependent on the solvent dielectricity and polarity. For example, the reflection color obtained from photonic gel film swollen by DI water, ethyl alcohol and saturated $CaCO_3$ solutions had reflection color were reddish, greenish-blue and deep red, respectively. In particular the drastic shift in reflectance and narrowing optical band-width were obtained by swelling with saturated $CaCO_3$ solutions [18].

The hybrid device without electric fields showed green color with the maximum reflectance peak at 563 nm. Figure 4 shows the UV-visible spectra of hybrid device with various annealing time under electric fields (2 V). Figure 5 shows reflection color as a function of electric fields generating time for the photograph of hydrogel-photonic gel hybrid device. The reflection color of hybrid device was shifted from green to orange depending on electric fields generating time. The maximum reflectance wavelength of hybrid device was shifted from 563 nm to 590 nm during electric fields generating time of 25 min. When electric fields were removed, the reflection color of the device was not recovered immediately. It took a day to be recovered, which means the shift by electric field is reversible, but slow process.

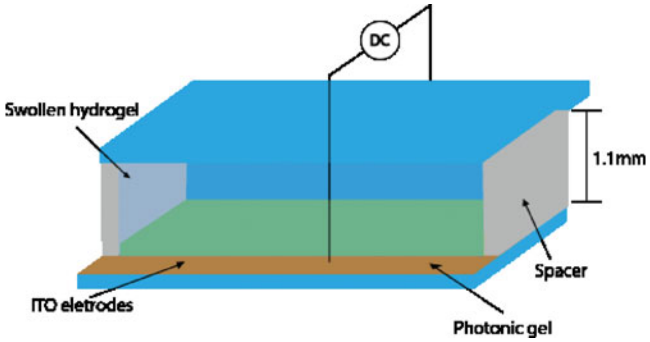

Figure 3. The schematic diagram of hydrogel-photonic gel hybrid device.

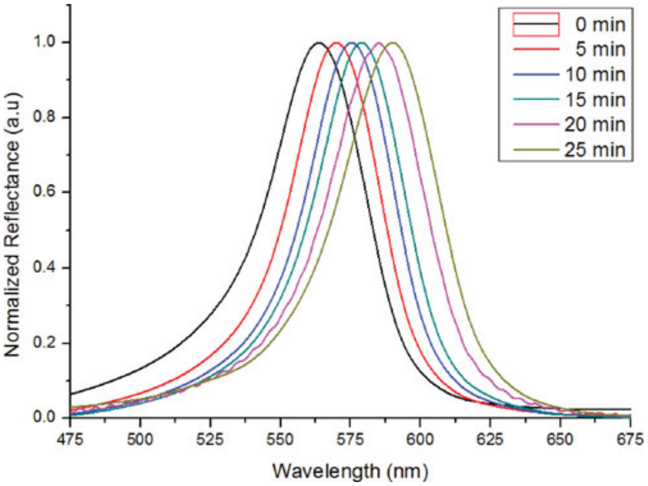

Figure 4. The UV-visible spectra of hybrid device with electric fields generating times.

The shift in Figure 4 was observed from a cell of cathode with the photonic gel and an anode with the hydrogel. However, it is interesting that similar behavior was observed from a cell with opposite current direction; a cathode with the hydrogel and as anode with the photonic gel. We hypothesized that two effects may play a role in changing color of the photonic gel. (1) Water molecules move under the electric fields [19]. (2) The ions transfer from hydogel to photonic gel or vice versa [20]. Both effects can lead to shift in the dielectric constant of the lamellar domains, or domain spacing by changing interaction between PS and P2VP. Here, we speculated that both effects occur simultaneously to affect reflection color.

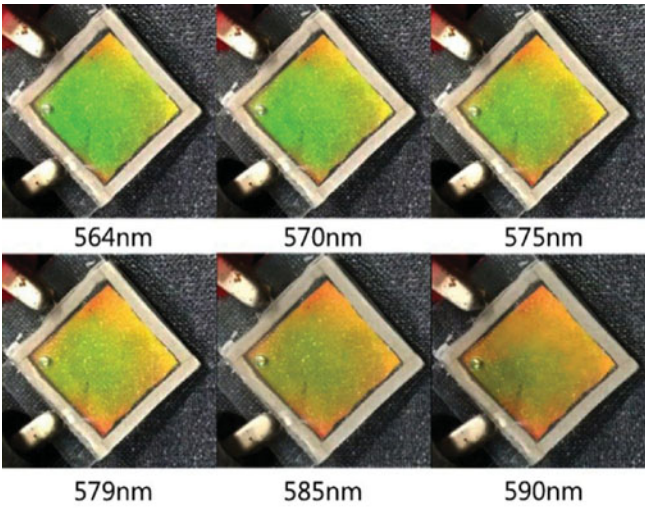

Figure 5. The photograph of change of reflecting color hybrid device with electric fields generating time at 0 min, 5 min, 10 min, 15 min, 20 min and 25 min.

4. Summary

Optical and electrical characteristics of the device using photonic gel and hydrogel were studied. PAAm-*co*-PAAc with potassium salts was synthesized for electric sensitive hydrogel that can interact with the photonic gel. It was observed that the reflection color changes from green to orange under the electric field. The maximum reflectance wavelength of the hybrid device shifted from 563 nm to 590 nm, and the band-width variation was very limited. We can control the reflection color of the hybrid device by moderate electric fields (e.g., 2 V) with reasonable time range. If the reflection color shifting time can be fast enough to confirm with the unassisted eye, we expect the range of photonic crystal's application would increase.

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