GDCh-Fortbildungskurs 665/11

Nanostrukturierte Polymermaterialien:
Nanokomposite, selbstorganisierte Strukturen, Charakterisierung
am Leibniz-Institut für Polymerforschung Dresden e. V.

Unterlagen nur zur eigenen Verwendung und zu Ausbildungszwecken

Strukturbestimmung mit Streumethoden

Prof. Dr. Manfred Stamm
1. Einführung in Streumethoden
2. Diskussion der Techniken
3. Grundlagen der Streutheorie
4. Vergleich der Techniken
5. Beispiele nanostrukturierter Materialien
   - semikristalline Polymere
   - Nanohybride
   - Polymer-Nanocomposite
   - nanostrukturierte Filme
6. Literatur
For the investigation of nanostructured materials one needs suitable characterization techniques, which can resolve structures in the range 0.1nm to 100nm. Scattering techniques can contribute here significantly, but a combination of techniques provides best results. Depending on material and topic one has to decide on the application of different types of radiation, x-rays, neutrons, light or electrons, as well as on scattering geometry and angular range. In the following a short review is given, but further details should be obtained from the literature given. The investigation of thin films, surfaces and interfaces is described in a different contribution and mentioned here only shortly.

**Introduction to Scattering**

In a typical scattering experiment a sample is hit by the radiation, which can be x-rays, neutrons, light or electrons, and the scattered intensity is recorded in a detector as function of the scattering angle $2\theta$. The incident beam has a well defined energy $E$, which is connected to the wavelength x-rays, neutrons, light or electrons,. It is the aim of a scattering experiment to determine from the characteristic diffraction pattern information on the nanostructure of the illuminated sample, and in that way to learn something about structure - properties relationships of the material.

![Schematics of a scattering experiment](image)

**Fig.1 Schematics of a scattering experiment**
Important aspects in such an experiment are relevant length scales, which can be resolved in the given set-up. One can use Braggs law to obtain a characteristic dimension $D$, which can be resolved in the experiment:

$$\lambda = 2D \sin \Theta \quad \text{or} \quad \frac{\lambda}{D} = 2 \sin \Theta$$

(1)

Please note that the experimental scattering angle (see Fig.1) is $2\Theta$. Since the angular range in most experiments is limited, also the range of characteristic dimensions $D$ to be resolved at a given wavelength $\lambda$ is limited. $D$ is inversely proportional to $\Theta$, and therefore large distances (with respect to $\lambda$) can be resolved at small angles and small distances at large angles. For that reason x-rays, neutrons and electrons are well suited to resolve truly nanostructures, since the wavelength can be chosen to be in the range of 1nm or below, while light has a wavelength of several hundred nm and therefore is less suited to resolve nano-scale. In the following we thus focus on those techniques.

A second important aspect is the contrast for scattering, which depends on the type of interaction of the chosen radiation with matter. It is determined for x-rays and electrons by the electron density, for light by the index of refraction, and for neutrons by the scattering length density. A contrast between structural elements of the sample needs a significant difference in those quantities, and only when this contrast is present, the corresponding structure can be seen in the scattering experiment.

Discussion of Techniques

For the investigation of a particular problem therefore the best suited technique has to be chosen. As an example the investigation of a semi-crystalline polymer is discussed.

Fig.2  Unit cell of a crystalline polymer with lattice parameters <1nm.

Since unit cell parameters are typically smaller than 1nm (Fig.2), one uses x-ray diffraction (WAXS) for this purpose. Only when the electron density difference
between atoms is not large enough or if hydrogen positions (very small electron density) have to be determined, also neutron scattering is applied. Looking at chain conformations at scales smaller than 30nm, however, small angle neutron scattering (SANS) is utilized. Here first the angular range is adopted and second a contrast between polymer chains in bulk is obtained by deuteration of some of the chains (Fig.3). From SANS the average dimension of the chains expressed by radius of gyration $R_g$ is obtained.

![Fig.3 One tagged deuterated chain in the lamellar morphology of other chains. Typical sizes of radius of gyration $R_g$ and long period $L$ are of the order of 10-20nm.](image)

The long period $L$ gives the distance between crystalline lamellae and is determined from small angle x-ray scattering or electron microscopy, where in both cases the difference in the electron density between amorphous and crystalline regions provides the contrast.

