

Biomimetic of Nature: Stimulus-Responsive Structural Coloration in Polymeric Photonic Crystals

Photonic crystals, such as butterfly wings, opals and bird feathers, are commonly observed in nature. They all exhibit fantastic and shiny colors that cannot be acquired on simply mixing pigments. This effect is attributed to the arrangements of long-range order of the self-assembled microstructures on a sub-micrometer scale. Because of the ordered arrays with varied refractive indexes, visible light traveling through such microstructures might encounter an inhibiting band that causes visible light to be reflected out, namely a photonic band gap. For light transport in photonic crystals with structures of long-range order, multiple Bragg reflections result in complicated photonic band gaps between photonic band structures, providing opportunities to control the light propagation. Many frontier and practical applications such as optical communication, highly reflecting materials, laser cavities and display pixels have been proposed. Biomimetic of nature, photonic crystals have drawn intensive attention of scientists. In 2015, a research team of Yeo-Wan Chiang (National Sun Yat-Sen University) reported an efficient and convenient means to fabricate polymeric photonic crystals of large microdomain through "bottom-up" methods, in particular from the self-assembly of block copolymers (BCP). They discovered an interesting red- and blue-shifting reflectance with stimulus-responsive and reversible optical properties in these BCP photonic thin films.

According to their recent reports,^{1,2} this team developed a facile, rapid and robust self-assembled technique to fabricate one-dimensional photonic crystal thin films of large area from polystyrene-block-polyisoprene (PS-PI) BCP of large molecu-

lar mass and featuring highly oriented lamellar microstructures. They found that unique red- and blue-shift reflective bands depending on solvatochromism could be produced in films of PS-PI BCP gels using a non-selective neutral solvent as an external stimulus. As the internal microstructures have size hundreds of nanometers, it is impractical to determine the morphology and packing structure of the microdomains using a regular microscopy and light-scattering methods. To investigate the mechanism of the color change of the photonic gel films associated with the microstructural orientation and solvent concentration, Chiang and co-workers hence conducted advanced ultra-small-angle X-ray scattering (USAXS) and grazing-incidence ultra-small-angle X-ray scattering at BL23A1. With a well controlled beam quality via careful calibration of the size, direction and intensity of the beam, information about the internal microstructures of size hundreds of nanometers in a visible photonic crystal became resolved in the ultra-small angle region, in which the distance between the sample and the 2D detector is 5 m, much larger than that in typical SAXS.

Microphase-separated morphologies of the PS-PI BCP as cast with molecular mass large but variable were then exam-

ined with a transmission electron microscope (TEM) and USAXS. The TEM micrographs show well ordered lamellar microstructures in PS/PI-260/278, PS/PI-340/363 and PS/PI-505/520 BCP (Figs. 1(a)-1(c)). In Fig. 1(d), the USAXS profiles show reflections at relative q^* ratios 1:2:3, confirming the formation of lamellar microstructures in these PS-PI BCP. A progressive shift of the first reflection maximum to smaller q also indicates an extension of the long periods with increasing BCP molecular mass. In general, the reflective color from a one-dimensional (1D) photonic crystal depends strongly upon the microstructural spacing. Accordingly, as the long period of the BCP lamellar microstructures expands, the wavelength of reflective electromagnetic waves also increases because of the increased optical thickness. Notably, the initially clear PS-PI solution (i.e., a homogeneous disordered phase) transforms into a colorful PS-PI gel phase after solution casting (see insets in Fig. 1). The appearance of color depends on the concentration and molecular mass of the PS-PI BCP.

