
8 Problems Associated with the Electron Microscopy of Polymers

This introductory chapter to Part II – which deals with preparation techniques – summarises the main problems associated with the investigation of polymers by electron microscopy. The irradiation sensitivity of polymers can be reduced by taking precautions with the instrumentation and the manner of operation. It should also be noted that the irradiation sensitivity of polymers can be utilised for special contrast development effects. The problem of the low contrast between structural details of polymers can be overcome through the use of chemical staining, physical effects or surface etching. The third problem is the preparation of ultrathin specimens from bulk polymers, which is successfully solved by applying (cryo)ultramicrotomy. Some additional methods are mentioned, and the applicabilities of various methods for studying the morphologies of several classes of polymers are summarized. All of these methods are described in detail in subsequent chapters in Part II.

8.1 Overview

The polymers that are studied by electron microscopy can take various shapes, forms and sizes. Examples include powders obtained directly from macromolecular synthesis and granules from compaction or a first extrusion step, and injection and extrusion-moulded test parts in the centimetre range or large pieces for different applications. In general, direct investigations of polymers by electron microscopy involve three problems:

1. The usual preparation techniques applied to inorganic samples, particularly for TEM investigations, cannot be applied, and the preparation of ultrathin specimens from bulk polymers is often difficult
2. Polymers (since they are organic substances) are particularly sensitive to electron beam irradiation
3. The contrast between structural details is often very low because polymers usually consist of the same light elements (C, H, O, and others) that interact only weakly with the electron beam (see Sects. 2.4 and 4.2.5).

Several preparation and investigation techniques have been developed to overcome these difficulties. These are reviewed in this chapter, and the main steps are discussed in detail in subsequent chapters in Part II.

8.2 Irradiation Sensitivity of Polymers

The effects of irradiation on polymers have been discussed in many papers and several reviews (e.g. [1–5]). The primary effects of the interaction of electrons with organic matter are inelastic scattering processes, which yield ionisation and break chemical bonds. Secondary effects are mainly chain scission or crosslinking, mass loss, fading of crystallinity, heat generation, and charging-up. The sensitivity to irradiation decreases with increasing carbon content in the polymeric samples; in other words in the sequence: PTFE, PVC, PMMA, PC, PE, PS [4]. Irradiation processes usually proceed very quickly during irradiation in EM, which means that investigations of polymers can often only be performed on badly damaged molecules. These damaged specimens are frequently well suited for investigating the supramolecular structure (the morphology) because the morphology is often unaltered by molecular processes. This generally holds for amorphous polymers, since image formation is based on differences in mass thickness (e.g. between different polymer phases, particles, domains). For semicrystalline polymers, however, the crystalline structure should also be investigated using diffraction contrast, which disappears upon molecular damage. The damage to the specimen can be reduced by taking precautions with the instrumentation and the manner of operation:

1. If possible, “low-dose” techniques should be used [6], which means focussing on one place on the sample and taking micrographs of a different (i.e. previously nonirradiated) place. Low-dose techniques involve performing adjustments to parameters such as the magnification, matching the dosage to the sensitivity of the viewing medium, and focussing on an area of the specimen adjacent to the feature. The beam is then moved with the beam deflection coils, and the shutter is closed to reduce the irradiation of the site adjacent to the feature. The beam is directed onto the feature only when it is being recorded.
2. The presence of evaporated thin carbon layers on both sides of the specimen improves the conductivity and can reduce specimen movements and the volatilisation of molecular fragments [7, 8]. The loss of contrast is small, and the increase in dosage has been shown to be as much as tenfold for organic crystals [9].
3. The sensitivity of the photographic material can be enhanced by using special emulsions with a higher silver halide content or special development techniques [10, 11], or the use of electron image intensifiers with coupled image recording can be helpful.
4. The application of a higher accelerating voltage for the electrons will lead to a reduction of the inelastic scattering cross-section. The corresponding enhancement of the radiation resistance upon changing from 100 to 200 kV is about 50%, and it increases about threefold upon changing from 100 kV to 1 MV [12–14]. (However, it should also be remembered that the exposure of the photographic film depends on ionisation process, and so the exposure time also increases).
5. In a HVTEM with an accelerating voltage of 1000 kV or more, the high energies of the electrons allow the use of highly sensitive photographic films, such as special X-ray films with a double coating of thick layers of emulsion and a higher

silver halide content [15]. Such films cannot be used in a usual TEM because of the lower penetration power of the 100–200 kV electrons.

