This introductory chapter provides an overview of the various techniques of microscopy that are available. Starting with the improvement in the resolution of microscopes during their historical development from optical microscopes up to high-resolution transmission electron microscopes and scanning tunnelling microscopes, the field of microscopy is classified based on the principles of imaging. The main techniques used to study the structures of surfaces, the internal structures of polymers and their chemical compositions are listed and discussed in detail in the subsequent chapters in Part I. An overview of additional techniques used to study the morphologies and micromechanical properties of polymers closes the chapter.

The structures and morphologies of polymers have been under investigation for more than 60 years. Early applications of transmission electron microscopy were concerned with the study of the spherulitic crystallisation of natural rubber and low-density polyethylene. After 1957 lamellar crystals of polyethylene crystallised from dilute solution were studied by transmission electron microscopy by Keller and Basnett and the folded chain hypothesis was advanced [1,2]. This was followed by a large number of contributions on the morphology of crystalline polymers. Techniques that allowed the use of transmission electron microscopy to investigate relatively complex structures, such as spherulites, polymer blends and block copolymers, were developed in the 1960s and 1970s. Scanning electron microscopy was introduced in the 1960s, and since then it has been used to investigate fracture surfaces, phase separation in polymer blends and crystallisation of spherulites. The recent availability of high-resolution electron microscopy, coupled with image processing techniques, or atomic force microscopy is now making it possible to view structures down to the molecular level.

The primary reason for developing electron microscopes was to improve the resolution of microscopes, and so one of the most important aspects of each microscope is its resolution power, which is the minimum distance between two adjacent object points that can still be imaged separately. It is well known that the resolution of optical microscopes is limited by the wavelength of visible light (it is half of the wavelength, about 0.2 μm). After the first development of optical microscopes in the seventeenth century, the improvements made mainly by Abbe, Zeiss and Schott at the end of the nineteenth century yielded microscopes with this resolution and physical evidence of the resolution limit. The development of electron microscopes in the 1930s resulted in 1934 in the creation of the first transmission electron microscope with a better resolution than an optical microscope. Since then there have been enormous im-
Recent advances in techniques used as well as in interpreting and processing the images have allowed resolutions of the order of 0.1 nm (= 1 Å) or better to be achieved for inorganic crystal structures.

However, the best resolution achieved in polymers is, in practice, poorer than this because of polymer-specific problems with high electron irradiation sensitivity and low contrast. The next jump in resolution came with the development of scanning tunnelling microscopy or, in general, scanning probe microscopy, which enabled the first ever three-dimensional imaging of solid surfaces with atomic resolution. Scanning probe microscopes do not belong in the field of electron microscopy. However, since they are usually used in close connection with electron microscopy and artefact-free evaluations of structures are easier to achieve when their results are compared with those from electron microscopes, they are discussed in this volume too. Field-ion microscopy, a special surface technique with atomic resolution, is not applied to polymers.

![Fig. 1.1. Improvements in the resolution of microscopy](image-url)
Electron microscopy (EM) can be divided into the techniques of transmission electron microscopy (TEM) and scanning electron microscopy (SEM). A comparison in terms of resolving power shows that scanning electron microscopes are somewhat intermediate between optical microscopes (OM) and transmission electron microscopes. A significant advantage of using SEM compared to TEM is that the former can image the surfaces of bulk samples with a large depth of focus. This large depth of focus also allows SEM to be used at low magnifications instead of optical microscopes.

It is necessary to use all of the microscopic techniques if we wish to study the large variety of morphologies and structures of polymeric materials, i.e. from the sizes and shapes of grains or powders up to crystalline structures; see Fig. 1.2. In general, all of the different types of microscopes can be classified according to whether imaging is

![Diagram showing resolutions and structures](image)

**Fig. 1.2.** Scheme of possible structures of different sizes present in polymers and resolutions attainable with the different microscopic techniques
achieved by irradiating the object with a “lamp” or to feeling the surface with a “finger” or “needle” (see Fig. 1.3):

1. A fixed beam of light or electrons is transmitted through the (thin) specimen (as a transmitted beam) in the transmission mode of the optical microscope and in transmission electron microscopes.

2. A stationary beam is reflected off the (bulk) specimen surface (as a reflected beam) in the reflection mode of the optical microscopes or in electron mirror microscopes (the latter are not used for polymers).

3. A focused beam is scanned across the specimen, passing through the (thin) specimen (scanning transmission EM) or resulting in a reflected beam (as in confocal laser scanning microscopy) or secondary or backscattered electrons in scanning electron microscopes.

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**Fig. 1.3.** Schematic representation of the principles of different types of microscopes (see text)
4. A mechanical tip is scanned across the specimen in order to make use of different physical properties in tunnelling microscopes and atomic force microscopes.

When studying the bulk material, the material's surface or its interior is the target of the microscopic investigations; see Fig. 1.4. The surface can be studied directly with scanning electron microscopy (SEM), atomic force microscopy (AFM) and, indirectly after replication, with transmission electron microscopy (TEM). Ultra- and semithin sections from the interior can be used for TEM and thicker sections for analytical TEM and SEM or for AFM.

The traditional electron microscopy technique is stationary-beam TEM, which has been applied to a wide range of materials, including polymers (Chaps. 2 and 3). The main limitation of this approach is that a transparent thin foil that is resistant to damage by the electron beam must be prepared. In addition to this conventional TEM method, special equipment has been developed to achieve high resolution (high-resolution TEM, HRTEM), to be able to use high (high-voltage TEM, HVTEM) or low accelerating voltages (low-voltage TEM, LVTEM), for scanning transmission (STEM), for holography and for spectroscopy or emission of X-rays in analytical microscopes (ATEM).

