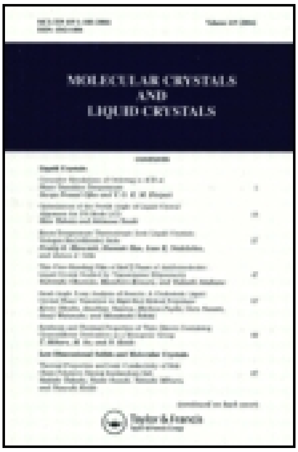

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The Effect of UV Irradiation on the Transmittance Bands of Polystyrene-block-2-vinylpyrimidine

Sung Woo Lee [a] , Jeesun Shin [b] , Jhoseph Shin [c] , Christine Shim [d] & Dong Myung Shin [a]

[a] Department of Chemical Engineering, Hongik University, Seoul, Korea

[b] Department of -Life Sceince and Biotechonology, Yonsei University, Seoul, Korea

[c] Department of Biological Science, State University of New York at Buffalo, NY, USA

[d] SeoulInternational School, Kyungki-do, Korea

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The Effect of UV Irradiation on the Transmittance Bands of Polystyrene-block-2-vinylpyrimidine

SUNG WOO LEE,[1] JEESUN SHIN,[2] JHOSEPH SHIN,[3]
CHRISTINE SHIM,[4] AND DONG MYUNG SHIN[1]

[1]Department of Chemical Engineering, Hongik University, Seoul, Korea
[2]Department of -Life Sceince and Biotechonology, Yonsei University, Seoul, Korea
[3]Department of Biological Science, State University of New York at Buffalo, NY, USA
[4]SeoulInternational School, Kyungki-do, Korea

Block copolymers have been investigated for fabricating functional nanomaterials due to their properties of self-assembly. 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. 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 5 wt% of iodomethane.

PS-b-P2VP films showed excellent photonic bands at 630 nm after swelling with ethanol and 661 nm with water after treated with Calcium Carbonate. We observed significant band shift from 663 nm (deep red) to 531 nm (green) during UV-irradiation for 40 seconds.

The phase separation process of BCP was very sensitive to the film thickness. The quarternized films with thickness varied from 0.43 μm (446 nm transmittance minimum) to 0.25 μm (478 nm transmittance minimum). This study shows that the total film thickness and UV irradiation effectively change the transmittance band by affecting the thickness of layers consisting of PS-b-P2VP photonic crystals.

Keywords Block copolymer; photonic crystals; poly(styrene-block-2-pyridine); UV irradiation

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]. Self assembly of BCP micro-domains leads to well-ordered structures, which have potential optical applications. The light passing through well ordered structures tends to bend, steer and interact with each other to generate other wave characteristics [4,5].

Address correspondence to Dong Myung Shin, Department of Chemical Engineering, Hongik University, Sangsu-Dong, Mapo-Gu, Seoul, 121-791, Korea. Tel. & Fax: (+82)2-320-1652; E-mail: shindm930@paran.com

Recent progress of self-assembly methods combined with lithographic processing facilities modulation of light frequency from infrared to visible range. The frequency range was dependent on the size of colloidal crystal arrays, artificial opals and inverse opals, hollow spherical micelles, and interlayer thickness of lamellar films [6]. The optical as well as mechanical properties required for desirable applications covers several polymeric characteristics, such as size of domains matches the optical frequencies of interest, long-range domain orders with appropriate orientations as well as sufficient dielectric constant between the domains.

Desirable photonic characteristics, such as optical wavelength, transmission band width, optical pathway and transparency of materials can be attained by modifying the structure of each monomer unit, blending with homopolymers, the relative ratio of each block, dielectric contrast between each domains, and interface characteristics [7–10]. The long range of periodicity goes with the molecular weight of blocks. However, very high viscosity of high molecular weight bcp retards the formation of periodic structures and requires high energy to overcome low mobility of long polymer molecules [11,12]. To facilitate intermolecular interactions for the phase separation of bcp and increase the range of periodicity, liquid crystalline blocks have been employed and accompanied with synthetic difficulties. Blending of homopolymers with bcp has been investigated experimentally and theoretically. Tailored domain spacing as well as processing advantage was obtained with employing the somewhat low molecular weight components [13–17].

Applications for the display devices have been investigated with poly(styrene-block-2-vinylpyridine), PS-b-P2VP have been investigated intensively. The reflectance band maxima varied from IR to UV range and were dependent upon the solvent reflective indices incorporated in P2VP layers [18–20]. Clarity of reflection bands dramatically increased after incorporation of Calcium Carbonate in P2VP layer. The inorganic materials in P2VP layer shift the absorption band to red [21,22].

In this study we applied UV irradiation on the swelled PS-b-P2VP bcp films and induced polymer modification followed by optical transmittance change in visible range. The results will apply for the optical components in the display devices.

