Chapter 10. Thermal Analysis & Microscopy of Polymers

10.1 Thermal analysis of polymers

* Summary of different thermal methods available

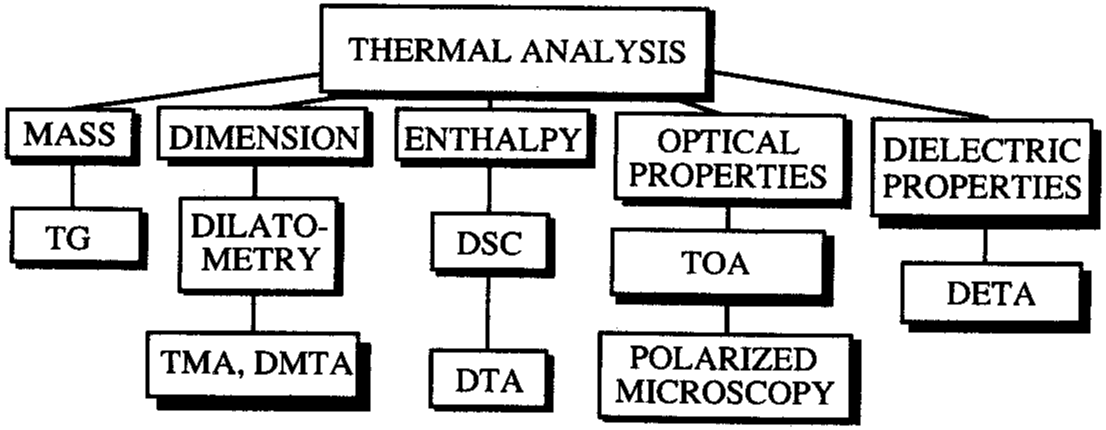


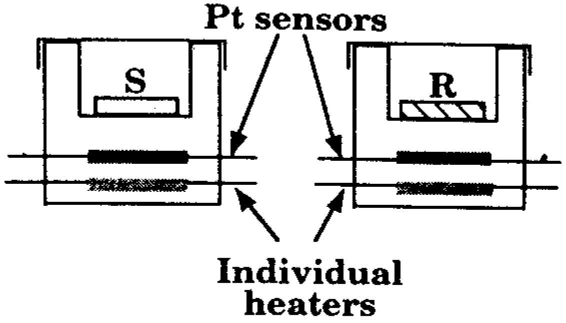
Figure 10.1 Thermo-analytical methods.

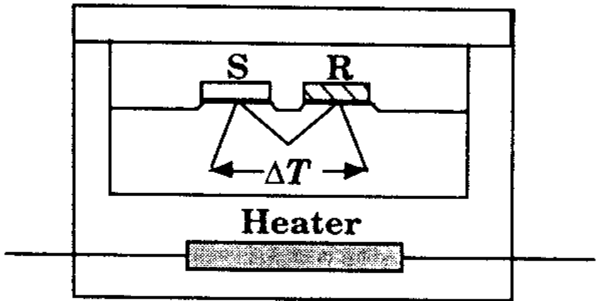
* **Differential scanning calorimetry (DSC)**

~ measures calorimetric properties

* **Differential thermal analysis (DTA)**

~ measures ΔT betw/ sample and reference





→ Schematic representation of DSC (left) and DTA (right),

where S and R denote sample and reference, respectively.