![Fig.4 SEM image of a polymer single crystal at μm-scale, where stacked crystal lamellae can be resolved.](image)

At still larger scale the lamellar morphology is obtained by electron microscopy, but also light scattering or optical microscopy may be used. The limit of small angle scattering is reached with some micrometers, where already ultra-small angles with special techniques have to be analyzed.

This discussion shows that depending on structural details, which are to be resolved, different techniques have to be applied. In many cases also contrast is a critical issue and particular preparation techniques are required. X-ray scattering on
polymers can be performed with bulk samples, where sample thickness can be 1mm. For transmission electron microscopy however the typical sample thickness is 50µm, and bulk samples have to be cut for instance by a microtome.

**Basics of Scattering Theory**

Scattering is based on the interference of waves as indicated in Fig.4.

![Fig.4](image)

*Fig.4* (left) *Superposition of 3 waves with and without phase shift; (right) scattering from 2 particles as superposition of 2 radial waves*

Therefore phase shifts between the waves are important and have to be calculated based on a given distribution of atoms in the sample. This is the basic principle of scattering theory, which is described in several books. As a result the amplitude $A$ of the scattered wave is obtained

$$A(q) = A_0 \sum_{n=1}^{N} f_n e^{-2\pi i r_n q}$$ (2)

$A_0$ is the amplitude of the incident wave, $N$ the number of scattering atoms, $f_n$ the form factor of the atoms, $r_n$ their position coordinates and $q$ the scattering vector,

$$q = 4\pi/\lambda \sin \theta$$ (3)

In the detector we measure the intensity $I$ of the scattered wave

$$I(q) = \int P(\vec{r}) e^{-2\pi i \frac{\vec{r} \cdot \vec{q}}{\lambda}} d^3 \vec{r}$$ (4)

where we have introduced a continuous scattering density distribution $\rho$ and the Patterson function $P$

$$P(\vec{r}^{'}) = \int \rho(\vec{r}^{'}) \rho(\vec{r} - \vec{r}^{'}) d^3 \vec{r}$$ (5)

Thus the intensity is the Fourier transform of the Patterson function, which contains the convolution of the scattering density distribution. The information on the detailed structure of the sample therefore cannot be obtained in a straightforward manner.
from the intensity because the phase cannot easily obtained from the experimentally measured intensity.

If we calculate the scattering from a crystal with a given unit cell and translational symmetry, two factors are obtained

\[ A = \sum_n e^{-2\pi i \mathbf{q} \cdot \mathbf{r}_n} \sum_m f_m e^{-2\pi i \mathbf{h} \cdot \mathbf{r}_m} \]

The first summation with index \( n \) is performed over the unit cells of the crystal located at position \( \mathbf{r}_n \), while the second summation with index \( m \) goes over the atoms in the unit cell at location \( \mathbf{r}_m \). In this way we obtain two separated terms \( G \) and \( F \), where the first one can be shown to contribute only at positions of scattering vector \( \mathbf{q} \) which correspond to a reciprocal lattice vector \( \mathbf{h} \).

Equ. (7) can be nicely illustrated by an optical simulation experiment, where first the scattering from a density distribution of one unit cell (corresponding to \( F \) in equ.(7)) is shown and then those unit cells are ordered in a crystal arrangement. The scattering pattern displays the superposition of the two terms \( F \) and \( G \): \( F \) determines the intensity and \( G \) the position of scattering maxima.

Fig. 5 Optical simulation of scattering experiment:
(a) single “8”, (b) scattering from “8”, (c) crystal of “8”s and (d) scattering pattern of crystal of “8”s (after 1).
Comparison of Techniques

The different types of radiation interact differently with materials and therefore also provide different scattering contrast. Some aspects of light, x-rays and neutrons are shown in tab.1. Light and x-rays are electromagnetic radiation of different energy and frequency, while neutrons represent particle radiation. The wavelength of light is large with respect to nanostructures, and light is therefore not well suited to resolve structures smaller than 100nm. X-rays and neutrons are very good in that respect. To study molecular dynamics on the other hand is well possible with light and neutrons, because here the energy (and energy resolution) is in the range of molecular und collective excitations.

