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Enhanced Reflectance Wavelength Shift of PS-*b*-P2VP Films Using Reactive Monomer and Photo-Initiator

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*The reactive monomers (RM) draw much attention due to many possible applications on the liquid crystal alignment in LCD. A photo-initiator (2,2-Dimethoxy-2-phenylacetophenone (DMPA)) decomposes to free radicals when exposed to UV light. Poly(styrene-*b*-2-vinyl pyridine) (PS-*b*-P2VP) lamellar film with alternating hydrophobic block-hydrophilic polyelectrolyte block polymers (52 kg/mol-*b*-57 kg/mol) were prepared for the photonic gel. The photophysical and photochemical effects of RM and DMPA to the PS-*b*-P2VP photonic gel film was studied. The reactive monomer added to the Photonic gel films increased the light scattering especially at blue region compared to the PS-*b*-P2VP photonic gel films. Irradiation of photonic gel containing RM and DMPA showed clear color. Swelling of films with ethanol (490 nm∼500 nm) exhibited shorter wave length reflection compared with those swollen with DI water (581 nm∼649 nm). This study showed that the water induced more hydrophobic and hydrophilic contrast compared to the Ethyl alcohol. The irradiation of photonic gel films with UV effectively controlled the reflecting color from red to blue (654 nm∼508 nm), DMPA (705 nm∼513 nm) and RM (637 nm∼405 nm). RM and DMPA additive increased the clarity of the film and give feasibility for color control of photonic gel.*

Keywords DMPA; photonic crystal; reactive monomer; swelling

1. Introduction

Photonic crystals contain periodic optical structures that are formed to affect the motion of photons. The wave phenomena of light in photonic crystals are very much similar as those in the periodicity of semiconductor crystals to the electron movement [1]. Responsive photonic crystals have been developed for the chemical sensors using the variation of optical properties caused by interactions with their environment.

The photonic crystals can be active components for display, sensory or telecommunication devices [2–4]. Since optical properties are the main physical properties for the application of photonic crystals, near-infrared to visible region is important for controlling and processing of light. The light interference occurred in between two different dielectric layers is dependent on the refractive indices difference and layer thickness of the layers. With appropriate refractive indices and the scale of periodicity of the dielectric

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layers to wavelength of incident light, the wavelength of reflected light can be managed. Many tuning methods of photonic band gap by changing the refractive index and/or layer thickness have been demonstrated [5–10]. Block copolymers have also been suggested as a material platform for producing photonic-crystal structures where self- assembly of high-molecular-weight block copolymers yields one-dimensional (1D), 2D and 3D periodic photonic crystals from lamellae, hexagonally packed cylinders and double gyroid micro domain structures [11–12]. Reflecting light wavelength of photonic gel films is dependent on the dielectric constant of liquid which penetrated into micro domains [13–14].

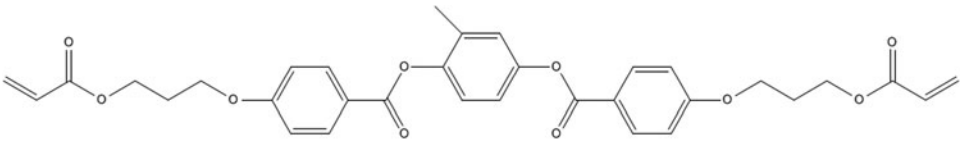
The Reactive monomer which is used to enhancing reaction rate of LCD cell by added to liquid crystal material [15]. When the photolysis of an applied initiator is known, it is not easy to predict the behavior of a photo-initiator incorporated into a polymer matrix, even if it is an efficient compound in the polymerization process. They retard polymer photo-degradation in some cases, but in other system and conditions, the same compounds act as sensitizers or catalysts. The colorless nature of DMPA makes it very attractive for the formulation of dental resins with improved esthetical properties. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) is a very efficient and frequently used free radical photo-initiator for thin photocurable coatings [16–18].

We studied the optical and physical properties of the photonic gel containing RM and photo-initiator compared that without those. The optical properties of photonic gel films after photo-irradiation, which were swelled with water, were studied.

