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Experiment Report for Prefectural Beamline

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Tracking sub-micron assembly in single-domain polymer opals using small angle x-ray scattering

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1. Summary

Single and multiple components polymer opals are 3D photonic crystals which are comprised of densely packed core-shell spheres. By using small angle x-ray diffraction technique, our experiment provides strong evidence of the effectiveness of the shear ordering process for polymer opals. Moreover, the experimental results enable us to gain insight into how random packed multi-component polymer opals system develops into highly ordered photonic crystal structures.

2. Purpose of experiment and background

Polymer opals are novel stretchable 3D photonic crystals comprised of densely packed core-shell spheres [1-3]. The spheres, with a hard polystyrene core and a low glass transition soft PEA shell, are pressed into thin films and sheared in solid phase without using any liquid solvent. By using small angle x-ray diffraction technique, the goal of the experiment is expected to be in two aspects: the first is to investigate the arrangement of the nanospheres in binary and ternary polymer opal films after shear ordering, and the second is to clarify the puzzles from our previous SAXS experiment on single component polymer opals, including peculiar intensity distribution along the tubes and large intensity contrast between spots at the same Q range. The experiment is supposed to be able to provide valuable information on ordered as well as disordered structures within the films, which therefore promises a deeper look on how spheres of either the same size or different sizes rearrange under shearing force in highly viscoelastic medium.

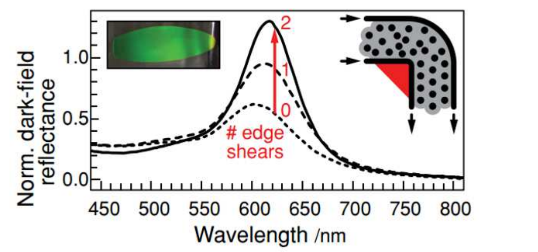

Figure 1. Dark-field spectra of polymer-opal films show improving order with BIOS process.

Compared to most of the top-down methods which are time costing and expensive, bottom-up assembly seems to be more promising and commonly used for fabricating low cost industrial applicable 3D photonic crystals. However, due to the intrinsic properties of the method, the existence of disordered structures is always a serious problem, which is detrimental for the optical performance and the potential applications. Shearing technique has been used for improving the order of self-assemblied colloidal structures, however, for those systems, viscosity of the medium is usually low, and shearing is done in liquid phase. Different from most of the colloidal systems, our efforts in recent years on making well-ordered polymeric opaline photonic crystals [4-11] show how shearing works in highly viscoelastic medium in solid phase. By using shearing force, we have fabricated industrial scale (>100m) flexible photonic crystal films which exhibit strong structural colours uniformly over large areas. Since optical properties of the film comes from the interplay of order and disorders of the structure, understanding how the spheres are arranged in bulk is of great importance for both science and applications [3,4,8,11]. However, due to the small size of the spheres (~200nm) as well as the low electron density contrast between the spheres and the medium, it has been a great challenge to characterize the structure. The setup of small angle x-ray diffraction in Saga provides very high resolution and intensity which facilitates the characterization of structures in submicron scale, which is a perfect technique for our polymer opal system.

3. **Experimental** (Note: Description of sample, method of experiment and analysis, etc.)

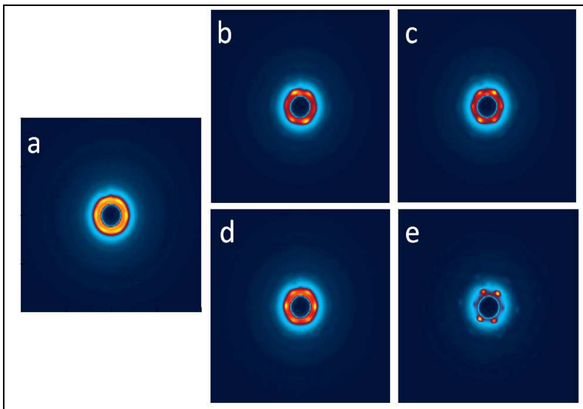

Figure 1. SAXS patterns of samples before and after shear ordering. a, before sheaing,b, biaxial shearing 5 passes, c, biaxial shearing 20 passes, d, uniaxial shearing five passes, e, uniaxial shearing 20 passes. Beam normal to the (001) plane.