Table 1. Some characteristic data of radiation types

<table>
<thead>
<tr>
<th></th>
<th>light</th>
<th>x-rays</th>
<th>neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>source</td>
<td>laser</td>
<td>x-ray source</td>
<td>reactor spallation source</td>
</tr>
<tr>
<td>mass</td>
<td>0</td>
<td>0</td>
<td>1.66 * 10^{-24} g</td>
</tr>
<tr>
<td>charge</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>spin</td>
<td>1</td>
<td>1</td>
<td>½</td>
</tr>
<tr>
<td>magnetic moment</td>
<td>0</td>
<td>0</td>
<td>1.93 µ</td>
</tr>
<tr>
<td>energy E example</td>
<td>1 – 10 eV</td>
<td>1 – 10 KeV</td>
<td>0.1 – 500 meV</td>
</tr>
<tr>
<td>frequencies ν=E/h</td>
<td>~ 10^{15} Hz</td>
<td>~ 10^{18} Hz</td>
<td>~ 10^{12} Hz</td>
</tr>
<tr>
<td>wavelength λ</td>
<td>100 – 2000 nm</td>
<td>0.1 – 1 nm</td>
<td>0.03 – 3 nm</td>
</tr>
<tr>
<td>energy resolution ΔE/E</td>
<td>10^{-8}/1 µeV</td>
<td>10^{-5}/100 meV</td>
<td>10^{-6}/0.1 µeV</td>
</tr>
<tr>
<td>typical intensities</td>
<td>10^{16}</td>
<td>10^{10}</td>
<td>10^{7}</td>
</tr>
</tbody>
</table>

X-rays are well suited for nano-structure investigations in the small and wide angle range (SAXS and WAXS) resolving structures in the range 0.1nm to up to 500nm. With synchrotron radiation and grazing incidence small angle x-ray diffraction (GISAXS) in thin films a wider range up to 3000nm can be covered. Neutrons are widely used for polymers because of their unique possibilities to generate a scattering contrast by deuteration (Fig.6). The neutron scattering lengths are b_H=-3.74fm and b_D=6.67fm, respectively. Replacement of H by D in a polymer molecule thus produces a significant scattering contrast, and the chain conformation
of a deuterated chain in the matrix of non-deuterated chains can be determined by small angle neutron scattering SANS.

Examples of Nanostructured Materials

(a) Semicrystalline Polymers
As an example the scattering from a semicrystalline polymer will be discussed, where different information on structure and conformation can be obtained by different techniques. A schematic picture of a semicrystalline polymer is shown in Fig. 7. Crystalline and amorphous regions are regularly spaced with a long period of typically 20nm and two extreme folding models are shown for the conformation of the chains. With SAXS, WAXS and SANS different aspects of this structure can be resolved.

Fig. 6 Schematics of nuclear interaction of a neutron with Hydrogen and Deuterium

Fig. 7
So first by SAXS the long period is obtained due to the density difference of amorphous and crystalline regions, which gives rise to a peak in the small angle region. WANS from crystalline regions reveals the crystal structure from an analysis of the Bragg peaks (Fig.8), while the ratio of Bragg peaks to amorphous halo provides information on the crystallinity. When chains are tagged by deuteration one can get information on the chain conformation of those chains in the matrix of the non-deuterated chains. In the Zimm representation 1/I versus q^2 the slope provides the radius of gyration R_g of the tagged chains
\[ \frac{x_0 x H K}{I_0 (q \to 0)} = \frac{1}{M_w} \left( 1 + \frac{R_g^2 q^2}{3} \right) \] (Zimm approximation)

With an analysis of the q-dependence of the scattering one then can distinguish between the two models of chain folding indicated in Fig.7, favoring for melt quenched polyethylene samples the statistical folding model for instance. A schematic scattering pattern of semicrystalline polymers is shown in Fig. 10. From the different angular ranges the information as indicated in Tab.2 is obtained.
Table 2 Characteristic information, which can be obtained from different regions of the scattering pattern