2. Experimental

We prepared polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer have 52 kg/mol-*b*-57 kg/mol, PS-*b*-P2VP film with 0.2 wt% reactive monomer(RM257) and PS-*b*-P2VP film with 0.01 wt% DMPA were prepared for photonic gel films (the structures of RM and DMPA are Figs. 1 and 2).

To manufacture the photonic gel, thin homogeneous films were prepared by spin-coating (MIDAS Model spin1200D) from a 5 wt% PS-*b*-P2VP solution in propylene glycol monomethyl ether acetate. The spin-coated films were annealed in chloroform vapor at 65°C for 24 hours and the film transformed to well oriented transparent lamellar films. Quaternization was performed with 5 wt% of iodomethane in n-hexane for 48 hours. The remaining iodomethane was immediately removed from the PS-*b*-P2VP film after quaternization using DI water and n-hexane. The quarternized photonic gel films were dried and saved for measurements. PS-*b*-P2VP was purchased from Polymer Source and



RM257

Figure 1. The structure of reactive monomer.

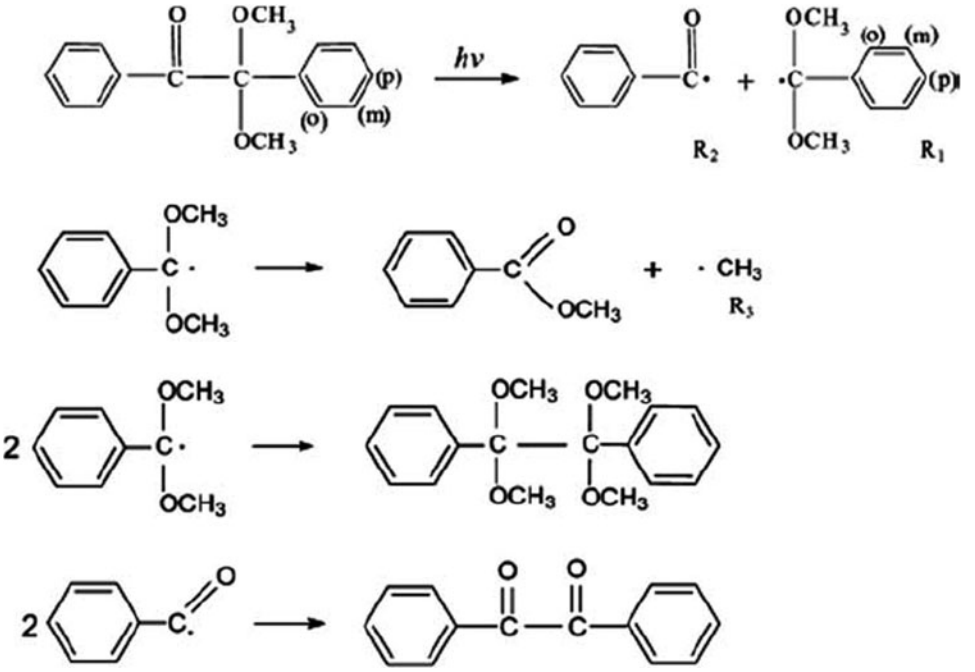


Figure 2. The structure of photo-initiator (DMPA) and the photodecomposition reactions for active materials.

iodomethane chemicals were purchased from Aldrich. These chemicals were used as it was without further purifications.

The photonic band gaps were measured with the UV spectrophotometer (Agilent Model 8435). The optical spectra of the photonic crystals were taken at swollen state by spreading distilled water and ethanol onto the film. To avoid drying during measurement of UV spectra, the films were covered with quartz cover glass. The UV lamp (FORCELAMP Model UVGL-58) was prepared for photo-irradiation.

