Fast electrically driven photonic crystal based on charged block copolymer†

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We have developed electrically driven photonic crystals (PCs) from a quaternized polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) block copolymer which can form a one dimensional periodic lamellar structure. The variation of applied voltage from −4.50 to +2.36 V on the PCs can lead to color display over the entire visible region with a sub-second fast response, where the periodic structure swells from 4.3 to 7 times that at dry state. The fast response is attributed to the charging of the P2VP block. Besides, the photonic crystal exhibits a reverse volatility behavior, that is, as the applied voltage increases, the reflective peak wavelength decreases. Such fast switching PCs are facilely prepared with low driving voltage and good durability. The PCs are expected to find applications in information technologies.

Introduction

Chromic materials with stimuli response attract increasing interests because of their practical applications such as in smart windows, displays, data storage, switches and sensors. Photonic crystals (PCs) are a new class of material with a periodic variation of dielectric constant.[1,2] They can manipulate and control light in their photonic band gap that forbids the propagation of electromagnetic waves in a certain frequency range. Recently, some structure color materials stimulated by heat,[3] electric field,[4–8] stretching,[9] UV light,[10] magnetic[11–13] and chemical environment[14,15] have been developed. Considering that electric field is the most facile approach to supply a stimulus in signal control among various external stimuli, electrically tunable photonic crystals have received much attention. However, only a few electrically tunable photonic crystals have successfully been prepared. Photonic crystals based on polypyrrole inverse opals are electrically tunable but they do not exhibit full color.[16] The electrically tunable photonic crystal made of a polyferrocenylsilane gel–silica opal composite with a reversible expanding and contracting lattice was reported to display full color.[4] Moreover, some polyferrocenylmethylvinylsilane and polyferrocenyldivinylsilane inverse gel opals exhibit fast response, however, their preparation procedure is complicated.[5]

Recently, several groups focused on one dimensional photonic crystals (1D PCs) of dynamic tunability.[14,15,17–20]

Generally, they are multilayers consisting of alternating high and low refractive index materials, and have high refractivity at the position of the photonic band gap known as Bragg stacks or Bragg reflectors or Bragg mirrors. Due to their simple architecture, the optical properties of 1D PCs can be readily manipulated by the thickness and refractive index of the film. Thomas *et al.*[14] reported that quaternized polystyrene-*b*-poly-(2-vinyl pyridine) (PS-*b*-P2VP) block copolymer with a one-dimensional periodic lamellar structure could form photonic crystals in that its lamellar layer thickness and refractive index can be adjusted by salt concentration or pH.[14] The optical hysteresis of the photonic crystal films proved to be controlled by the ionic strength.[21] Organic/inorganic photonic crystals with lamellar structure can also be prepared by using the block copolymers as a template.[22] The chemically tunable PCs can exhibit a large reversible optical change from ultraviolet to near infrared. Recently, electrically tunable PS-*b*-P2VP PCs were successfully prepared.[6,7,23] They have advantages over other PCs because of their facile preparation, low driving voltage and broad continuously tunable wavelength range from invisible ultraviolet to invisible near infrared. Electrically tunable photonic crystals with nonvolatile photonic colors were also developed. The volatility of the photonic crystals was tuned by controlling their hysteresis strength and the pK_a value, which depend on the species of anions pairing with pyridinium groups.[7]

In the present work, we have developed electrically driven 1D PCs with fast switching based on the charged block copolymer, quaternized PS-*b*-P2VP. The PCs have a response less than one second, namely, the switching is about 1000 times faster than that of the PCs made of PS-*b*-P2VP without quaternization. Also, the wavelength and brightness of the diffracted light of the newly developed PCs can be tuned continuously from ultraviolet through visible to the near infrared.

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Experimental section

Materials

Polystyrene-b-poly(2-vinyl pyridine) diblock copolymer (PS-b-P2VP) was purchased from Polymer Source. The number average molar mass (M_n) of either PS or P2VP block is 1.90×10^5 g mol^{-1}. The polydispersity index (M_w/M_n) is 1.10. Acetonitrile, lithium nitrate and propylene glycol monomethyl ether acetate (Aladdin) as well as chloroform (Sinopharm) were used as received.