For practical applications, a highly aligned BCP

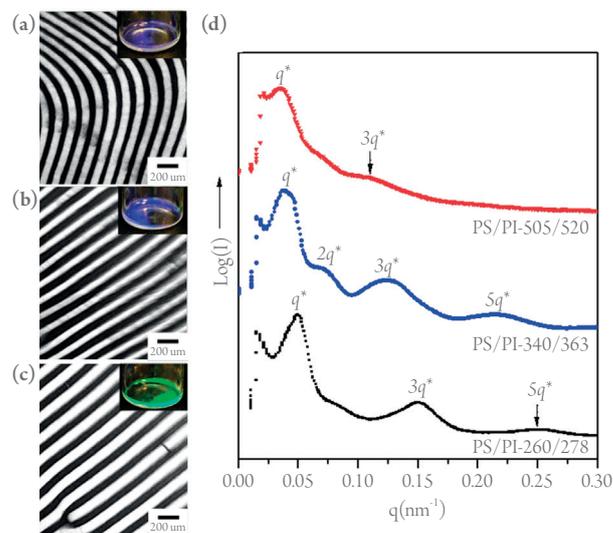


Fig. 1: TEM micrographs and 1-D USAXS profiles of photonic PS-PI BCP. (a) PS/PI-260/278, (b) PS/PI-340/363 and (c) PS/PI-505/520 BCP. [Reproduced from Ref. 1]

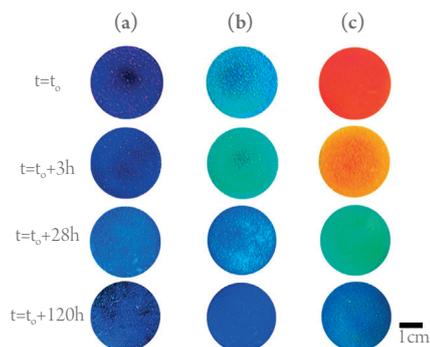


Fig. 2: Time-dependent optical photographs and corresponding reflectivity profiles for shear-aligned (a) PS/PI-260/278, (b) PS/PI-340/363, and (c) PS/PI-505/520 BCP photonic gel films. Here t_0 denotes the initial time of measurement of the reflectance after shearing. [Reproduced from Ref. 1]

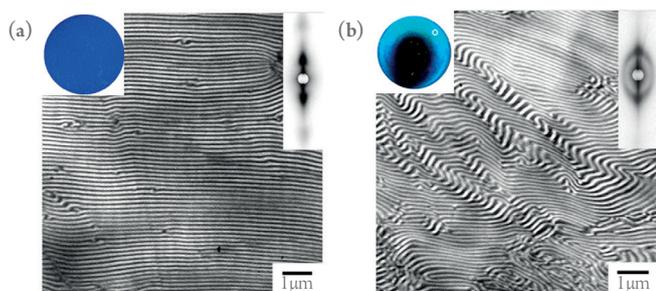


Fig. 3: Cross-sectional TEM micrographs of shear-aligned PS/PI-340/363 films after complete evaporation of the solvent. The inset shows the corresponding USAXS pattern. [Reproduced from Ref. 1]

photonic film is critical and necessary. For instance, with varied viewing angles, one can see varied coloration of butterfly wings or opals, i.e., reflective light of varied wavelength because of distinct structural orientations. This team performed a facile process, oscillatory shearing, to generate 1D BCP photonic crystals of large area with highly aligned microstructures, which can give more uniform reflectance with narrow bandwidth. After shearing, the optical properties of the BCP photonic gels were examined with a spectrometer microscope equipped with an optical spectrometer. In Fig. 2, the shear-aligned PS-PI BCP photonic gel films all exhibit uniform and strongly reflective colors over the entire area in the state as sheared (t_0). Most interestingly, the time-dependent reflectivity spectra show that the red-shift reflective bands are obtained first and blue-shift reflective bands arise subsequently during the evaporation of the solvent or with elapsed time. The reason is a consequence of the variation of the BCP lamellar long period resulting from the competition between the swelling due to increased segregation strength and the contraction due to solvent evaporation for the BCP long period.

Through the observation of reflective colors for the PS-PI BCP gels, the effect of molecular mass on the reflected wavelength is also significant. With increasing molecular mass, reflective bands are found at longer wavelength. As observed, the maximum positions of the reflective bands for shear-aligned PS/PI-505/520, PS/PI-340/363 and PS/PI-260/278 are 666, 509 and 460 nm. Interestingly, these PS-PI BCP films can still exhibit uniform reflective colors for the entire area even though time is protracted ($t = t_0 + 120$ h), indicating that highly aligned lamellar microstructures of large area are preserved after evaporation of the solvent. The cross-sectional TEM micrograph and anisotropic 2D USAXS pattern confirmed the long-range and highly aligned lamellar microstructures to be oriented parallel to the shear direction (Fig. 3(a)), which differs significantly from the disoriented lamellar morphology in the unsheared sample (Fig. 3(b)). As a result, PS-PI BCP photonic crystals of large area can be implemented using an oscillatory shear stress.