- DSC thermogram of an undercooled, semicrystalline polymer

endothermal

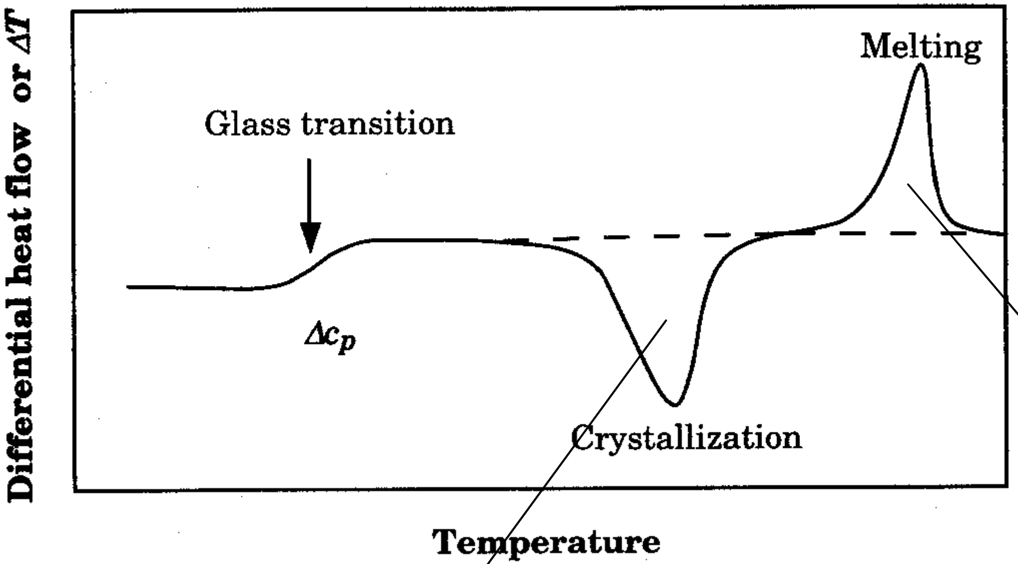


Figure 10.4 Schematic DSC traces showing three transition types.

area under
endothermal peak
= melting enthalpy

area under exothermal peak
= crystallization enthalpy

- DSC thermogram of an immiscible mixture of SAN & PB (ABS)

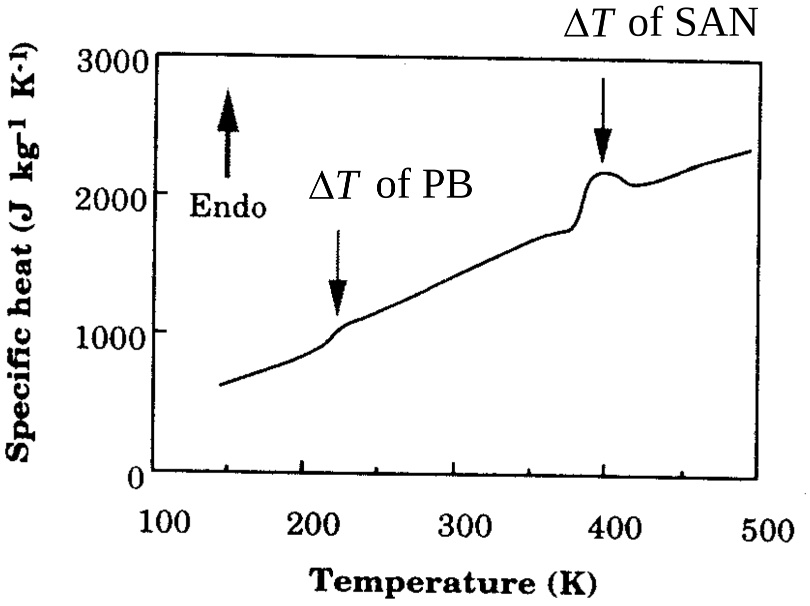


Figure 10.21 DSC thermogram of ABS showing two glass transitions. Drawn after data from Bair (1970).

* **Thermogravimetry (TG)** or **thermogravimetric analysis (TGA)**

~ is carried out in thermobalance permitting the continuous measurement of sample wt. as a ft'n of temperature/time.

Components: recording balance, furnace, furnace T controller & computer

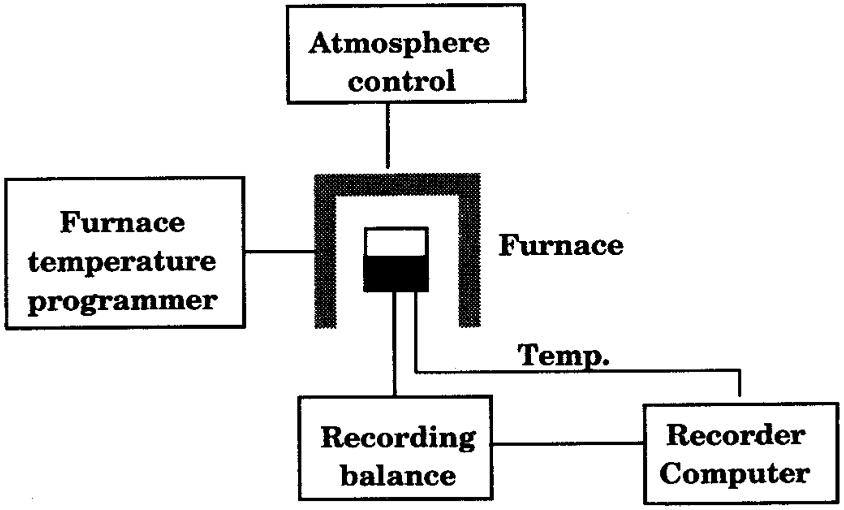


Figure 10.5 Schematic presentation of a TG apparatus.