Lamellar film preparation

The details about preparation of the lamellar film can be found elsewhere.[14] Generally, each film was prepared on an indium tin oxide (ITO) glass with a KW-4A spin coater (CHEMAT Technology, Inc.), starting from a 5 wt% PS-b-P2VP solution in propylene glycol monomethyl ether acetate. After the solution was uniformly dropped on the ITO glass surface, it was spun at 3000 rpm for 15 s. Then more PS-b-P2VP solution was added and spun at 500 rpm for at least 75 s. Such prepared film was annealed in chloroform vapor at 53 °C for 24 h. The thickness of the film was mediated by the concentration of polymer solution and the speed of the spin coating. Generally, the thickness of the film increases with the concentration but decreases with the speed of spin coating. The concentration used here is 5 wt%. The formation of quaternized P2VP blocks were prepared by using 1-bromoethane (5 wt%) in hexane at 50 °C for more than two days which follows the same procedure as in the previous report.[14,24] FTIR measurements indicated that all pyridine groups converted to pyridinium groups.

Measurements

A simple two-electrode electrochemical cell was used. The film on ITO served as the working electrode and another bare ITO plate was used as the counter electrode. The electrodes were separated by a polytetrafluoroethylene coated rubber O-ring. The film was immersed in the mixture of acetonitrile and water (20/1, v/v) with 0.19 M lithium nitrate. The electrical potential dependent reflective spectra were recorded on a UV/Vis spectrophotometer (Unico 2802PCS) in the transmission mode. Color analysis was carried out by taking the red, green and blue (RGB) values from video frames at the center of the photonic crystal film in the rubber O-ring. The RGB values span a range from 0 to 255 obtained by PhotoStudio (Arc Soft). The transfer matrix method was used to compute the theoretical spectra of the photonic crystal film. The refractive index (n_{PS}) of the PS layer is 1.52. The refractive index (n_{PVP}) of the quaternized P2VP layer with various thicknesses can be calculated by using $n_{PVP} = 1.62(t_{PVP0}/t_{PVP}) + 1.34(1 - t_{PVP0}/t_{PVP})$, where t_{PVP0} and t_{PVP} are the thickness of the quaternized P2VP layer in its dry state and swollen state in the mixed solvent, respectively. The thickness of the PS or P2VP layer is 30 nm and the film thickness is about 1 μm.[23]

Results and discussion

The peak position of the reflected light varies with the solvent composition. In a preliminary experiment, we found that the reflective peak shifts towards longer wavelength (red) as the acetonitrile fraction increases because acetonitrile is a good solvent for quaternized P2VP. On the other hand, the salt can screen the charges on the quaternized P2VP. Thus, as the salt concentration decreases, each quaternized P2VP layer becomes more swollen, and the lamellar periodicity increases. Meanwhile, the refractive index of the quaternized P2VP decreases with salt concentration. Here, we fixed the concentration of lithium nitrate at 0.19 M in the mixture of acetonitrile and water (20/1, v/v) so that the reflected light is in the visible region.

Fig. 1 shows how the wavelength of the reflective peak changes with the applied voltage. The reflected light changes from green ($\lambda_{max} = 550$ nm) to blue ($\lambda_{max} = 486$ nm) when a positive potential is applied. Upon applying a negative potential, the reflected light changes from green ($\lambda_{max} = 550$ nm) to red ($\lambda_{max} = 664$ nm). Namely, the PCs have a full color display. Actually, the reflective peak can even shift into the near-infrared region with its high order Bragg peaks in the visible region when a negative potential lower than −4.5 V is applied. In contrast, the reflective peak shifts into the ultraviolet region which shows transparent to visible light when a positive potential higher than +2.4 V is applied. Clearly, we can observe a continuum of the accessible color over a voltage range of a negative applied potential (−3.50 to −4.50 V) and positive potential (+2.00 to +2.36 V). Moreover, the photonic crystal exhibits a reverse volatility behavior. Namely, as the applied voltage increases, the peak wavelength decreases. This is quite different from that regarding photonic crystals made of quaternized PS-b-P2VP with low salt concentration (~0.5 mM) or PS-b-P2VP without quaternization, where the peak wavelength increases with the voltage.[7,23] This is because the P2VP blocks in quaternized PS-b-P2VP with higher salt concentration are surrounded by charged ions and electrostatic interaction between the salt and the quaternized P2VP layer plays a critical role in changing the color. In contrast, for photonic crystals made of quaternized PS-b-P2VP with low salt concentration or PS-b-P2VP without quaternization, the color change is mainly controlled by the interaction between the P2VP layer and the electrode. When a positive voltage is applied to a quaternized PS-b-P2VP photonic crystal, nitrate ions with negative charges bind to the thin film due to the Coulombic interaction. As the concentration
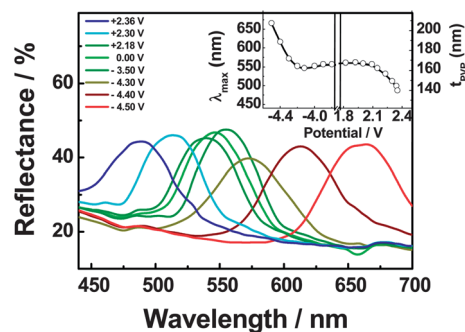
Fig. 1 Electrical potential dependence of reflective spectra of a quaternized PS-b-P2VP thin film (photonic crystal). The inset shows the voltage dependence of the first Bragg peak position (λ_{max}) and the corresponding thickness of the quaternized P2VP layers (t_{PVP}).

