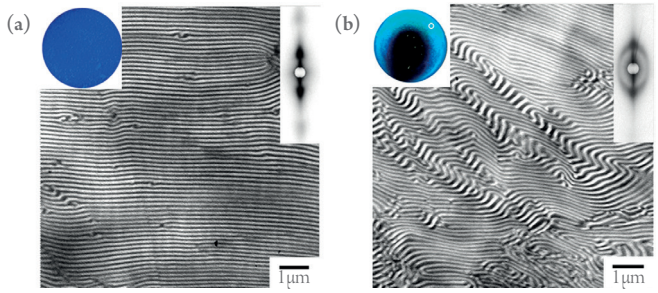

Fig. 3: Cross-sectional TEM micrographs of shear-aligned PS/PI-340/363 films after complete evaporation of the solvent. The inset shows the corresponding USAXS pattern. [Reproduced from Ref. 1]

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_o). 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 Macromolecues ***48****, 4004 (2015).*

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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)-carbamoyl] (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-

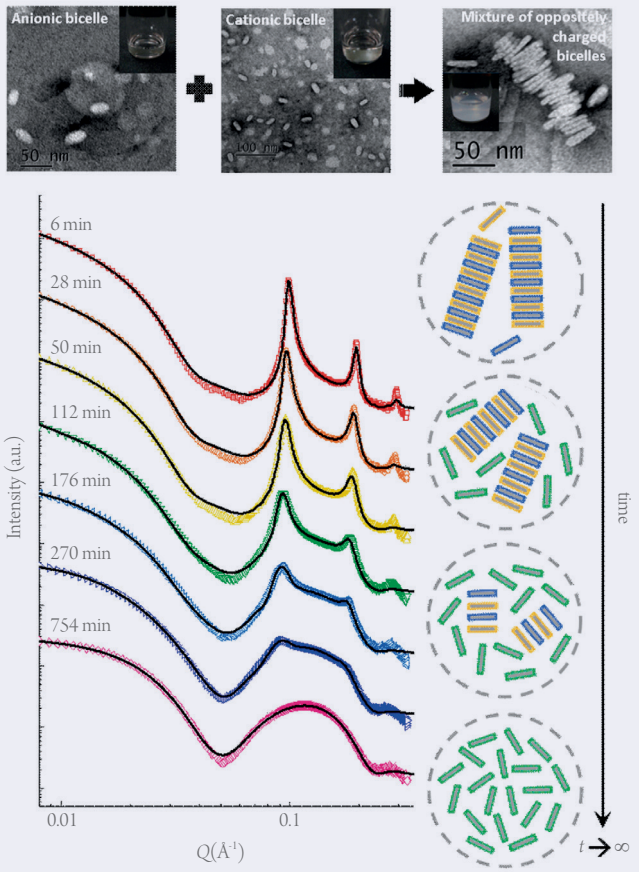

Fig. 1: Top: TEM images and photos of both negatively and positively charged bicelles (15 % charge doping with DPPG and DC-cholesterol, respectively) before mixing, and the mixture a few minutes after mixing. Bottom: Time-resolved SAXS profiles from a mixture of oppositely charged bicelles as a function of the interval after mixing. The schematic of structural evolution is shown also to illustrate the gradual dissociation of the bicelle stacks into free bicelles as a result of gradual neutralization of the charged bicelles due to exchanging the charged lipids. [Reproduced from Ref. 3]