- Schematic TG trace for a filled polymer

  Finely ground samples ~ preferred

  (∵ reduce a delay in mass loss due to diffusion obstacles)

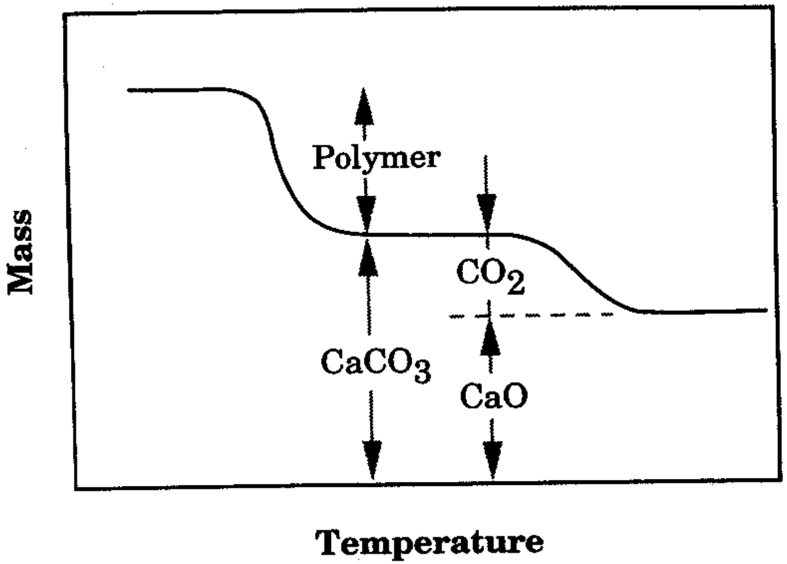
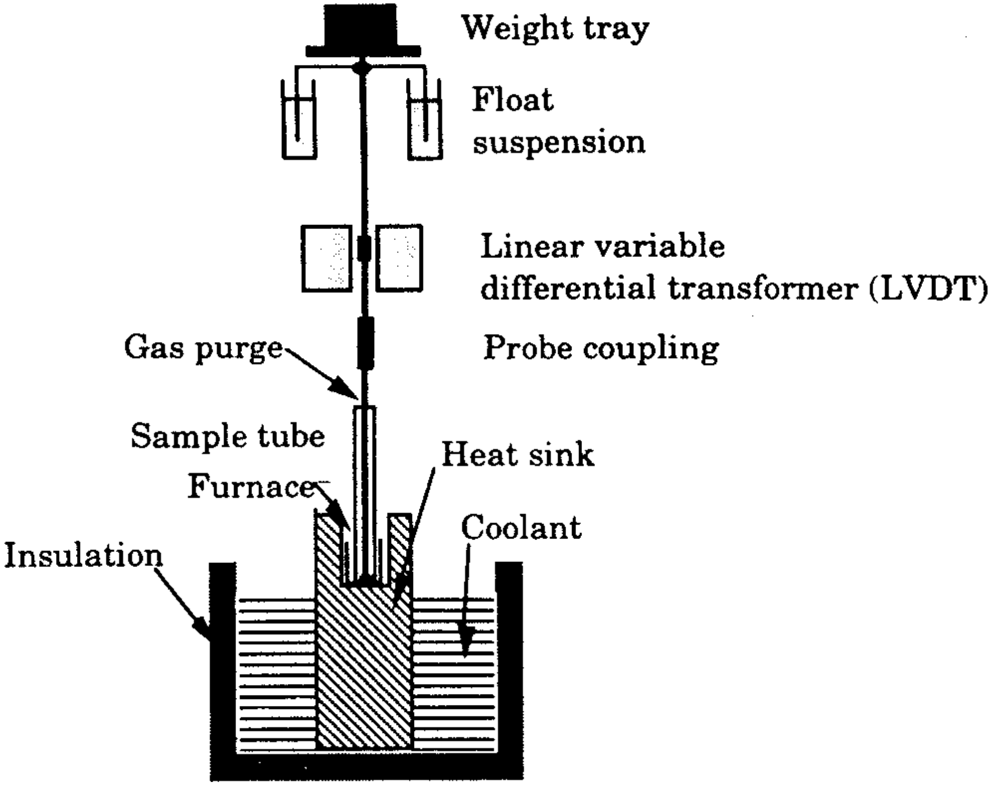


Figure 10.6 Sample mass as a function of temperature. Schematic curve of a polymer filled with $CaCO_3$.