2. Experimental Section

To obtain well-oriented lamellar film Polystyrene-b-poly (2-vinyl pyrimidine) (PS-b-P2VP) lamellar films which is hydrophobic block-hydrophilic polyelectrolyte block polymer were spin-coated (MIDAS Model spin 1200D) from a 5 wt% PS-b-P2VP (57 kg/mol-b-57 kg/mol) solution in propylene glycol monomethyl ether acetate (PGMEA). The spin-coated films were annealed in saturated chloroform vapor at for 48 hours. After the annealing, we could observe well-oriented lamellar films showed significant color by swelling with ethanol. Quaternization was performed with 5 wt% of iodomethane solubilized in n-hexane. Iodomethane were reacted with pyrimidine groups in PS-b-P2VP at for 72 hours. The quaternized photonic gel films were then immersed into saturated $CaCO_3$ for 2 days (Fig. 1).

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 ethanol. To observe UV light effect on the photonic gel films were UV light (intensity 1000 mW/cm^2) from 25 seconds to 50 seconds at dried state. The UV-visible absorption and transmission spectra were measured in the

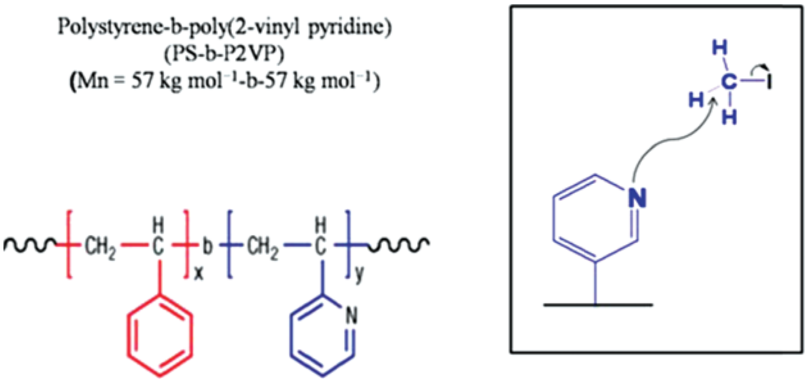

Figure 1. Structure of PS-P2VP block copolymer and quarternization reaction scheme.

range of 350–800 nm. In order to prevent evaporation during measurement of film spectra, we covered the films with cover glass after swollen with ethanol.

3. Result and Discussion

PS-b-P2VP films were spin coated at ambient temperature and annealed at the elevated temperature for the movement of polymer chain rearrangement. The 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.

The absorption maxima the films swollen with ethanol located at 510 nm after the quaternization process, which facilitated the swelling and changed the dielectric constants of the swelled layers. Especially, water can penetrate easily into the films after quaternization. After the films were treated with the saturated Calcium Carbonate solution for 2 days and spread water onto the film, a deep red color developed, Figure 2. Calcinations with Calcium Carbonate shifted the transmittance bands at shorter wavelengths. The band shifts were significant and the clarity of the films were enormously improved. This is due to the dielectric constant contrast between two layers, polystyrene and poly(2-vinyl pyrimidine) containing Calcium Carbonate, and clear interfaces which reduce the scattering at shorter wavelength.

The films treated with Calcium Carbonate showed absorption maxima at 630 nm after swelling with ethanol. The shorter wavelength compared to the films swollen with water. The films swollen with water showed significant red color, Figure 2. The shorter wavelength shift was due to the decrease in dielectric contrast between two different layers.

The films swollen with water were effectively change color under UV irradiation. After the UV irradiation, the transmittance bands shifted gradually to shorter wavelength as increasing the irradiation time, Figure 3.We observed significant band shift from 663 nm to 531 nm during UV-irradiation only for 40 seconds. The significant

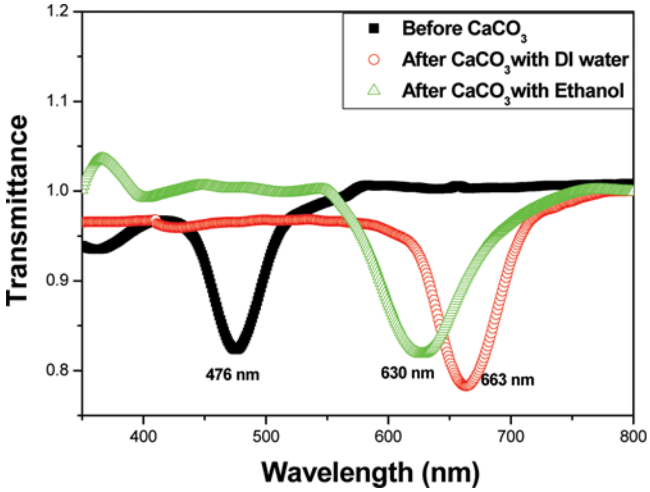

Figure 2. UV-vis. transmittance spectra of PS-P2VP photonic gel before, after treated with $CaCO_3$ and the films were swollen with water (663 nm maximum) and ethanol (630 nm maximum).

