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 acidic propronic substance. Photonic films reacting ultraviolet or visible light were prepared by spin-coating polystyrene-b-poly(2-vinylpyridine) (PS-P2VP) block copolymer \( M_1 = 12\,000, f_{\text{ps}} = 0.60 \) and immersing the spin-coated films in 1,3-bis(sulfopropoxy)propane (SA)/tetraethyleneglycol (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 whose 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 crys-

To prepare photonic films, PS-P2VP (\( M_1 = 121k, f_{\text{ps}} = 0.60 \)) 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 solute of tetraethylene glycol (TEG) at \( 40^\circ\text{C} \) 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 TEG alone (0 mM) probably because of reflection from 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 \( \lambda \) from the direction perpendicular to the film is reflected by the layered structure, where \( \lambda = 2(\pi d_i n_i) \) for the alternating multilayer stack of components 1 and 2 [2]. 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, \( \lambda \) is approximately 3D, where \( D = d_i + d_j \) \( \lambda \) estimated by reflectivity measurements and \( D \) determined by U-SAXS nearly satisfied the relationship \( \lambda = 3D \), 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 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].

REFERENCES

BEAMLINE
BL-15A2
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