6. The use of a scanning transmission electron microscope (STEM) instead of a fixed-beam microscope can reduce the damage somewhat [16].
7. By cooling the specimens to low temperatures (cryomicroscopy), the mobility of the polymer molecules and all secondary processes (e.g. mass loss, amorphisation rate of crystals, crosslinking) can be reduced. Cooling specimens to the temperature of liquid nitrogen only has a small effect [1, 2], but cooling to liquid helium temperatures yields a significant increase in the polymer lifetime [8, 17, 18]; see also Sect. 3.3.2. However, it is still quite difficult to use liquid helium in a special cryomicroscope, and this rules it out as a routine operation for polymer samples.

On the other hand, it is also possible to make use of the irradiation sensitivities of polymeric materials for special effects of contrast development:

- In the case of polymer blends, the different sensitivities of the polymeric components can result in a stronger mass loss in one component than in another, yielding a the development of contrast at the start of irradiation in the EM. An example is shown in Fig. 17.13.
- In the case of semicrystalline polymers, the primary irradiation processes (rupture of chemical bonds, ionisation, etc.) are the same, but the secondary processes of crosslinking may be stronger in the amorphous regions than in the crystalline ones. This gives rise to some other effects, and the result is the development of contrast between the amorphous and crystalline parts; see Sect. 13.3.1 with Figs. 13.10–13.12.

As mentioned above, the irradiation-induced changes (at the macromolecular level) often do not impede morphological investigations performed at the supramolecular level. Moreover, the morphologies of specimens can be stabilised by applying chemical fixation and staining treatments – essentially by crosslinking the macromolecules and incorporating atoms of heavy elements – which is often necessary when preparing ultrathin sections for TEM or surfaces for SEM investigations. Another common and serious problem is poor performance during in situ deformation tests, although this problem can be overcome by implementing several precautions; see Chap. 12.

The total avoidance of any irradiation-induced effects is only possible if replicas of the materials of interest are investigated (see Sect. 9.5) or if an AFM is used.

8.3 Low Contrast of Polymers

A second problem associated with the direct investigation of polymers by transmission electron microscopy (TEM) is the low contrast between structural details. However, there are several methods that can be used to enhance the contrast:

1. The chemical staining of details can be achieved through the selective incorporation of heavy elements. Different structural details (lamellae, amorphous regions, interfaces, regions of different molecular packing densities or different free volumes, several polymer phases, and others) possess different reactivities to staining media. Also, different staining media are applicable to different materials (e.g. osmium tetroxide, ruthenium tetroxide, phosphoric-tungsten acid, chlorosulfonic acid).
2. In addition to the commonly used method of chemical staining, there are some physical methods that enhance the contrast between structural details. One method is based on the abovementioned different irradiation sensitivities of different polymeric components. Irradiation-induced changes can also enhance the contrast of semicrystalline polymers; for instance the structure and lamellar arrangements inside spherulites. Another physical method involves developing the contrast between different polymeric components by mechanically straining the sample (this is known as “straining-induced contrast enhancement”).
3. Structures at surfaces can be “developed” by chemical or physical etching methods. The contrast of structural details can also be enhanced by evaporating metal atoms at small angles (shadowing).

These chemical and physical methods of contrast enhancement will be discussed in detail in Chap. 13, and the methods of structural development at surfaces are explored in Sect. 9.3.

8.4 Methods of Investigating the Morphologies of Polymers

8.4.1 Powders, Particles, Fibres

Powders, other small particles or fibres can be investigated “as is”, i.e. without any additional treatment. After mounting the material on a sample holder, its shape, size, and surface structure can be studied directly in SEM or ESEM. Dispersions of very fine particles or fibres can be mounted on a (C-coated) grid for direct TEM inspection. Embedding and ultramicrotomy of the particles is usually needed to reveal the internal particle structure in TEM (see Chap. 10).