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of nitrate ions increases, the positively charged photonic crystals shrink due to the screening of nitrate ions. The shrinking of each P2VP layer leads the lamellar periodicity to decrease but causes the difference of refractive index between PS and the quaternized P2VP layer to increase. This is why the reflective peak exhibits a blue shift. When a negative voltage is applied, lithium ions bind to the polymer film so that the local concentration of lithium ions around the film increases. Since P2VP is positively charged, the photonic crystal swells due to the repulsion between the positively charged pyridinium groups and lithium ions. Accordingly, the photonic crystals exhibit a red shift of the reflective peak. The reflective peak shift occurs when the voltage reaches a critical value, that is, it is below −3.50 V for a negative applied potential and above +2.00 V for a positive potential. The chain entanglement and the Coulombic interactions are responsible for such critical voltage. When a positive electric potential is applied on the polymer film, the positively charged P2VP layers repel the positively charged electrode. Nitrate ions are attracted to the electrode so that the film is surrounded by negative charges. The critical value +2.00 V is the result of competition between Coulombic interactions of the quaternized P2VP layers/electrode and the quaternized P2VP layers/nitrate ions. On the other hand, when a negative electric field is applied, the positively charged quaternized P2VP layers are attracted by the negatively charged electrode. Meanwhile, the lithium ions are also attracted to the electrode so that the thin film is surrounded by positive charges. The photonic crystals are swollen due to the repulsion between the charge on the P2VP block and lithium ions. The polymer chains are entangled with each other at such a high concentration, and the swelling of the layers requires the chain disentanglement. As a result, the absolute critical value of the negative applied voltage (−3.50 V) is somewhat higher than that of the positive one (+2.00 V).

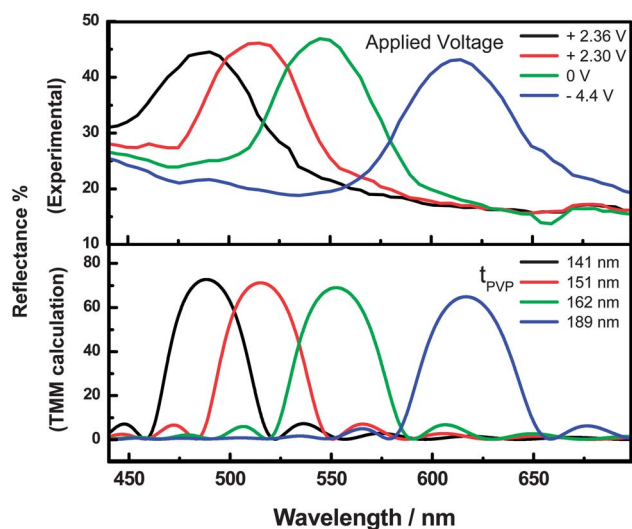Fig. 2 shows the change in thickness of the quaternized P2VP layer calculated by the transfer matrix method (TMM). The

Fig. 3 Photographs of color switching of a quaternized PS-b-P2VP thin film (photonic crystal) at different applied voltages.

periodic number of the film is 16 since the film thickness is 1 μm and the thickness of the PS or P2VP layer in dry state is 30 nm. The theoretical spectra of the thin film were computed with different thicknesses of quaternized P2VP layer. The peak position can match the experimental results. However, the peak widths from the experiment are broader than the theoretical values. This is due to the defects and misorientation of the lamellar structure.[14] The inset of Fig. 1 also shows peak wavelength as well as the change of thickness of the P2VP layers at different applied voltage obtained by TMM simulation. The P2VP layer can swell from ca. 4.3 to 7 times in terms of its thickness (ca. 30 nm) in dry state as the film color changes from blue to red.