3. Results and Discussion

The domain spacing of dried photonic gel films was not wide enough to show any color from the films. Addition of aqueous solution to the films immediately exhibited color due to layer thickness and refractive index change. Figure 3 showed the reflectance of the photonic crystal films with and without RM and DMPA. The visible absorption spectra represented the sum of the reflected light and scattered light from the film surface. The standard photonic gel films swollen by DI water has reflectance peak at 649 nm and the film showed red color. The film swollen by ethyl alcohol exhibited reflectance peak at 490 nm and appeared blue color. The photonic gel films with RM swollen by DI water has reflectance peak at 581 nm and the film showed red color. The film swollen by ethyl alcohol exhibited reflectance peak at 499 nm and appeared blue color. The photonic gel film with DMPA swollen by DI water has reflectance peak at 662 nm and the film showed red color. The film swollen by ethyl alcohol exhibited reflectance peak at 500 nm and appeared blue color. Ethyl alcohol influenced photonic band gap to the shorter wavelength due to low

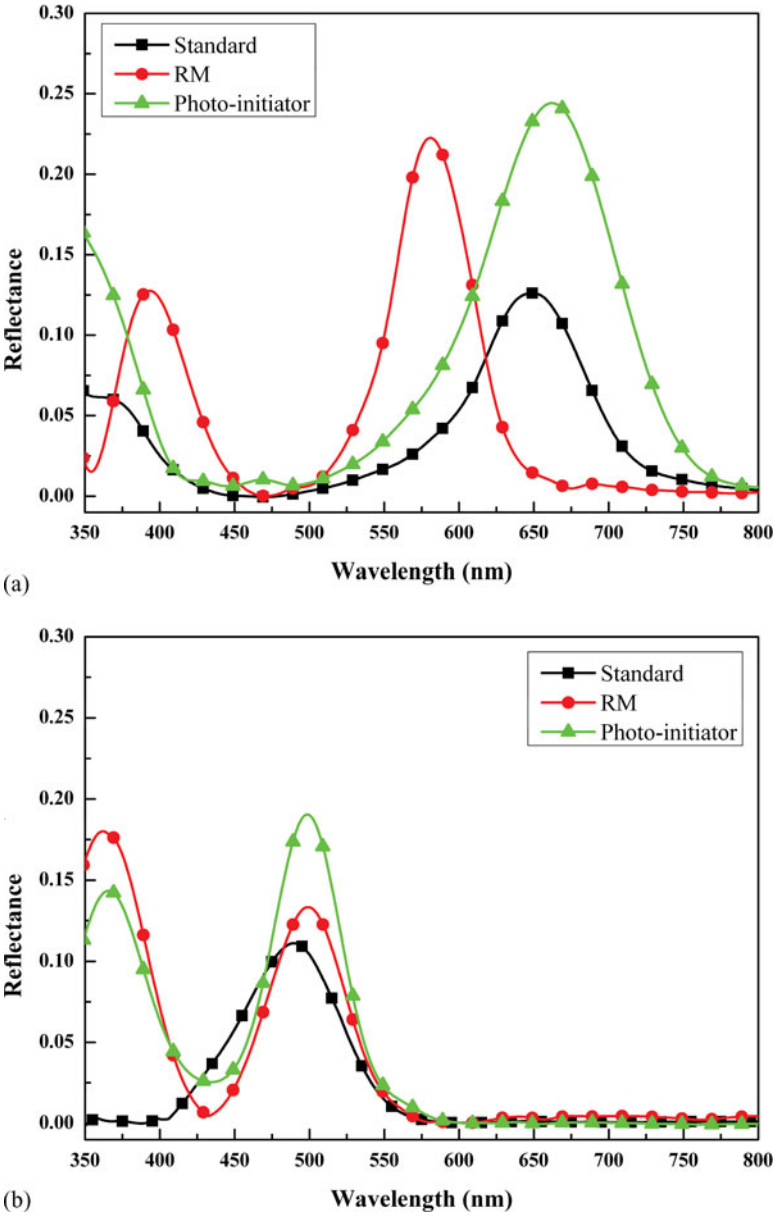


Figure 3. Ultraviolet-visible-near-infrared reflectance spectra of PS-*b*-P2VP photonic gel films and the photonic gel films containing RM and photo-initiator were swollen by (a) DI water, (b) ethyl alcohol.

dielectric constant and thin layer thickness. The photonic band gap was highly influenced by the swelling solvents.