* **Dilatometry/Thermal mechanical analysis (TMA)**

~ measure *V*, linear thermal expansion coefficient & modulus as a ft’n of *T*



→ Schematic presentation of TMA

10.2 Microscopy of polymers

Microscopy: a group of experimental methods which permit magnification of morphological structures

- Optical microscopy (OM)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Infrared microscopy
- Ultraviolet microscopy
- Atomic force microscopy (AFM)
- Acoustic microscopy

- Structural information from microscopy and scattering pattern

TEM ~ observes crystal lamellae directly

SAXS ~ requires the use of a model

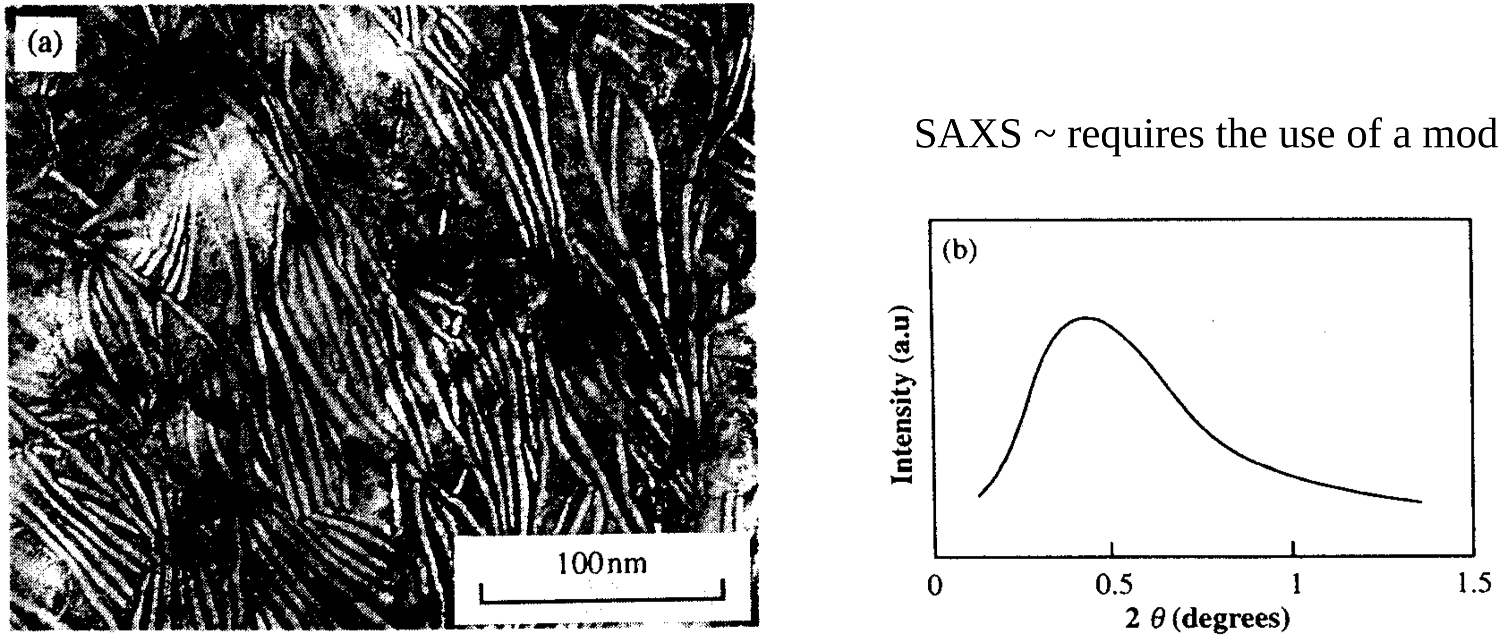


Figure 11.1 (a) Transmission electron micrograph of chlorosulphonated polyethylene. (b) Small-angle X-ray scattering pattern of the same polyethylene sample. Intensity is plotted on an arbitrary units scale. Unpublished data of M. Hedenqvist, Dept of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.

