Small-angle X-ray Scattering studies of macromolecular and colloidal systems

Hutten, Paul Frederik van

S U M M A R Y

This thesis deals with the basic principles of Small-Angle X-ray Scattering (SAXS), and describes various experimental applications.

Scattering of X-rays at angles smaller than those at which the diffraction effects due to the atomic ordering are observed, is the result of a non-homogeneous density on the "colloidal" level. Density fluctuations of colloidal extent are, of course, to be found in dispersions of colloidal particles, but also in solutions of macromolecules, due to the large dimensions of the latter. Solid systems consisting of more than one phase may give rise to considerable SAXS intensity as well. The only essential requirement is the presence of a difference in (electron) density.

For two-phase systems, SAXS can be used to characterize the spatial extent of the different regions and the nature of the phase boundary. The density difference may also be determined. SAXS permits the calculation of particle dimensions and interaction parameters (second virial coefficient) in dispersions. In dilute systems, where the volume fraction of the dispersed phase is low, the scattering is characteristic of an (average) individual particle. In that case, parameters such as the radius of gyration and the particle volume can be calculated, and in more favourable cases the shape and mass of the particle too. Several real systems will deviate from the ideal picture with two homogeneous phases, but in many cases appropriate corrections can be made.

In this work the Kratky camera with a slit-collimated X-ray beam was used, which allows measurements to be made at very small angles corresponding to a Bragg distance of ca. 10000 Å. Slit collimation has strong implications for the interpretation and analysis of the experimental data, however, and therefore calls for an adapted theoretical framework.

The characterization of fibres by means of SAXS requires special measures, because of the strong anisotropy in properties and morphology. In general, polymer fibres are marked by a periodic alternation of ordered (crystalline) and less well-ordered domains in the fibre direction. This gives rise to one or more discrete intensity maxima centred on the meridian (a line from the centre of the SAXS pattern parallel to the fibre axis). A detailed SAXS pattern can be interpreted in terms of the dimensions and ordering of the domains (lamellae), and the degree of microfibrillarity. The so-called one-dimensional approximation is based on a strongly idealized model for the lamellar stacks. It is usually employed when the SAXS pattern shows little detail, in particular when a broad orientation distribution is found. For oriented systems, the use of slit collimation too involves a considerable loss of information, and the analysis of lamellar ordering will be essentially one-dimensional.

The experimental part of this thesis describes the characterization of polyethylene shish-kebab fibres, prepared from dilute solution by means of two different techniques to induce crystallization. From previous studies it is known that the fibres are made up of elementary fibrils, each consisting of a continuous backbone overgrown with lamellae. The backbone is an extended-chain crystal possessing defect regions from which parts of chain molecules emanate. These "cilia" have crystallized into the folded-chain lamellar overgrowth during the process of fibre preparation. The lamellar overgrowth prevents a close packing of the elementary fibrils, and this results in a porous macrofibre. This, in turn, gives rise to a high SAXS intensity. For the characterization of the lamellar overgrowth the slit-collimated Kratky camera has to be used, since the lamellae are spaced 700 to 1500 Å apart.

The results of SAXS and electron microscopy (EM) clearly agreed for extreme cases, such as the highly overgrown free-growth fibres and the smooth high-temperature surface-growth fibres. When small differences are concerned SAXS is considered to be representative of the fibre samples, and to be more objective than EM results.

SAXS showed a decrease in the amount of overgrowth with increasing tension in the fibre during preparation. The amount of cilia will be reduced by a more effective stretching of the molecules when the backbone is formed, the dangling chains being pulled in by a creep mechanism in the entanglement network. The meridional SAXS maxima could be described by rather broad distributions for both the lamellar thickness and the interlamellar spacing, according to the one-dimensional paracrystalline model. Nevertheless, the SAXS curves showed that the position of the lamellae on the backbones is far from random, and hence not a result of random nucleation. If the fibre sample is inhomogeneous, as was inferred from the comparison of experimental with calculated scattering curves, the regularity along individual backbones will be even higher than that given by the distributions.