The photophysical characteristics of the films with and without RM and DMPA were compared. Figure 3 showed the higher background shorter wavelength reflectance indicates increased scattering and enhanced phase separation due to RM. All type of photonic gel films

has similar reflectance peak positions when the films were swelled by ethyl alcohol. The reflectance peak of PS-*b*-P2VP film with RM shifted from 649 nm to 581 nm. The photonic gel film with RM exhibited about 68 nm shorter wavelength reflectance due to RM had moderate polarity. The photonic gel film with RM and DMPA had higher reflectance than standard photonic gel film. The hydrophobicity of RM and DMPA influenced reflectance peak position to shorter wavelength and higher reflectance peak intensity, which appeared more pronounced color.

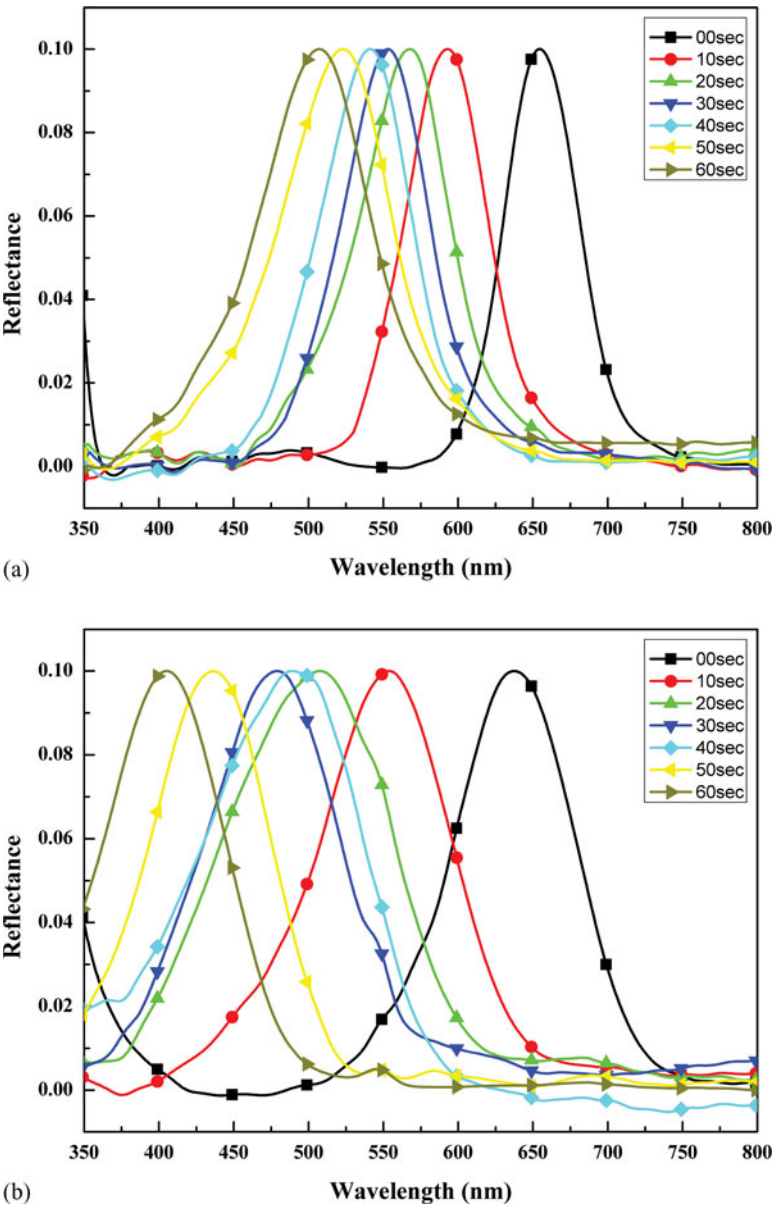


Figure 4. Ultraviolet-visible-near-infrared reflectance spectra of UV irradiation to the PS-*b*-P2VP photonic gel films (a) standard (b) RM (c) with DMPA, were swollen by DI water. *(Continued)*