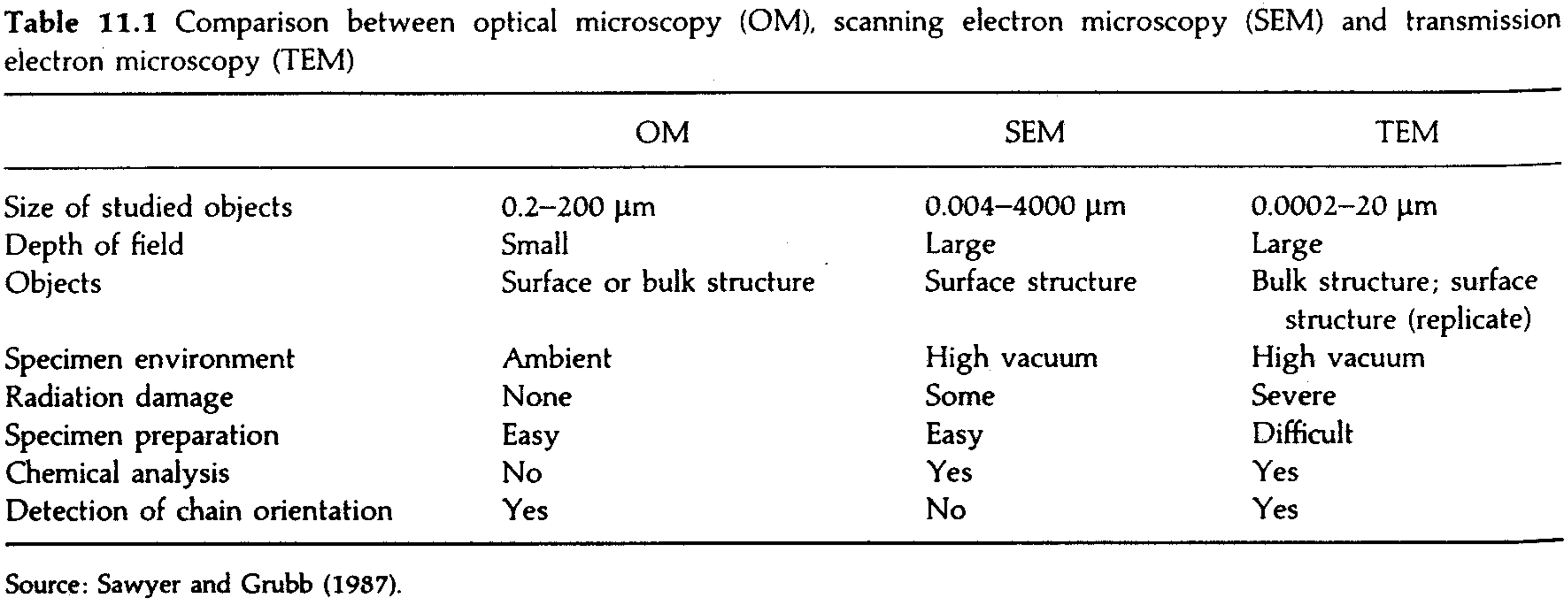


Table 11.1 Comparison between optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

	OM	SEM	TEM
Size of studied objects	0.2–200 μm	0.004–4000 μm	0.0002–20 μm
Depth of field	Small	Large	Large
Objects	Surface or bulk structure	Surface structure	Bulk structure; surface structure (replicate)
Specimen environment	Ambient	High vacuum	High vacuum
Radiation damage	None	Some	Severe
Specimen preparation	Easy	Easy	Difficult
Chemical analysis	No	Yes	Yes
Detection of chain orientation	Yes	No	Yes

Source: Sawyer and Grubb (1987).

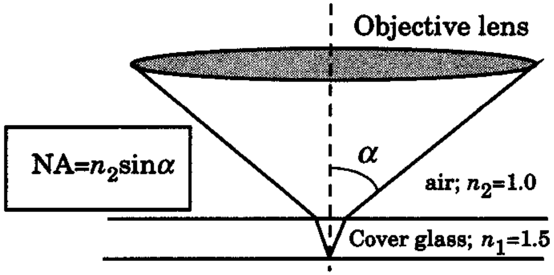
* **Optical microscopy (OM)**

~ maximum magnification is about 2000X.

Bright-field microscopy & Dark-field microscopy

Resolution (d) :

$$d = \frac{\lambda}{NA_{obj} + NA_{cond}}$$



λ : the wavelength of the light

NA_{obj}, NA_{cond} : the numerical aperture of the objective and the condenser

defined as $NA = n\sin\alpha$ α : half the acceptance angle

→ High resolution is obtained with high numerical aperture & short wavelength of light.