8.4.2 Bulk Polymers

The sizes of the supramolecular structures or morphological features of bulk polymers range from the smallest details that are just above the molecular level (smaller than 1 nm) up to structures that are larger than 100 μm – a range of more than five orders of magnitude. Several different preparation techniques and microscopic methods are available for studying structure. However, there is a general methodology for structure determination that should be applied to all microscopic investigations. The various steps included in preparation and investigation methods, as well as the corresponding results obtained, are schematically illustrated in Fig. 8.1.

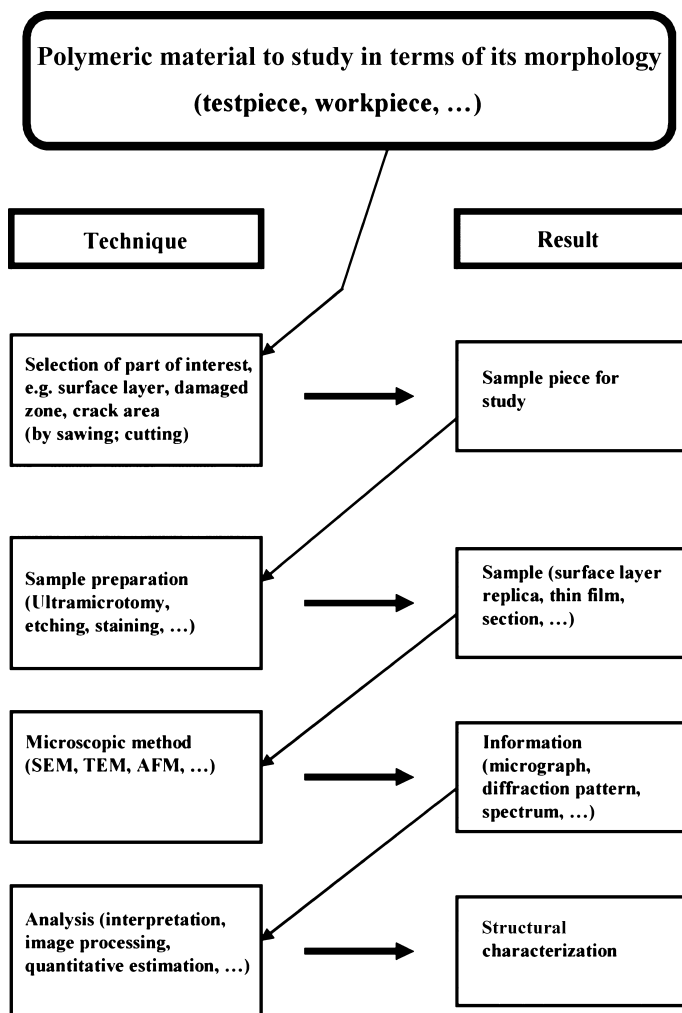


Fig. 8.1. Illustration of the steps involved in sample preparation and investigation methods, and the corresponding results from them during structure determination

Preparation methods for investigating the morphologies of bulk polymers differ from the techniques used for inorganic materials. The usual technique applied to inorganics – chemical or electrolytical thinning – is not applicable to polymers because they swell in solvents and therefore cannot be thinned continuously. Three methods for investigating the morphologies of polymers are generally available (Fig. 8.2):

1. The preparation of special surfaces (e.g. brittle fracture surfaces, smooth and selectively etched surfaces) that yield information on the internal structure of the material. These surfaces are investigated by means of replicas in the TEM or directly in the SEM or AFM.

2. The preparation of thin sections by ultramicrotomy, generally after special fixation and staining procedures have been performed. Investigations are carried out by conventional TEM, HVTEM or AFM.
3. The preparation of special thin films [solution-cast films, focussed ion beam (FIB) sections] with an additional staining treatment (as used for ultramicrotomy) and then studying by TEM or AFM.