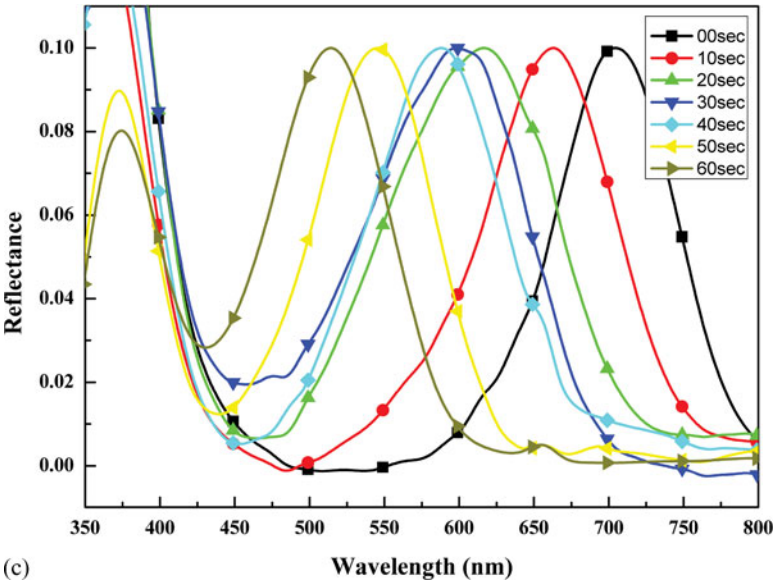


Figure 4. (Continued)

The photonic gel films were irradiated by UV light for 10 second at dry condition without any solvent. The UV irradiated condition was 1.8 mW/cm^2 at 6 cm. The reflectance of the film was measured by the UV spectrophotometer after swelling with DI water. After the reflectance measurement, photonic gel film blew dry by N_2 gas for the photo-irradiation. We repeated these process 6-times. Figure 4 showed that the reflectance peak of photo-irradiated film shifted to shorter wavelength with UV irradiation time. The wavelength shift was more pronounced when the standard films were swelled with DI water, 654 nm to 508 nm. The shift was from 637 nm to 405 nm when the films with RM were swelled by DI water. Longer irradiation of reactive monomer in the polyimide film forced many photoreactions, such as [2+2]dimerization and reverse reaction, radical formation by decomposition of carbonyl group and addition reactions of reactive monomer to the polymer chain. The complex photoreactions produced inhomogeneous film, which made optical scattering of the polyimide film. The shift was from 705 nm to 513 nm when the films with DMPA were swelled by DI water. DMPA was generated free radicals when UV irradiation and free radicals promoted reflectance wavelength shift. The difference in wavelength shift was also due to the enhanced hydrophobic and hydrophilic contrast by UV irradiated film when swelled with water. Figure 4 showed dramatic color shift of the photonic gel film with UV irradiation.

The photo-decomposition of PS-*b*-P2VP upon UV-irradiation is more favorable reaction mechanism. Both RM and DMPA additives decrease reaction film and more hypsochromic shift.

4. Conclusions

We have studied the effect of reactive monomer in PS-*b*-P2VP film. The reflectance peaks were compared by swollen solutions. Adding RM and DMPA to the photonic gel increased the reflectance maximum compared with the standard film. The RM added to the photonic

gel film increased the light scattering especially at long wavelength region. The photonic gel containing the RM and DMPA showed pronounced color. It can be used to control visibility of photonic gel film. The swelling solution, influence the photonic gel film colors. The color of photonic gel film showed hypsochromic shift by UV irradiation. The UV irradiation affords to control the color of photonic gel film. We expect that the light management of photonic gel will lead to display devices.

Since photo-decomposition reaction is the only decomposition pathway from the DMPA, the similar results from the additive suggests that the photo-decomposition reaction is the major pathway.

Acknowledgment

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