- Related techniques

: polarized microscopy, phase-contrast microscopy, differential interference-contrast microscopy

* Electron microscopy (SEM & TEM)

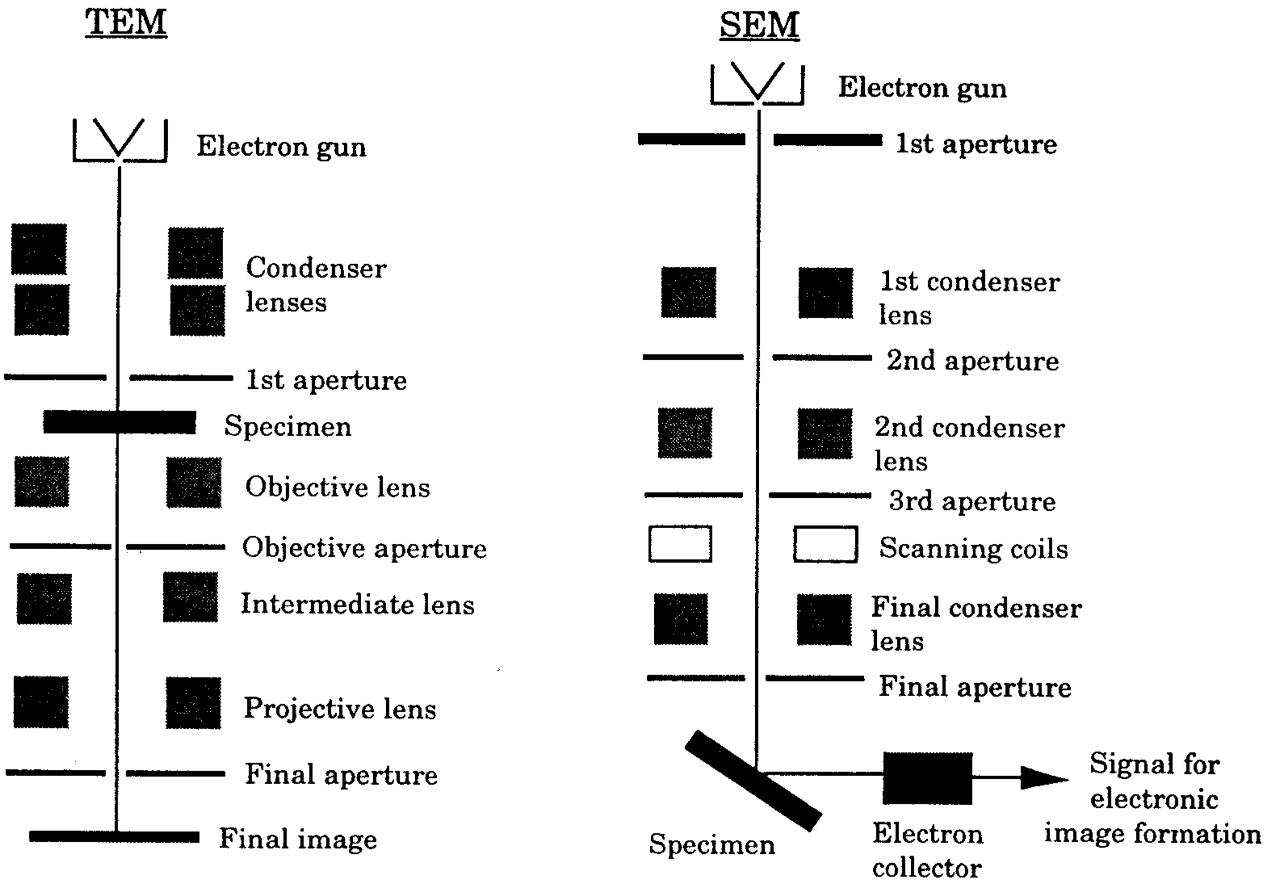


Figure 11.7 Schematic description of conventional TEM and SEM.