<table>
<thead>
<tr>
<th>region</th>
<th>q, D</th>
<th>information</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA</td>
<td>&gt; 10 nm⁻¹</td>
<td>- crystal structure</td>
</tr>
<tr>
<td></td>
<td>&lt; 1 nm</td>
<td>- crystallinity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- RDF of amorphous regions</td>
</tr>
<tr>
<td>SA II</td>
<td>1–10 nm⁻¹</td>
<td>- correlation between chain segments</td>
</tr>
<tr>
<td></td>
<td>1-10 nm</td>
<td>- type of chain folding</td>
</tr>
<tr>
<td>SA I</td>
<td>&lt; 1 nm⁻¹</td>
<td>- long period</td>
</tr>
<tr>
<td></td>
<td>&gt; 10 nm</td>
<td>- radius of gyration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- molecular weight</td>
</tr>
</tbody>
</table>

Polymer nanocomposites can be investigated by scattering techniques to obtain information on the size, form, crystall structure, orientation, dispersion etc. of the nanoparticles in the polymer matrix. In addition changes of the structure of the polymer matrix can be detected. The contrast for x-ray scattering is usually high when inorganic nanoparticles are used. A first information is the radius of gyration $R_g$ of the particles, which is obtained in the Guinier range at very small scattering angles ($qR_g < 1.2$).

$$I(q) = (\Delta n_e)^2 e^{-q^2R_g^2/3} \quad \text{(Guinier)} \quad (9)$$

$\Delta n_e$ is the scattering contrast. For two phase systems (particles, phase separated blends etc.) at larger scattering angles ($qD>3$) the Porod law can be used to obtain information on the total surface $S$ of the system.
Deviations from the $q^{-4}$-law are attributed to diffuse interfaces or fractal behavior. There are several other approximations and scattering laws known for particles of different shape (rods, discs, spheres etc.). An example is given in Fig. 11 for spheres, where also the Guinier and Porod regimes are indicated.

\[
\lim_{q \to \infty} I(q) = (\Delta n_e)^2 S \frac{2\pi}{q^4}
\]  
(Porod) (10)

Therefore a phenomenological approach is used for the description of the scattering of nanocomposites, where a Guinier and Porod-like scattering is combined. For more complex systems several weighted terms with different $R_g$ and exponents $p$ may be used.

\[
I(q) \equiv Ge^{-q^2R_g^2/3} + B\left(\text{erf}\left(\frac{qR_g}{\sqrt{6}}\right)/q\right)^p
\]  
(Beaucage) (11)

$G$ and $B$ are weighting factors. It should be kept in mind that this form is only an approximation to obtain an estimate on the particle or cluster scales. Exponent $p$ and $R_g$ are coupled in the Beaucage approach which is not the case in the true Porod analysis.

(b) Ti-oxo-nanohybrids

As a first example we will discuss the investigation of epoxy-nanohybrid materials, containing Ti-oxo-nanoclusters linked to the polymer chains (2) (fig.12a). From a fit to the experimental scattering curves with the Beaugage equation containing two size scales (fig.12b) one obtains the mean size of the primary particles with sharp interface as well as the clusters with diffuse interface.
A model is developed to understand the cluster formation by statistical attachment of particles. Depending on the Ti-oxo-nanoparticle concentration in those nanohybrids the stiffness in the glassy state is significantly enhanced and thermal stability improved.

(c) Polyamide-Nanocomposites

Several nanocomposites of polyamide with ZnO and Al₂O₃ nanoparticles are investigated by SAXS (3). PA is a semicrystalline material and nanoparticles are incorporated into the structure. Changes in the scattering with increasing concentration of nanoparticles are observed mostly at small angles (fig.14) and the long period peak of PA disappears (fig.15). Nanoparticles are therefore not preferentially incorporated into the amorphous or crystalline regions (fig.16), and clusters are formed. In a Beaucage fit two length scales have to be used (fig.17).
Fig. 14 SAXS pattern on area detector of PA and PA nanocomposites (3)

Fig. 15 SAXS pattern after radial average for different nanoparticle concentrations (3)

Fig. 16 Model of semi-crystalline polymer

Fig. 17 Beaucage fit to SAXS pattern indicating different contributions (3)
For ZnO nanocomposites $R_g1$ and $R_g2$ are decreasing with nanoparticle concentration while they stay constant for Al$_2$O$_3$. From WAXS investigations the crystallinity and crystal structure of the nanoparticles is obtained (fig.18). While ZnO nanocomposites show a significant increase in elastic modulus and yield strength, there is almost no change in Al$_2$O$_3$ nanocomposites (fig.19).