Equatorial scans yielded values for the thickness of the backbone of about 150 Å, which reasonably agrees with the results from line-broadening of wide-angle X-ray and electron diffraction reflections. Both methods showed only a slight decrease in the fibril dimensions with increasing preparation temperature. It was clearly demonstrated that the fibres give rise to multiple scattering, but this did not seriously affect the determination of the cross-sectional dimensions.

The nature of the lamellar overgrowth was investigated by means of "in situ" heating, dissolution and crystallization experiments. Upon heating in vacuum the overgrowth appeared to be metastable. Above 80°C the lamellar period increased, reorganization continuing until the lamellae finally melted around 140°C, where the fibre loses its porosity. The way in which the molten lamellae crystallize upon cooling depends on the maximum temperature attained, as well as on the crystallization temperature. A large supercooling produced two independent long periods, 700 Å and 400 Å. This is thought to be connected with the location of the defect regions in the backbone, from which the cilia emanate. The cilia crystallize so as to form a chain-folded phase, exhibiting a temperature-dependent SAXS which is tentatively ascribed to "surface melting".

The dissolution of the lamellar overgrowth could be followed in the SAXS set-up as well. For a sample in dodecane, no reorganization was observed up to 115°C; at higher temperatures the lamellar-period peak disappeared. Equatorial curves suggested an increase of the backbone diameter, possibly due to swelling of defect regions. The recrystallization of the dissolved cilia onto the backbone in a shish-kebab fashion could be directly demonstrated at various crystallization temperatures between 110°C and 90°C.

Drawn surface-growth fibres were also investigated. Fibres drawn at 150°C were non-porous and showed a broad long-period maximum around 500 Å. The amount of chain-folded phase was found to decrease with increasing draw ratio, which suggests a transformation of the original lamellar overgrowth into extended-chain crystals. SAXS of fibres drawn at 90°C showed that the overgrowth is strongly affected even for small draw ratios, indicating that the elementary fibrils are interconnected by lamellae, which are sheared upon drawing. The observations imply the presence of many weak spots in the elementary fibrils. Drawing to higher ratios at higher temperatures will require a considerable local elongation of the backbones, and a mechanism for this "micro necking" is proposed in which lamellae are transformed into extended-chain crystals in the backbone.

In the appendices, a variety of SAXS applications is briefly surveyed, in

which attention is paid to more specific aspects.

SAXS can be used to calculate the particle-size distribution in colloidal dispersions. Contrast variation is a method to determine the internal structure of particles. Interaction and structure formation in more concentrated systems can also be studied. Experiments on silica suspensions showed the particles to be homogeneous spheres, with a narrow diameter distribution around 1800 Å. Measurements on microemulsions showed ordering phenomena depending strongly on concentration.

Biomacromolecules in solution can be investigated to determine their unique but complex shape and substructure. Solvation can be studied, but specific interactions with a multicomponent solvent affect the scattering curve in a complex way. Experiments on tubular polymers of β-haemocyanin confirmed the shape found from EM: a hollow cylinder with a diameter of ca. 350 Å.

Solutions of flexible chain molecules have traditionally been studied in the dilute region to obtain over-all molecular parameters. SAXS investigations of more concentrated solutions allow the testing of recent thermodynamic theories of segment-segment interactions.

In materials science, SAXS is often applied to systems that are not very well-defined, which prevents a rigorous theoretical treatment. The characterization of semi-crystalline polymers is often restricted to the determination of the long period. Nylon-6 serves as an experimental example. SAXS clearly showed lamellar thickening as a result of annealing, this process being highly dependent on the water content of the sample. For other types of solid polymers, SAXS gives very different information.

SAXS from substances of low molecular weight allows the study of defects (in solids), phase transitions and critical phenomena. For binary systems, thermodynamic quantities concerning the mixing behaviour can be obtained. Measurements on an Al-Zn alloy showed the formation of precipitates for different conditions of phase separation.