- Resolution of electron microscope ~ depends on the voltage applied

The wavelength of the accelerated electrons: $\lambda = \frac{h}{mv}$ (de Broglie eq'n)

where h: Planck's constant, m: the mass of an electron, and v: the velocity of the electron

For an electron with charge e subjected to a voltage U, the following expression holds:

$$eU = mv^2/2$$

Insertion of the above eq'n into the de Broglie eq'n: $\lambda = \sqrt{\frac{h^2}{2meU}}$

The highest resolution (d) of the electron microscope is due to the short wavelength of electrons:

$$d = \sqrt{\left(\frac{0.61\lambda}{\alpha}\right)^2 + \left(C_s\alpha^3\right)^2}$$

where α : half the angular aperture and C_s : the spherical aberration coefficient

ex) Resolution of a 100kV TEM : d=0.5nm.

← λ =0.0037nm, α =0.006 rad, and C_s=1.6mm

- Contrast is obtained by staining or by etching followed by replication

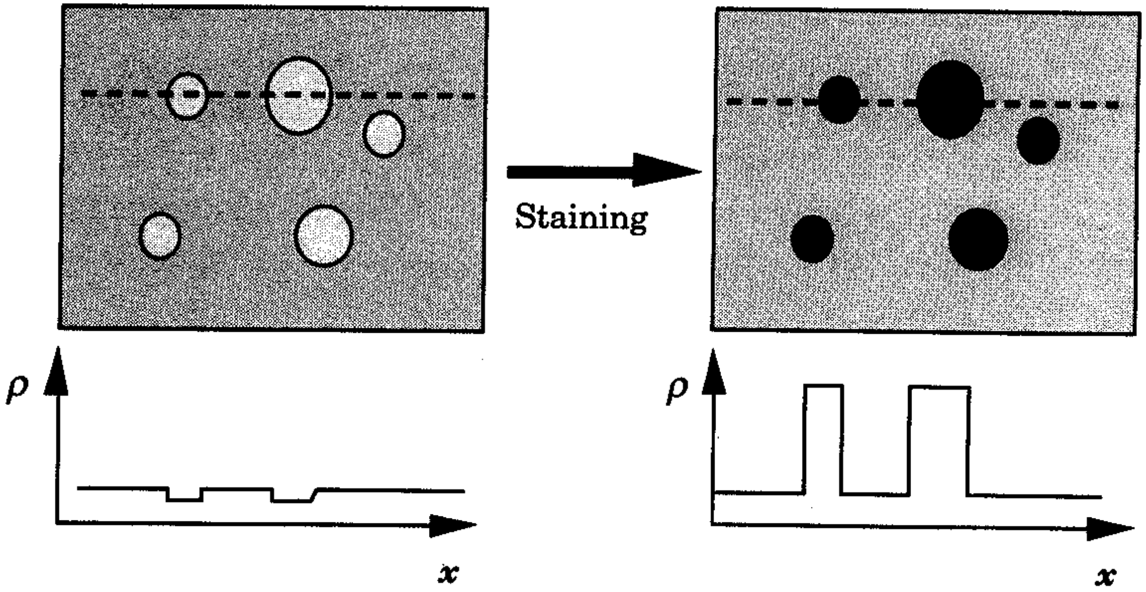


Figure 11.9 The effect of staining. The heavy element is added only to the discrete phase.

Ex) OsO_4 ~ able to stain polydienes

used on ABS, HIPS, SBS copolymers, rubber-containing plastics and PET

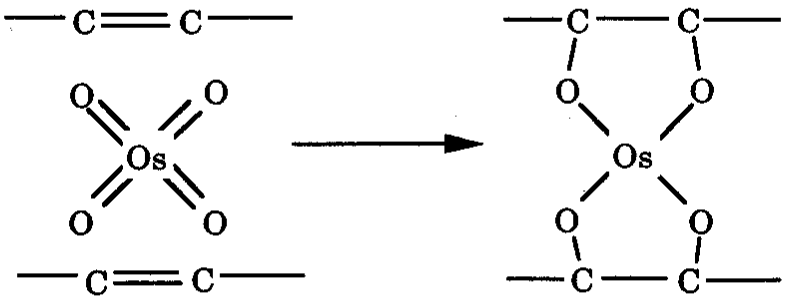


Figure 11.10 Simplified reaction scheme for how OsO_4 is added to unsaturated polymer chains.

Atoms of higher elements ~ achieve different electron density

→ Better contrast can be obtained.