**Fig. 1.4.** Application of different microscopic techniques to study the surface and interior of a bulk polymeric material
Scanning electron microscopy (SEM) is currently the most popular of the microscopic techniques (see Chap. 4). This is due to the user-friendliness of the apparatus, the ease of specimen preparation, and the general simplicity of image interpretation. The obvious limitation is that only surface features are easily accessible. With SEM, the chemical analysis of different elements is usually possible (energy dispersive or wavelength dispersive analysis of X-rays, EDXA, WDXA).

As mentioned above, scanning probe microscopy techniques cannot be classified as types of electron microscopy. However, because of the wide application of atomic force microscopy (AFM) and the fact that it is often used in combination with electron microscopic techniques, it is discussed in Chap. 5. There are some other techniques of electron microscopy, such as emission EM, mirror-EM, field-electron or field-ion microscopy, which cannot be applied to polymers.

In the past, the central reason for using EM was structure and morphology determination, but it is also currently of importance for investigating different processes, i.e. changes in the material caused by interactions with several factors, such as heat, electric or magnetic fields and environmental liquids or gases. Of particular interest is the study of micromechanical processes of deformation and fracture, as discussed in Chap. 6 (on in situ microscopy).

Valuable methods for improving images and quantitatively estimating structures are included in the final chapter of Part I, Chap. 7 (on image processing).

There are a number of reviews and monographs that discuss the different techniques in more detail, e.g. [3–11], and their application to polymers, e.g. [12–14]. A good overview of microscopically determined structures present in polymers is provided by A.E. Woodward [15].

Besides the techniques of EM and AFM discussed in this volume, there are other techniques that are used to study the morphologies and mechanical properties of polymers [16]. The most important of these techniques are:

- Optical microscopy with magnifications of up to about 1000×, which is very useful for gaining an overview and as a first step in any morphology analysis
- Laser scanning and optical near-field microscopies (scanning beam techniques; see Fig. 1.3), which have improved resolution compared to optical microscopes
- Macromolecular orientations can be visualised using optical birefringence;
- Acoustic microscopy (ultrasound microscopy) is based on the reflection of ultrasound in the sample, which yields information on density differences, microvoids, cracks, etc., with sizes of less than 1 μm
- Small-angle light scattering (SALS) can be used if the polymers are capable of scattering light due to density or birefringence fluctuations of the order of the wavelength of the light, and is a useful method for studying textures that are larger than about 1 μm, e.g. spherulites in semicrystalline polymers
- Classical methods of light-optical interference are used to detect small details on the order of the wavelength of the light in transparent materials; in particular, the micromechanics of crazes at crack tips in transparent glassy polymers can be investigated
Small-angle X-ray scattering (SAXS), the traditional technique used to study periodicities in semicrystalline polymers (e.g. long periods of fibrils or lamellae) and also to detect microcavities (e.g. microvoids between craze fibrils and interfibrillar spacing).

Wide-angle X-ray scattering (WAXS) yields information on the crystallinity (type and size of crystals and lattice defects) in polymers.

Rheo-SAXS experiments using X-ray radiation from a synchrotron source allow us to measure in situ changes in structure and crystallinity and to perform real-time measurements at low speeds and frequencies.

Small-angle neutron scattering (SANS) characterises the fluctuations in the density, concentration, and magnetic properties of the material and yields information on the conformation, size and mobility of the macromolecular coils, but is far from a routine technique.

Infrared (IR) and Raman spectroscopy characterise the type and constitution of the macromolecules present.

Rheo-optical methods include a mechanical test performed under static conditions which is carried out simultaneously with optical measurements; among other optical methods, Fourier transform infrared spectroscopy (FTIR) has become one of the most frequently applied tools in rheo-optics, since it enables changes in molecular orientations in polymers and different types of macromolecules in polymer blends to be identified.

Dynamic mechanical analysis (DMA) is a very helpful tool for determining relaxation processes, glass transition temperatures and mixing or phase separations of different polymer constituents in blends and copolymers.

Differential scanning calorimetry (DSC) measures melting or crystallisation temperatures and degrees of crystallinity.

Microindentation hardness gives information on crystallisation behaviour, local mechanical properties, and micromechanical processes.

Positron annihilation spectroscopy (PAS) allows us to estimate the local concentration of free volume or the size of nanovoids.

Electron spin resonance (ESR) and nuclear magnetic resonance (NMR) measure, for instance, radical formation and macromolecular mobility.

The advantage of all of these techniques is that they can be used to investigate larger material volumes and to give integral parameters for the measured structure. On the other hand, their major disadvantage is that they cannot clarify variations in structural or morphological parameters, such as the size distributions of lamellae or particles, orientation differences, local concentrations of additives, deviations in phase separation, and many others. In order to gain an understanding of mechanical properties, in particular strength, elongation at break or toughness, it is not sufficient to measure the “average morphology”, since these properties depend strongly on the variation in structural elements and, for instance, on extreme values of them. Therefore, microscopic techniques with high local resolution are exceptionally important for polymer research and the development of materials with improved mechanical properties. To maximise the information obtained about a particular material, a com-
Combination of electron microscopy (with its high local resolution of structures and variations in details) with some of other integral techniques that provide average values of structures should be utilised if possible.

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