The measurements are performed using the photon energy of 8.2 keV and a Rigaku high resolution detector. The radius of the beam stop is just at the edge of an acceptable level for imaging the reciprocal space lattices, which gives us as much information as we want but at the same time generated some distortions over the diffraction patterns.

Polymer opal films with different degrees of structural order as well as different ordering techniques have been characterized. Clear SAXS patterns were observed on both single component and multi-component polymer opals which are comprised of pure polymeric spheres embedded in medium of a different polymer with very low electronic density contrast between them.

4. Results and Discussions

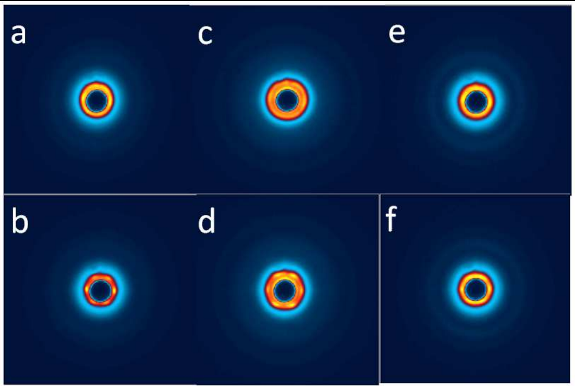

Figure 2. SAXS patterns of binary polymer opals. a&b, R/G binary opal before and after ordering, c&d, B/G binary opal before and after ordering, e&f, B/R binary opal before and after ordering. Beam normal to the (001) plane.

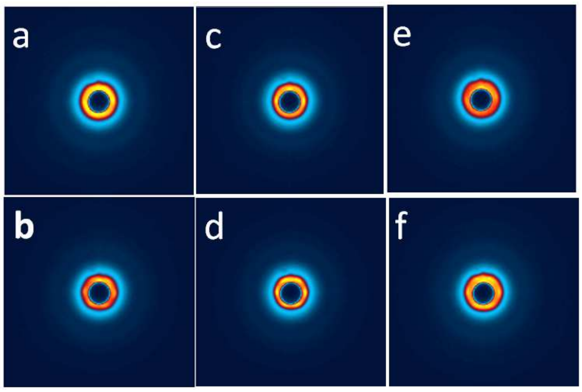

Figure 3. SAXS patterns of ternary polymer opals. a&b, R/G/B 1:1:1 ternary opal before and after ordering, c&d, R/G/B 3:2:1 ternary opal before and after ordering, e&f, R/G/B 1:2:3 ternary opal before and after ordering. Beam normal to the (001) plane.

The results show that before applying the ordering process, the structure of the film is completely disordered (Fig 1a) but do show pronounced rings presumably originating from (short-range) positional correlations between the particle positions. Clear crystalline features appear after applying the ordering process, then these features become more and more significant with increasing number of the ordering passes (Fig 1b-1e) which indicate better structural order and alignment. Shearing process shows the same effect on both binary and ternary polymer opals (Figure 2, 3). Careful analysis of the data will help us understand more about how the spheres rearrange from jammed state to crystalline structure under shearing force with extremely large polydispersity.

Preliminary analysis of the results of the experiment provides strong evidence of the effectiveness of the shear ordering process for polymer opals. Meantime, the information enables us to gain insight into how random packed multi-component polymer opals system develops into highly ordered photonic crystal structures.

5. Future issues

1. Characterization of inter-plane structural order by aligning the beam parallel to the planes
2. Tilting the samples in different orientations in order to get more information

of the 3D reciprocal lattice strucuture
3. Obtaining the form factor of core-shell spheres from experiments by using very dilute suspensions

6. References

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7. Publications, patents (Note: Typical deliverables related to this proposal.)

The experimental data obtained in this work will be submitted to an international scientific journal.

8. Keywords (Note: 2-3 words about samples and experimental methods.)

Polymer opals, SAXS, Shearing, Order and disorders

9. About the publication of research results

Please delete either item ① or item ② indicated below, according to a user’s choice of publications as described in ※2. Also, please fill in an expected date of publication of a refereed journal article or an expected date of submission of a SAGA-LS Research Report. For example, deadline of both publications corresponding to the proposals performed in the fiscal 2013 is by the end of fiscal 2015 in both ① and ②.

① Publication of a refereed journal article (the date of publication : 2015)