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A mesoporous pattern created by nature: A SAXS and micro-SAXS study

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Marine sponges deposit hydrated silica in needle-like objects called spicules. These spicules also contain a protein axial filament which plays an important role in silica deposition. This presentation deals with the structural study of the organization of the axial filaments in spicules from different sponges, carried out using a SAXS setup with synchrotron radiation. The collected images show diffraction spots sharper than what can be expected from a regular polymeric fiber, indicating that the protein units in the spicule axial filaments must form highly ordered patterns. The analysis of the position and distribution of the spots reveals a hexagonal arrangement with different possible bi- and tri-dimensional dispositions of the units along the main axis of the spicules. The micro-diffraction of a single spicule and of the circular section of the cut spicule confirmed the presence of an hexagonal structural order in the cavity. Analysis after thermal treatments reveals a structural ordering accompanying the thermal degradation of the organic material. This confirms that the order can only be indirectly related to the arrangement of the protein units, and strongly support our hypothesis of the presence of an ordered siliceous mesophase inside the spicules, where the protein units act as templates. Our results suggest the following possible mechanism for the biosilicification process in spicules. The initial step consists in the formation of a very ordered disposition of the protein units, forming a regular mesoporous arrangement in a silica matrix, similar to that found in synthetic materials. In a second step the biosilicification process continues with a deposition of amorphous silica on the outer walls of the mesoporous core.

Keywords: biomineralization, microdiffraction, porous materials

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Deformation behavior of drawn polymer spherulite studied by simultaneous micro SAXS-WAXS and POM

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The clarification of the deformation mechanism of hierarchical structures of crystalline polymers during drawing, particularly the identification of the sequence of stress focusing in the polymer structure, is one of the most important issues in the polymer processing field. However, the hierarchical structure of crystalline polymers generally has a spatial inhomogeneity and they are non-uniformly deformed under drawing. Furthermore, a lamella structure inside of a polymer spherulite sometimes has very complex morphologies such as twisting and cross-hatched structures. To obtain detailed information on the deformation behavior of the hierarchical structure in such complex polymer systems, a combinatorial approach of microbeam small- and wide-angle X-ray scattering simultaneous measurement was used, in which a unique method provides us the structural information in a wide-scale hierarchy at a local region. We applied microbeam SAXS-WAXS and POM to the observation of the deformation behavior at a fixed local region of an isotactic polypropylene spherulite having cross-hatch structure [1] and a spherulite of poly(caprolactone)/Poly(vinyl butyral) blend having beautifully twisted lamella sturucture during hot drawing. Microbeam SAXS-WAXS was performed at BL40XU of SPring8, which is a high-flux beamline equipped with a helical undulator. We generated a microbeam of about 5 micrometer diameter by merely inserting a micro-pinhole (2 micrometer diameter) combined with a large guard pinhole. With detailed analyses of microbeam SAXS-WAXS during deformation, we clearly identified the sequence of stress focusing inside the cross-hatched and banding structure during hot drawing and constructed their detailed deformation model.
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Guest-responsive structures and properties of porous coordination polymers

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The recent advent of porous coordination polymers (PCPs), as new functional microporous adsorbents, have attracted the attention of chemists due to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage, for separation and in heterogeneous catalysis.1 One of the advantages of PCPs is flexibility, which provides a variety of frameworks with guest-responsive properties. This prominent feature leads us to expect that PCPs provide us with soft porous crystals. Here, we have found superb sorption of gas molecules such as C2H2 on the functionalized and mobile surface of PCPs and show an enhanced “confinement and/or recognition effect”, applicable to a highly stable, selective adsorption and separation system.2 In addition to this confinement phenomena, we have found flexible porous frameworks,3,4 which respond to specific guests, common in PCPs but dissimilar to the conventional porous materials.
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