

shear-induced orientation of bcc-spheres such as described below, at temperatures well above OOT temperature where bcc-spheres are thermodynamically stable: twinned bcc-spheres with the twinning plane parallel to the shear plane, and with their  $\langle 111 \rangle$  axes parallel to the shear direction. We shall then discuss shear-induced OOT from the oriented bcc-spheres described above to the oriented hex-cylinders, such as described below at a temperature slightly above OOT temperature where bcc-spheres are still stable thermodynamically in quiescent state: the cylinders orienting with its axis parallel to the shear direction and its  $\{110\}$  plane parallel to the shear plane.

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**Keywords:** block copolymers, microdomains, time(phase)-resolved small-angle X-ray scattering

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#### Supramolecular Structures Via Self-assembly of A $\beta$ Congeners

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One pathological manifestation of Alzheimer's patients is the deposits of amyloid plaques in the brain. The primary component in the plaques is a peptide (A $\beta$ ) consisting of 39-43 amino acid residues. Due to its unique amphiphilic character, the peptide self-assembles in aqueous media leading to the formation of well-organized fibrillar structures. Understanding the detailed mechanism of self-assembly of A $\beta$  variants solution and the structure of these resulting assemblies have been useful for the development of methods for altering or preventing the process of fibrillogenesis. By using solid-state NMR, CD, EM, AFM, biochemical assays and SANS/SAXS, a detailed atomic scale structure of the fibrils formed by A $\beta_{10-35}$  has been developed. Using the detailed framework of the fibril structure, further insight on the role of metal ions in the nucleation and growth of the fibrils has been achieved. The formation of extremely large tubular structures by the self-assembly of smaller variants of the A $\beta$  peptide (A $\beta_{16-22}$ ) sheds light on the relationship between the length of the peptide and the extent of lamination of the  $\beta$ -sheets. These unique supramolecular self-assemblies formed by the variants of A $\beta$  peptide may have interesting and useful applications in nanotechnology.

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**Keywords:** amyloid peptides, nanotubes, SANS/SAXS

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#### Real-time Observation of Anisotropic Structure of Aggregates in Stretched Rubber by 2D-USAXS

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Addition of filler such as carbon black and silica to an elastomer shows the reinforcement effects [1]. The mechanism of the reinforcement has not yet been clarified in spite of numerous studies. Two-dimensional Ultra-Small-Angle X-ray Scattering (2D-USAXS) has a large potential as a tool for the observation of structural change in a size scale of 100 nm - 10  $\mu$ m. In the present study, we have performed the 2D-USAXS of filled rubber under elongation and investigated structural changes of the filler aggregation.

Experiments were performed at BL20XU, SPring-8 (Hyogo, Japan). The camera length was 160.5 m and an X-ray CCD detector coupled with X-ray Image Intensifier [2] was used as the detector. The combination of the high-brilliance X-ray source, the sensitive 2D-

detector, and the long camera length enables us to observe 2D-USAXS patterns in a real-time mode. Samples used were Styrene-Butadiene Rubber filled with silica particles. The 2D-USAXS images showed corresponding hysteresis to that of stress-strain curve, which suggest the morphology of the aggregate affects the viscoelasticity of rubber. The 2D-USAXS clarified the aggregate structure in stretched rubber for the first time, which had been only speculated based on viscoelastic experiments.

[1] Ferry J.D., *Viscoelastic Properties of Polymers*, John Wiley & Sons, New York, 1980. [2] Amemiya Y., et al., *Rev. Sci. Instrum.*, 1995, **66**, 2290-2294.

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#### Spherulites for Polar Dye Organization

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Melts of D-sorbitol form remarkably transmissive, radially-symmetric, polycrystalline spherulites. Recent reports by Yu suggest that these structures arise from concomitant crystallization of two polymorphs at room temperature.<sup>[1]</sup> Spherulites grown at higher temperatures consist of a single polymorph. There is considerable interest in the material science community to generate polar order in achiral optically responsive molecules for use in high-speed electrooptic modulators. As the propagating crystal interface of the spherulites invariably orients dyes dissolved in the melt, we seized upon the opportunity to utilize these structures as an entirely new method for generating polar media.

DAST, a well known non-linear optical dye, is highly soluble in the sorbitol melt and readily oriented by the spherulite matrix. Characterization of the linear and non-linear optical properties of these materials includes linear birefringence and dichroism imaging, polarized absorption, and second harmonic generation microscopy. Dyed spherulites exhibit pronounced absorption anisotropies (dichroic ratios  $> 3$ ), as well as second harmonic generation nearly 70 times that of the undyed samples. Effects of polymorph fractionation on growth and optical properties will also be discussed.

[1] Yu L., *Cryst. Growth Des.*, 2003, 967.

**Keywords:** nonlinear optical materials, noncrystallographic symmetry, dye compounds