小角X線散乱法によるポリマーオパールの構造秩序評価

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Polymer opals are novel stretchable 3D photonic crystals comprised of densely packed core-shell spheres. 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. The studies in recent years on making well-ordered polymeric opaline photonic crystals show how shearing works in highly viscoelastic medium in solid phase. By using shearing force, industrial scale (>100m) flexible photonic crystal films have been fabricated which exhibit strong structural colours uniformly over large areas. Since optical properties of the film come 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. In this research, both single and multi-component polymer opal films processed with different degrees of biaxial bending induced oscillatory shearing and uniaxial bending induced oscillatory shearing methods have been characterized by using small angle x-ray scattering setup at BL11 of SAGA-LS. Clear hexagonal patterns were observed in all the sheared samples with different degrees of structure order. Asymmetric intensity distribution between (10) and (1-1) spots was also observed, and it varies depending on different shearing methods and degrees of shearing.

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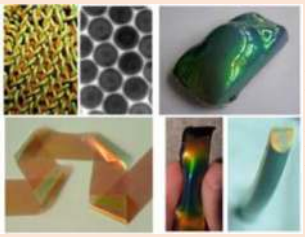
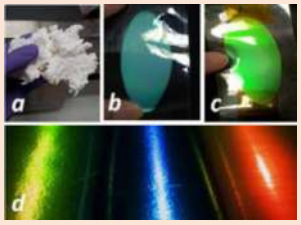
Background and Objective

Full 3D bottom-up assembly of sub-micron components into well-defined architectures is a major challenge for nano-photonics, nano-electronics, plasmonics and metamaterials. Even simple structures such as opaline photonic crystals based on face centred cubic (fcc) colloidal lattices have optical properties dominated by defects. Baumberg . have recently reported a significant advance in high-quality polymer opal thin-films exhibiting tunable structural colour across visible wavelengths.

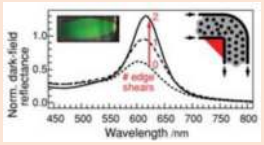


Mono-domain polymer photonic crystal films in a variety of forms display new functional photonic properties. (Quantum regime in tunnelling plasmonics, Nature 491, 574 (2012), Geometrically locked vortex lattices in semiconductor quantum fluids, Nature Communications 3, 1243 (2012), Coupling quantum tunnelling with cavity photons, Science 336, 704 (2012))

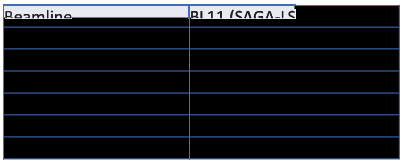
Polymer opals are novel stretchable 3D photonic crystals comprised of densely packed core-shell spheres. The spheres, with a hard polystyrene core and a low glass transition soft PEA shell, are pressed into thin films and sheared in solid phase without using any liquid solvent. The studies in recent years on making well-ordered polymeric opaline photonic crystals show how shearing works in highly viscoelastic medium in solid phase. By using shearing force, industrial scale (>100m) flexible photonic crystal films have been fabricated which exhibit strong structural colours uniformly over large areas. Since optical properties of the film come 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.

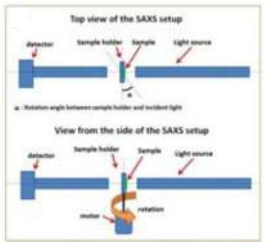


a, aggregates of the spheres
b, after being pressed into a thin film
c, after shear ordering
d, polymer opal films on fabric.



Experimental technique





By fitting the diffraction patterns with 2D Gaussian model, detailed analysis has been done, which provides insight into how spheres are rearranged with different shearing methods.

In this research, both single and multi-component polymer opal films processed with different degrees of biaxial bending induced oscillatory shearing (B-BIOS) and uniaxial bending induced oscillatory shearing (U-BIOS) methods have been characterized by using small angle x-ray scattering (SAXS) setup at BL11 of SAGA-LS.

Experimental results

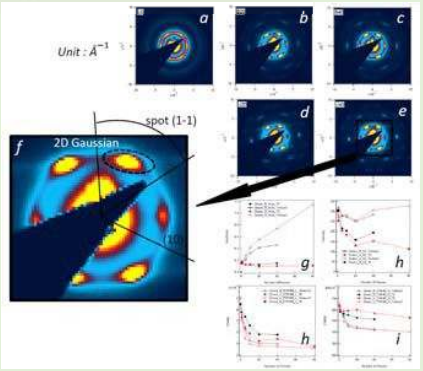


Figure 1. 2D SAXS patterns of polymer opals with different shear ordering methods. (a) before shearing, (b) biaxial-BIOS 20 passes, (c) biaxial-BIOS 40 passes, (d) uniaxial-BIOS 20 passes, (e) uniaxial-BIOS 40 passes, (f) zoom in of the first ring in (e), spots are analyzed with 2D Gaussian fit, (g)-(i) amplitude and integrated intensity of (10) spot and (01) spot for different samples with different shearing methods and number of shearing.

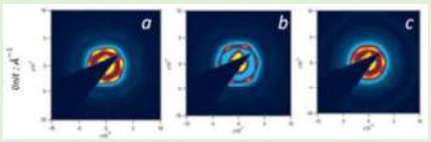


Figure 2. 2D SAXS patterns of binary polymer opal films ordered with uniaxial 20 passes. (a) : = 1.2, (b) : = 1.2, (c) : = 1.4.

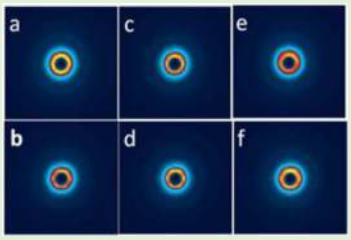


Figure 3. SAXS patterns of ternary polymer opals.
a&b, R/G/B 1:1:1 ternary opal before and after ordering,
c&d, R/G/B 3:2:1 ternary opal before and after ordering,
e&f, R/G/B 1:2:3 ternary opal before and after ordering.
Beam normal to the (001) plane.

- Both B-BIOS and U-BIOS methods improved the structural order of polymer opals significantly.
- While integrated intensity of (1-1) spot remains approximately constant, amplitude increases drastically with increasing amount of shearing which is also accompanied with a rapid drop in FWHM.
- With same amount of shearing, structure order improves more effectively with U-BIOS.
- FWHM in radial direction (narrow axis of the spot) drops much slower than the hoop direction (long axis of the spot), which indicates orientational order improves much fast than positional order.
- Significant difference between (10) spot and (1-1) spot has been observed, which needs further investigation.
- Overall order of the films reaches a saturated level after approximately 40 passes of shearing with both methods, while structural order improves most effectively in the first ten passes.
- BIOS method can also be used in fabricating binary or ternary opal structures.
- Fig. 2 & 3 show clear hcp arrangement in binary polymer opals comprised of spheres with different sizes.

Summary

Both single and multi-component polymer opal films processed with different degrees of biaxial bending induced oscillatory shearing (B-BIOS) and uniaxial bending induced oscillatory shearing (U-BIOS) methods have been characterized. Clear hexagonal patterns were observed in all the sheared samples with different degrees of structure order. Asymmetric intensity distribution between (10) and (1-1) spots was also observed, and it varies depending on different shearing methods and degrees of shearing.