Nonvolatile Photonic Block Polymer Films Swollen with Acidic Liquid

We report on the nanostructures and optical properties of block copolymer photonic films swollen with a nonvolatile acid/nonvolatile protic solvent. Photonic films reflecting ultraviolet or visible light were prepared by spin-coating polystyrene-b-poly(2-vinylpyridine) (PS-P2VP) block copolymer (M_n = 121000, ϕ_{PS} = 0.60) and immersing the spin-coated films in 1,3-bis(sulfopropoxy)propane (SA)/tetraethylene glycol (TEG) solutions as nonvolatile acidic solutions. Ultra-small angle X-ray scattering revealed that the domain periodicity of the PS-P2VP/(SA/TEG) film increases with an increase in the concentration of SA. Moreover, the wavelength of reflected light from PS-P2VP/(SA/TEG) films was found to be tunable by varying the concentration of SA.

Block copolymers that form periodic, ordered nanostructures (i.e., nanophase separated structures) have attracted a lot of attention, since they are useful for preparing high functional materials. One application example of nanophase-separated block copolymers is photonic crystals. A photonic crystal is a structural array where materials with different refractive indices are arranged periodically [1, 2]. The simplest photonic crystal is a one-dimensional photonic crystal, also referred to as an optical multilayer stack. Lamellar nanophase-separated structures of block copolymers can act as such one-dimensional photonic crystals [3]. Recently, we reported the fabrication of nonvolatile photonic crystal films that reflect light in the near-ultraviolet light to near-infrared range by immersing the lamellar-forming polystyrene-b-poly(2-vinylpyridine) (PS-P2VP) block copolymer in a nonvolatile protic ionic liquid, where the P2VP blocks are selectively dissolved in the ionic liquid [4]. In this study, by immersing PS-P2VP thin films into a nonvolatile protic liquid containing a nonvolatile acid to partially protonate the pyridyl groups of P2VP, we fabricated nonvolatile, anhydrous photonic films with large interdomain distance D (> 100 nm) (see also Fig. 1).

To prepare photonic films, PS-P2VP (M_n = 121k, f_{PS} = 0.60) thin films were prepared on a glass or polyimide substrate by spin-coating. Then, PS-P2VP thin films were immersed in a nonvolatile protic liquid, i.e., a mixture of nonvolatile sulfonic acid of 1,3-bis(sulfopropoxy) propane (SA) and nonvolatile protic solvent of tetraethyleneglycol (TEG)) at 40°C for 12 h, producing a light-reflecting photonic thin film.

Ultra-small angle X-ray scattering (U-SAXS) measurements were performed at BL-15A2, to determine D quantitatively. The camera length was 3.6 m with an X-ray wavelength of approximately 0.172 nm. In all the profiles (Fig. 2), integer order peaks were observed, indicating lamellar structures. Swelling occurred by addition of SA/TEG, while the lamellar structure was maintained. Furthermore, as the acid concentration was increased up to around 10 mM, the first order peak position, q_1, of the U-SAXS profile shifted to the lower q side, which means an increase in D from 114 nm to approximately 210 nm, as deduced from the relational expression $D = 2\pi/q_1$. For the sulfonic acid concentration of 10 mM and above, the peak position became substantially constant.

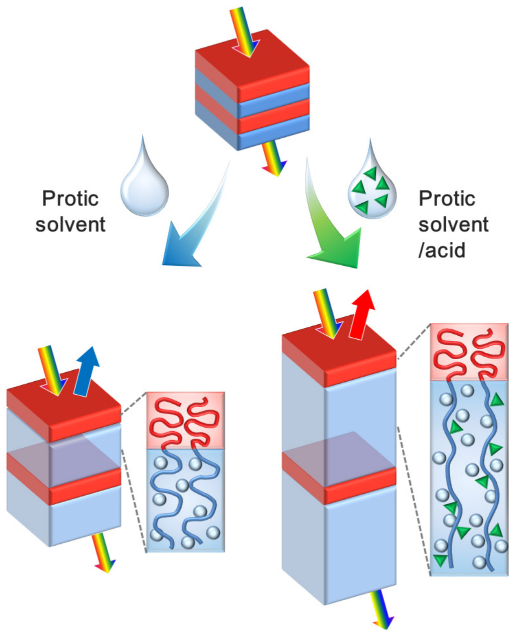

Figure 1: Schematic illustration of photonic films swollen with a neat protic solvent or acid/protic solvent. See also reference [5].