Taking advantage of the photo-induced cross-linking characteristics of PS and PI blocks toward UV irradiation, a well defined photopatterned thin-film photonic crystal can be generated via masking. The exposed region can exhibit either a lower red-shift reflectivity or an unresponsiveness toward an external stimulus (i.e., solvent) through control of its duration of exposure to UV irradiation. This approach appears to be a facile and efficient means to design patterns for stimulus-responsive thin-film photonic reflectors. (Reported by We-Tsung Chuang)

This report features the work of Yeo-Wan Chiang, Edwin L. Thomas and their co-workers published in Macromolecules 48, 4004 (2015).

References

1. Y.-W. Chiang, C.-Y. Chou, C.-S. Wu, E.-L. Lin, J. Yoon, and E. L. Thomas, *Macromolecules* **48**, 4004 (2015).
2. Y.-W. Chiang, J.-J. Chang, C.-Y. Chou, C.-S. Wu, E.-L. Lin, and E. L. Thomas, *Adv. Optical Mater.* **3**, 1517 (2015).

Charged Lipid Exchange Between Oppositely Charged Bicelles

Recent work in National Tsing Hua University yielded the results of the first study on charged lipid-exchange kinetics using novel disc-shaped bicelles (lipid bilayer micelles). Lipid transport and lipid exchange are important biological processes to maintain the lipid composition. Defects in lipid trafficking and an incorrect lipid distribution in membranes can result in severe disease, but knowledge of lipid transport or exchange kinetics is limited; it is essential to understand the lipid-exchange mechanisms. The movement of lipids among various bilayers is diversified. Intra-bilayer lipid transfer includes lateral diffusion and flip-flop between the two leaflets of the bilayer. For inter-bilayer lipid exchange, several paths include monomer diffusion through the aqueous phase, inverse flip-flop via transient contact, lateral diffusion when hemifusion occurs and direct insertion. Several factors are also found to affect significantly the lipid-exchange kinetics, such as concentration, temperature, ionic strength and lipid species, as well as the presence of other molecules.

In conventional experiments, the lipid exchange is monitored using vesicles or supported lipid bilayers. Using time-resolved neutron scattering with deuterated lipids, the evolution of scattering intensity due to the exchange of the protonated and deuterated lipids between the originally protonated and deuterated vesicles can reveal the lipid exchange and flip-flop kinetics. Apart from investigating the movement of zwitterionic lipids using neutron scattering, the present work with time-resolved small-angle X-ray scattering (SAXS) that monitors the structural evolution of mixed oppositely charged bicelle complexes extracts only the inter-bilayer exchange of charged lipids. Because of the symmetric structure of the disc bilayer, the effect of flip-flop on the lipid exchange becomes eliminated. Unlike using vesicles, the planar structure of the disc bilayer also eliminates the effect of curvature on the lipid-exchange kinetics. The disc-shaped bicelles of diameter about 20 nm are large enough to mimic the lipid membrane, which is ideal for study of the lipid-exchange kinetics. The bicelles can be doped with charged lipids to control their surface charge density for study of the charged-lipid exchange kinetics.

When the prepared bicelles of equal concentration but oppositely charged were mixed at equal volume, they immediately formed one-dimensionally stacked bicelle aggregates, with the positively charged and negatively charged bicelles in alternating order; the solution became slightly opaque. Figure 1 shows transmission electron microscope (TEM) images of 15% charged cationic and anionic bicelles, before mixing and the mixture of cationic and anionic bicelles a few minutes after mixing. The anionic and cationic bicelles are doped with 1,2-dipalmitoyl-sn-glycero-3-phospho-(10-*rac*-glycerol) (DPPG) or cationic cholesterol 3b-[N-(N0,N0-dimethylaminoethane)-carbonyl] (DC-cholesterol) respectively. The bicelles in the aggregate are in close contact with each other because of the strong electrostatic attraction between the oppositely charged bicelles. The exchange of charged lipids between the oppositely charged bicelles gradually decreases the net bicelle surface charge density and weakens the electrostatic attrac-