Fig. 3 shows the switching time of the photonic crystal. The display area inside the rubber O-ring is about 1 cm² and the film is surrounded by a liquid reservoir in the cell. Photographs were taken under an 18 W desk lamp which can be treated as a normal lightening condition. When the electric potential is added to the electrode, the color of the thin film rapidly changes from green to red or blue (see ESI, Video S1 and S2†). In

Fig. 2 Electrical potential dependence of reflective spectra of a quaternized PS-b-P2VP thin film (photonic crystal) and the theoretical spectra calculated by transfer matrix method.
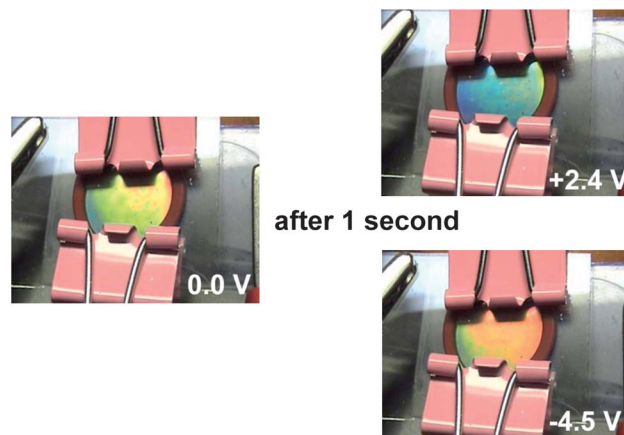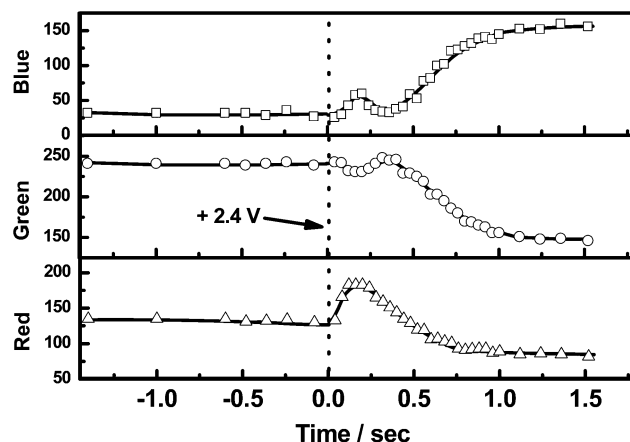

Fig. 4 RGB color analysis from Video S1 of color switching of a quaternized PS-b-P2VP thin film (photonic crystal) at a positive applied voltage (+2.4 V).
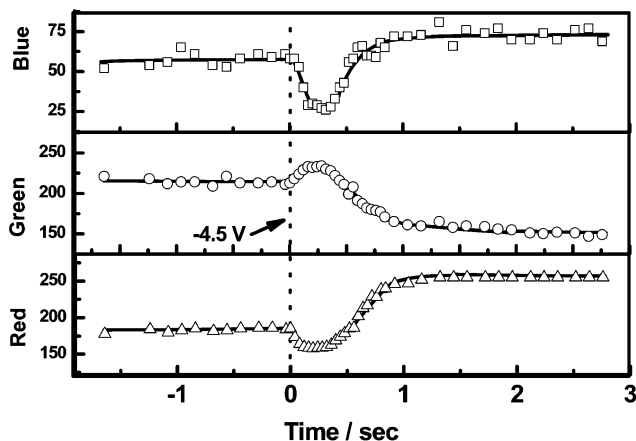
Fig. 5 RGB color analysis from Video S2 of color switching of a quaternized PS-*b*-P2VP thin film (photonic crystal) at a negative applied voltage (−4.5 V).
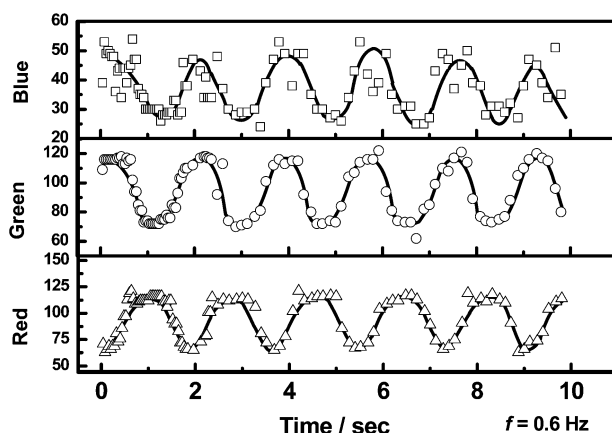