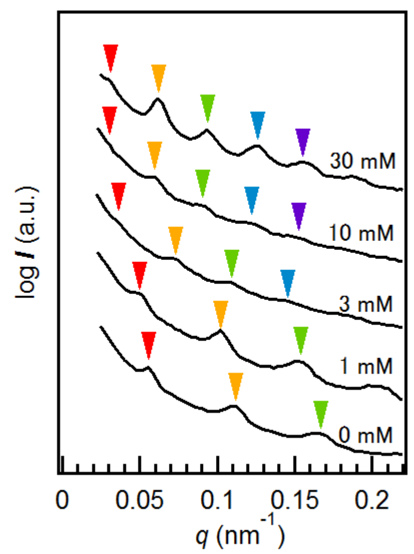

Figure 2: U-SAXS profiles of PS-P2VP/(SA/TEG). The concentration of SA in TEG was varied from 0 mM to 30 mM. See also reference [5].

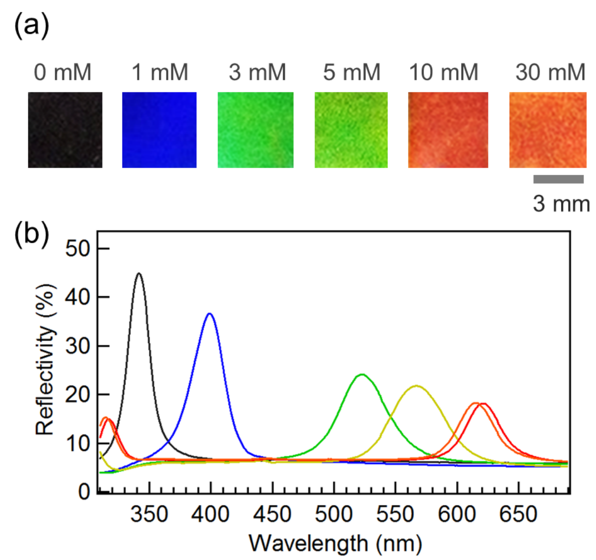

Figure 3: (a) Appearance of PS-P2VP/(SA/TEG). (b) Reflectivity spectra of PS-P2VP/(SA/TEG). The concentration of SA in TEG was varied from 0 mM to 30 mM. See also reference [5].

Figure 3a shows the appearance of the PS-P2VP/(SA/TEG) photonic films on a black cloth as background. No visible color appeared from the film swollen by TEG alone (0 mM) probably because of reflection in the UV. On the other hand, with an increase in acid concentration, reflections in the visible regime appeared in the order of blue, green, yellowish green, and red. Reflectivity measurements were also performed and demonstrated that the peak wavelength of the reflected light shifts from the ultraviolet region to the red light region with increasing acid concentration (Fig. 3b). The wavelength values of the reflected light became substantially constant above an SA concentration higher than approximately 10 mM, which is in agreement with the results of U-SAXS.

According to Bragg's condition, incident light with a specific wavelength λ from the direction perpendicular to the film is reflected by the layered structure, where $\lambda = 2(n_1d_1 + n_2d_2)$ for the alternating multilayer stack of components 1 and 2 [3]. Here, d_i is the thickness of component i and n_i is the refractive index of component i. Since the refractive index of a typical organic material is approximately 1.5, λ is approximately 3D, where $D = d_1 + d_2$. λ estimated by reflectivity measurements and D determined by U-SAXS nearly satisfied the relationship $\lambda \sim 3D$, which proves that these films swollen with SA/TEG are quantitatively 1D photonic crystals reflecting UV/vis light.

In summary, by immersing neat PS–P2VP films in the nonvolatile liquid containing a protic solvent and sulfonic acid molecules that can protonate the pyridyl groups, photonic films that reflect visible light were prepared. The combination of U-SAXS and reflectivity measurements also confirmed that by varying the degree of swelling by changing the concentration of sulfonic acid, the interdomain distance of internal structure could be tuned in the range of 114–210 nm as well as the wavelength of the reflection light in the range of 340–620 nm. The findings of this study will facilitate the preparation of nonvolatile, anhydrous block copolymer photonic films [5].

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