reflection band shift is due to the decrease of interlayer thickness or the deswelling of the films. However, the solvent swelling for the UV irradiated films showed the same transmittance band and the color retained for few days. This clearly indicated that the UV irradiation incurred decomposition of polymer chains which eventually collapsed the layer structure without changing the polymer dielectric constants. The block copolymer films came off after long irradiation time, which also indicated the photo-degradation of the polymers. There are many photo-labile sites on the

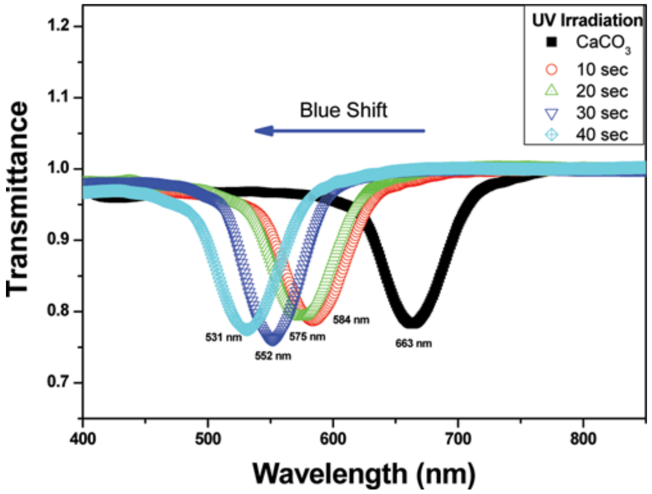

Figure 3. UV-vis. transmittance spectra of PS-P2VP photonic gel obtained during UV irradiation for 40 sec.

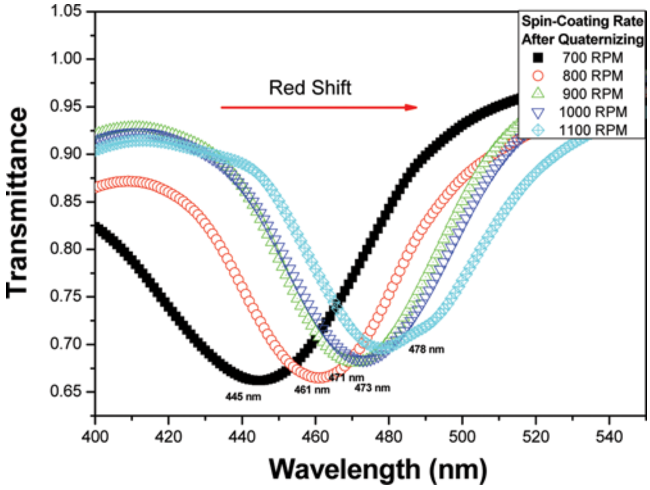

Figure 4. Visible transmittance spectra of PS-P2VP photonic gel with variation of total film thickness.

PS-b-P2VP including benzylic position connected to the styrene and pyrimidine rings.

The phase separation of BCP can be very sensitive to the film thickness. The films thickness was measured after quarternization of the PS-b-P2VP films, which were originally spin coated at variable spin rate. The film thickness measured by alpha step instrument. The films spin casted at low spin rate are thick. When the spin rate was 700 rpm, thickness of the quarternized film was 0.43 μm, which became 0.25 μm for highest speed spin rate. The transmittance maximum shifted from 446 nm for the thicker film to 478 nm for the film made with the maximum spin speed. The band shift with film thickness indicates that the layer thickness is dependent upon the total film thickness. The vanished scattering around 400 nm observed from non-calcinated films clearly indicated sharp interface for the calcinated film which accompanied with thickness change.

4. Conclusion

PS-b-P2VP films showed excellent photonic bands, which can be more clear and transparent after calcinations with Calcium Carbonate. The films treated with Calcium Carbonate showed transmittance maxima at 630 nm after swelling with ethanol and 661 nm with water. The deep red color films can be transformed to green to blue color films with UV irradiation. We observed significant band shift from 663 nm to 531 nm during UV-irradiation for 40 seconds. The significant reflection band shift may be due to the decreased layer thickness with decomposition of the polymers.

The phase separation process of BCP was very sensitive to the total film thickness. The quarternized films thickness decreased from 0.43 μm to 0.25 μm with increasing spin rate. The transmittance minima shifted from 446 nm for thicker film to 478 nm for thin film, Figure 4 and Table 1. This study shows that the total film thickness and UV irradiation effectively change the transmittance band by affecting the thickness of layers consisting of PS-b-P2VP photonic crystals.

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

Speed (rpm)	Thickness (μm)	Transmission Minimum (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

Acknowledgment

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