The methods used to prepare surfaces are covered in the next chapter, while those used to prepare ultrathin or semi-thin sections are discussed in Chaps. 10 and 12 and the preparation of special thin films is reviewed in Chap. 11.

These three groups of preparation techniques are generally applicable to various polymers; however, some are more convenient for some groups of polymers while others are better for other polymer groups. A rough summary of the applicability of the preparation techniques to various types of polymers is provided in Table 8.1.

Whether or not these different preparation and investigation methods are successful depends on the kind of sample under examination and its structural details, and they do not work to the same extent for all morphological types. Therefore, to perform a full structural determination it is often necessary to apply several techniques. This approach is illustrated for semicrystalline polymers in Fig. 14.9. Additionally, different techniques enable different maximum resolutions in EM. Figure 13.17 shows resolution that can be obtained for semicrystalline, lamellar polyethylene when it is prepared with different techniques and contrast enhancements.

The structures observed in electron micrographs will usually be estimated qualitatively or semiquantitatively in order to derive information about shapes, distributions, arrangements or types of structural components. Quantitative information about structural details, such as the diameters of particles, the thicknesses of lamellae, or others, are usually determined directly from the micrographs using a PC. The automatic analysis of structural details is covered in the discussion of image processing in Chap. 7.

8.5 Methods for Studying Micromechanical Processes

Due to the variety of different structural details that can occur in polymers, there are also a wide variety of micromechanical processes that can appear under load. These include changes to individual macromolecular segments (on a nanometer scale), localised plastic yielding in the form of crazing or shear bands (at the micrometre scale), up to crack propagation and macroscopic fracture (at the millimetre scale); see Fig. 12.1. Therefore, different techniques for studying these processes are required, which are discussed in detail in Chap. 12.

There are additional advantages of using micromechanical testing for morphology determination:

- Components with different mechanical properties can show enhanced contrast due to their different deformabilities (e.g. soft, rubber-like particles in a stiffer