![Fig.18 WAXS pattern of nanocomposites at different nanoparticle concentrations (3)](image)

![Fig.19 Stress-strain curves of nanocomposites at different concentrations (3)](image)

Scattering investigations are used in many more examples for the investigation of different nanocomposites mostly in combination with electron microscopy. Recent examples are for instance the determination of hierachical structures of carbon black in polybutadiene (4) or the self-assembly of gold-nanoparticles in diblock copolymers of PS-b-PVP (5). SAXS and WAXS results provide a representive average over the sample, are used without dedicated sample preparation and can also be applied in-situ for instance under deformation, heating or solvent annealing conditions. Since the SAXS data analysis is not unique and needs model assumptions, it is always advisable to combine the scattering experiments with selective electron microscopy investigations.
(d) Multilayers and Nanostructured Thin Films

Scattering and reflectivity techniques for the investigations of nanostructures at surfaces, interfaces and in thin films are discussed in another contribution and therefore will be mentioned here only briefly. The structure perpendicular to the film surface can be tested with x-ray or neutron reflectivity (6) (fig.20). So for instance the interface between two films can be analysed as well as a multilayer structure determined. Reflectivity is also sensitive to surface or interface roughness or waveness, and therefore highly smooth samples have to be used.

Fig.20 Schematics of an x-ray or neutron reflectivity experiment from a double layer film sample to determine the buried interface between the two polymer films (6)

As an example the nicely ordered structure of a diblock copolymer film of PS-b-PMMA in a thin film is shown (7), where the scattering density profile of ordered lamellae parallel to the silicon substrate is obtained from a fit to the neutron reflectivity curve. The PS block is deuterated for contrast reasons.

Fig.21 Neutron reflectivity curve of a diblock copolymer thin film PS(D)-b-PMMA on a silicon substrate (7).
If there are lateral structures in the film or at the surface, grazing incidence scattering has to be used. An example is the scattering from the morphology of a diblock copolymer forming cylinders perpendicular to the substrate (8) (fig.22). In the so-called out-of-plane scan with a highly focused synchrotron beam the nanostructure of the copolymers in the thin film are resolved (fig.23). The empty cylinders are also resolved by scanning force microscopy (fig.24). In-situ grazing incidence small angle x-ray scattering (GISAXS) allows to investigate the solvent vapour induced orientation switching in PS-b-P4VP block copolymer thin films (9). The supramolecular assembly of block copolymers can be used for fabrication of ordered nanomaterials where metallic nanodots are deposited inside the preformed nanotemplates (10).

Nan

**Fig.22** Copolymer morphology with perpendicular orientation of cylinders in a thin film. One component is removed to obtain empty cylinders (8).

**Fig.23** GISAXS out-of-plane scan from a nanostructured diblock copolymer film. The peak corresponds to a spacing of 24nm.

**Fig.24** AFM image of the copolymer film. The dark spots correspond to empty cylinders of 8nm width.

In conclusion scattering techniques are well suited to resolve nanostructures in bulk materials as well as in thin films and at surfaces. Depending on contrast and
technique particular structural aspects of the sample can be investigated, covering a range from 0.1nm to 2000nm for structural details. Since in most cases scattering techniques do not provide unique information, a combination with microscopy techniques is advisable.

References

1) S. Haussühl, Kristallphysik, Dt. Verlag Grundstoffindustrie (1983)


Reviews and Books


M. Hoffmann, H. Krömer, R. Kuhn, Polymeranalytik I/II, G. Thieme Verl., Stuttgart (1977)


M. Stamm (ed.), Polymer Surfaces and Interfaces, Springer (2008)

I. C. Sanchez (ed.), Physics of Polymer Surfaces and Interfaces, Butterworth-Heinemann, Boston (1992)