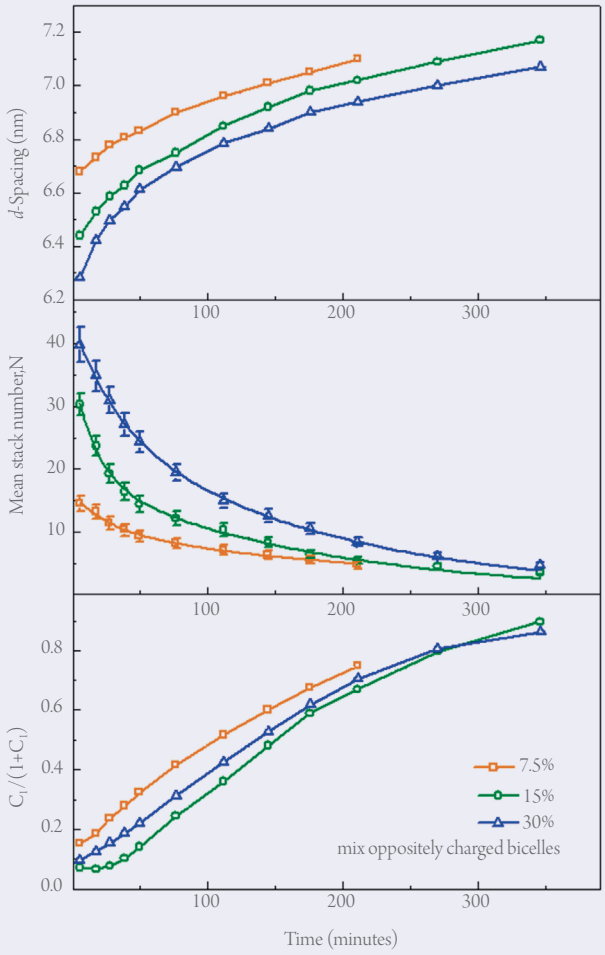

Fig. 2: Plots of deduced *d*-spacing, mean bicelle stack number and fraction of free bicelles as a function of time after mixing. [Reproduced from Ref. 3]

tion between the oppositely charged bicelles; as a result, the bicelle stacks become shorter. The bicelles in a stack also become less tightly bound, resulting in an increasing *d*-spacing (repeat distance of the bicelles in the stack). Eventually, all bicelles become free isolated bicelles with a net charge about zero. The dissociation of the bicelle stacks is detectable with SAXS. The SAXS profiles showed that the lamellar diffraction peaks of the bicelle stacks gradually disappear into the form factor structure of isolated free bicelles. Figure 1 shows the SAXS profiles for the case of 15 % doping charge at several intervals together with schematics of the structural evolution.

By carefully model-fitting the SAXS profiles, the number of stacked layers, *d*-spacing of bicelles in the stack and the fraction of free bicelles can all be derived, as shown in Fig. 2. The number of stacked layers decreases with increasing time because of the gradual neutralization of the bicelles. The *d*-spacing gradually increases with time, which indicates that the average water gap between bicelles in the stack gradually becomes larger due to the weakening electrostatic attraction between the oppositely charged bicelles in contact. The fraction of free bicelles gradually increases as the bicelle stacks gradually dissociate. The exchange of charged lipids was found to possess exchange kinetics of two kinds; a rapid mode dominates at the beginning and a slow mode succeeds at a later stage. Initially, at a large density of surface charge with almost no free water layer, only bound water, between the bicelles in the stack, rapid exchange dominates. At a later stage with a smaller surface-charge density and wider water gaps, with a free water layer between the bicelles in close contact, slow exchange ensues. Such two-stage exchange kinetics has here been observed in lipid bilayer systems for the first time. Exchange modes of these two kinds fit well with the lipid exchange models of transient hemi-fusion for the rapid mode and monomer exchange through the aqueous phase (the free water layer) for the slow mode. The hemi-fusion is a much more rapid process; its time scale is tens of minutes. The monomer exchange mode would have a much longer time scale of order hours as the lipids must first escape from the bilayer, then diffuse through the water phase and enter the other bicelles again. Both the water gap with or without a free water layer and electrostatic interactions are critical factors to determine the charged-lipid exchange kinetics between lipid membranes in close contact. The present observations can be useful for understanding mechanisms of membrane fusion and lipid exchange during vesicle collisions. This work could be extended to include the role of proteins in inducing membrane fusion, at which proteins are thought to decrease the distance between two bilayers during vesicle contact. The bicelle interactions investigated here should also be useful in applying bicelles to study various membrane interactions with antimicrobial peptides and amyloid peptides. (Reported by We-Tsung Chuang)

This report features the work of Po-Wei Yang, Tsang-Lang Lin and U-Ser Jeng published in Soft Matter ***11****, 2237 (2015).*

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