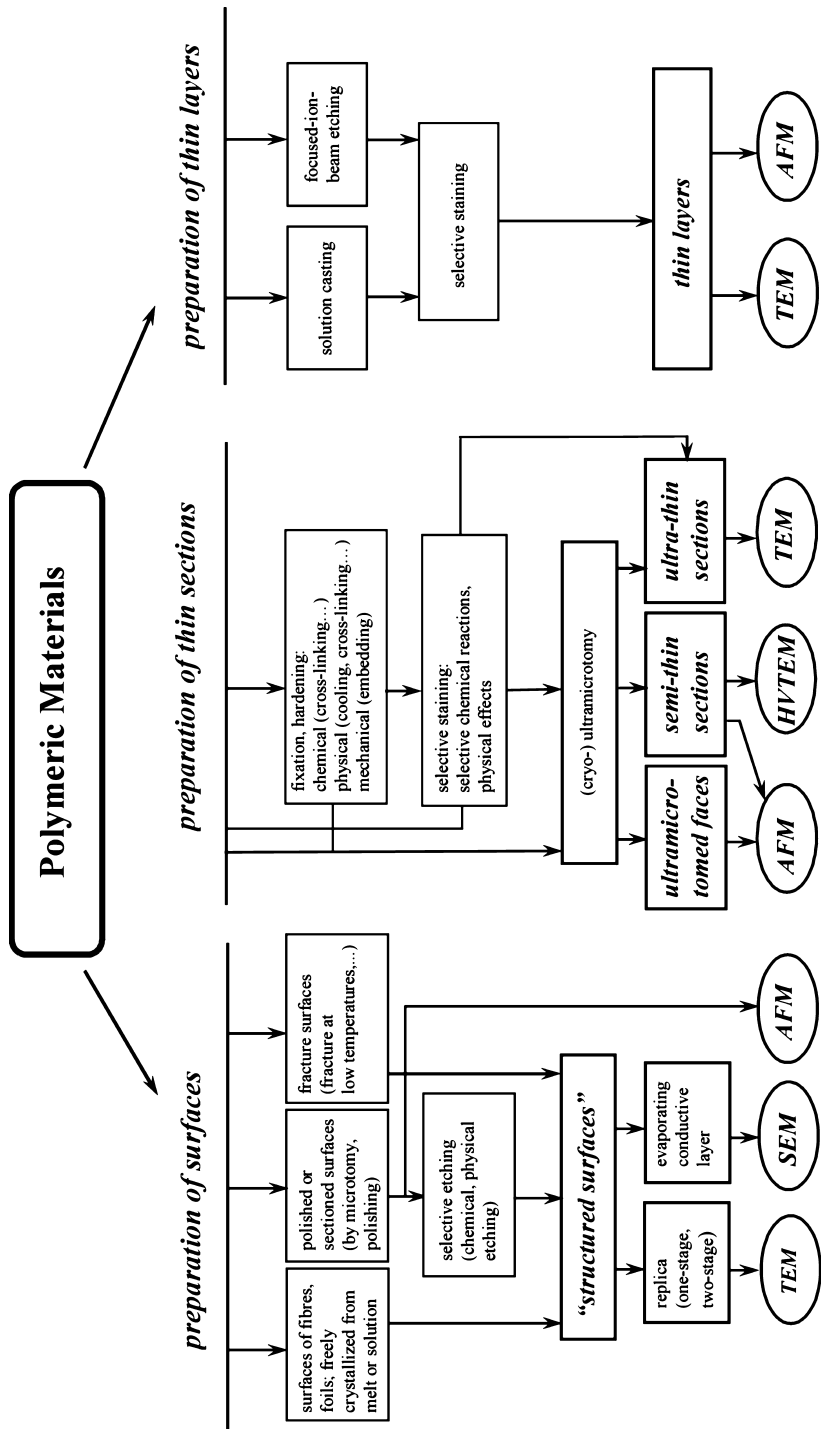


Fig. 8.2. Overview of the preparation techniques and electron microscopic methods often used to investigate the morphologies of bulk polymers

Table 8.1. Summary of the specimen preparation techniques used for EM investigations of the morphologies of different classes of polymers

Preparation technique and EM method	Applicable for				
	Amorphous polymers	Semicrystalline polymers	Polymer blends, Block copolymers	Composites	
1. Preparation of “structure developed surfaces” and study of (single-stage or two-stage) replicas by TEM, studying directly by ESEM, AFM or after coating by SEM (see Chap. 9)					
a) Surfaces “as is” if they show a structure, e.g. after free crystallisation of films or foils from melt or solution		x			
b) Smooth (polished or sectioned) surfaces and selective etching (chemically using solvents or physically using ion beams or glow discharge)	x	x	x	x	
c) Fractured surfaces from low-temperature fracture, brittle fracture		x	x	x	
d) Surfaces from “melt fracture” (high-temperature fracture, soft matrix fracture)			x	x	
2. Preparation of ultra- or semi-thin sections by (cryo)ultramicrotomy after chemical or physical fixation and study by TEM, STEM, HVTEM or AFM (see Chaps. 10, 13)					
a) Sufficient density differences exist for contrast between structural details			x	x	
b) Enhancement of contrast by chemical treatment (with one chemical agent, by combined attack of several media, or after physical activation)	x	x	x		
c) Enhancement of contrast via physical effects					
– irradiation-induced contrast enhancement		x			
– straining-induced contrast enhancement	x		x		
d) Use of diffraction contrast, preparation of thin sections with cryoultramicrotomy		x			
3. Preparation of special thin films with additional staining procedure (see Chap. 11)					
a) Solution-cast films	x	x	x		
b) Thin sections cut with focussed ion beam (FIB)					x

matrix). This effect is termed “straining-induced contrast enhancement” (see Sect. 13.3.2).

- The strengths of interfacial layers in heterogeneous polymers can be checked through straining. In particular, a low interfacial strength will result in interfacial rupture (phase decohesion, unbonding, see Fig. 21.6) under strain. This can allow, for instance, the effects of using surface treatments or coupling media to be evaluated.

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