Fig. 6 RGB color analysis from Video S3 of color switching of a quaternized PS-*b*-P2VP thin film (photonic crystal) at an alternating voltage (4.1 V, 0.6 Hz).

comparison with PS-*b*-P2VP PCs without charging,[23] quaternized PS-*b*-P2VP PCs exhibit a more than 1000 times faster switching.

Considering that the fast switching is difficult to characterize by UV-Vis, we use the color analysis of the videos to interpret the change in color of the film (in Video S1, S2 and S3

in the ESI†). The red, green or blue (RGB) value is obtained from the center of the display area of the film to the video frame. The RGB value varies with the film color triggered by the voltage (Fig. 4 and 5). In Fig. 4, as the color of the film turns from green to blue, the red and green contents of the color decrease while the blue content increases. A small dip for blue and red content or a small spike for green content is observed at 0–0.3 s after the voltage is applied to the film. This behavior can be attributed to the competition of the electrostatic interactions between the quaternized P2VP groups on the film and the nitrate ions, as well as P2VP groups and the electrode. When a positive voltage is added to the electrode, the substrate is instantly positively charged and the pyridinium groups on the film tend to repel the substrate, leading to a red shift with the increase of the red content at 0–0.3 s after the voltage trigger. However, the nitrate ions are also attracted by the substrate and move to the film, and screen not only the electrostatic interaction between the film and the substrate but also the interactions between the quaternized P2VP groups on the film. The latter causes the film to collapse and decreases its periodic length. As a result, a blue shift happens. The film color turns blue with the RGB content leveling off after about 0.8 seconds. Similar behavior can also be found when a negative voltage is applied (Fig. 5). The red and blue shifts are complete within one second, which shows the fast migration of lithium ions through the film. The fast ion migration and the electrostatic interaction between the film and ions in solution are likely to be responsible for the fast response. On the other hand, the pores and the dislocation defects in lamellar structures formed due to the charging of the P2VP block behave like effective high-transport-rate channels for solvents and ions across the polystyrene layers,[14] further accelerating the response. The facts indicate that the quaternized P2VP block is very sensitive to chemical environment. We also examined the performance of the PCs upon application of an alternating current. When an alternating current ($f = 0.6$ Hz, $V_{max} = 4.1$ V) is added to the film, a fast and periodical switching of colors can be clearly observed (ESI, Video S3†). The color analysis is shown in Fig. 6. In addition, all the RGB contents of the film reach the same value, indicating the film exhibits good persistence of electric response, durability and reversibility. Fig. 7 schematically illustrates the potential induced conformational change of the quaternized PS-*b*-P2VP thin film.
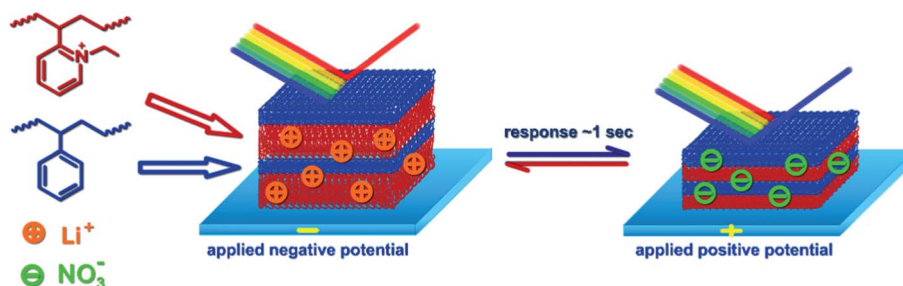

Fig. 7 Illustration of the potential induced conformational change of quaternized PS-*b*-P2VP thin film at different applied potentials.

Conclusion

We have developed electrically tunable photonic crystals by a facile procedure. They can exhibit full color with wavelength shifts traversing the ultraviolet, visible and near infrared region upon a low driving voltage. In particular, they have a fast switching. The photonic crystals also exhibit reverse volatility behavior regarding applied voltage and the reflective peak wavelength. They should find applications in information technologies.

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