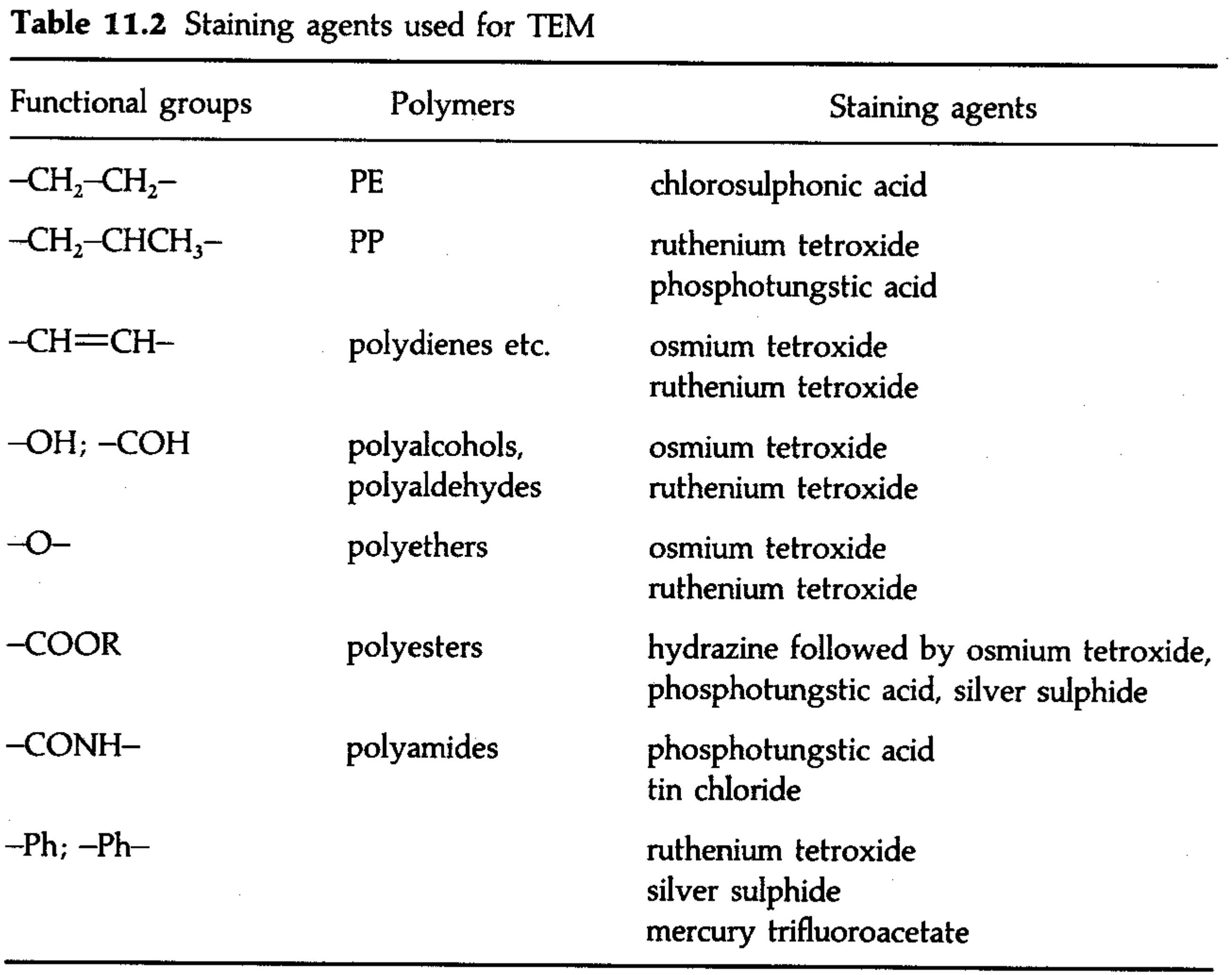


Table 11.2 Staining agents used for TEM

Functional groups	Polymers	Staining agents
$-CH_2-CH_2-$	PE	chlorosulphonic acid
$-CH_2-CHCH_3-$	PP	ruthenium tetroxide phosphotungstic acid
$-CH{=}CH-$	polydienes etc.	osmium tetroxide ruthenium tetroxide
$-OH$; $-COH$	polyalcohols, polyaldehydes	osmium tetroxide ruthenium tetroxide
$-O-$	polyethers	osmium tetroxide ruthenium tetroxide
$-COOR$	polyesters	hydrazine followed by osmium tetroxide, phosphotungstic acid, silver sulphide
$-CONH-$	polyamides	phosphotungstic acid tin chloride
$-Ph$; $-Ph-$		ruthenium tetroxide silver sulphide mercury trifluoroacetate

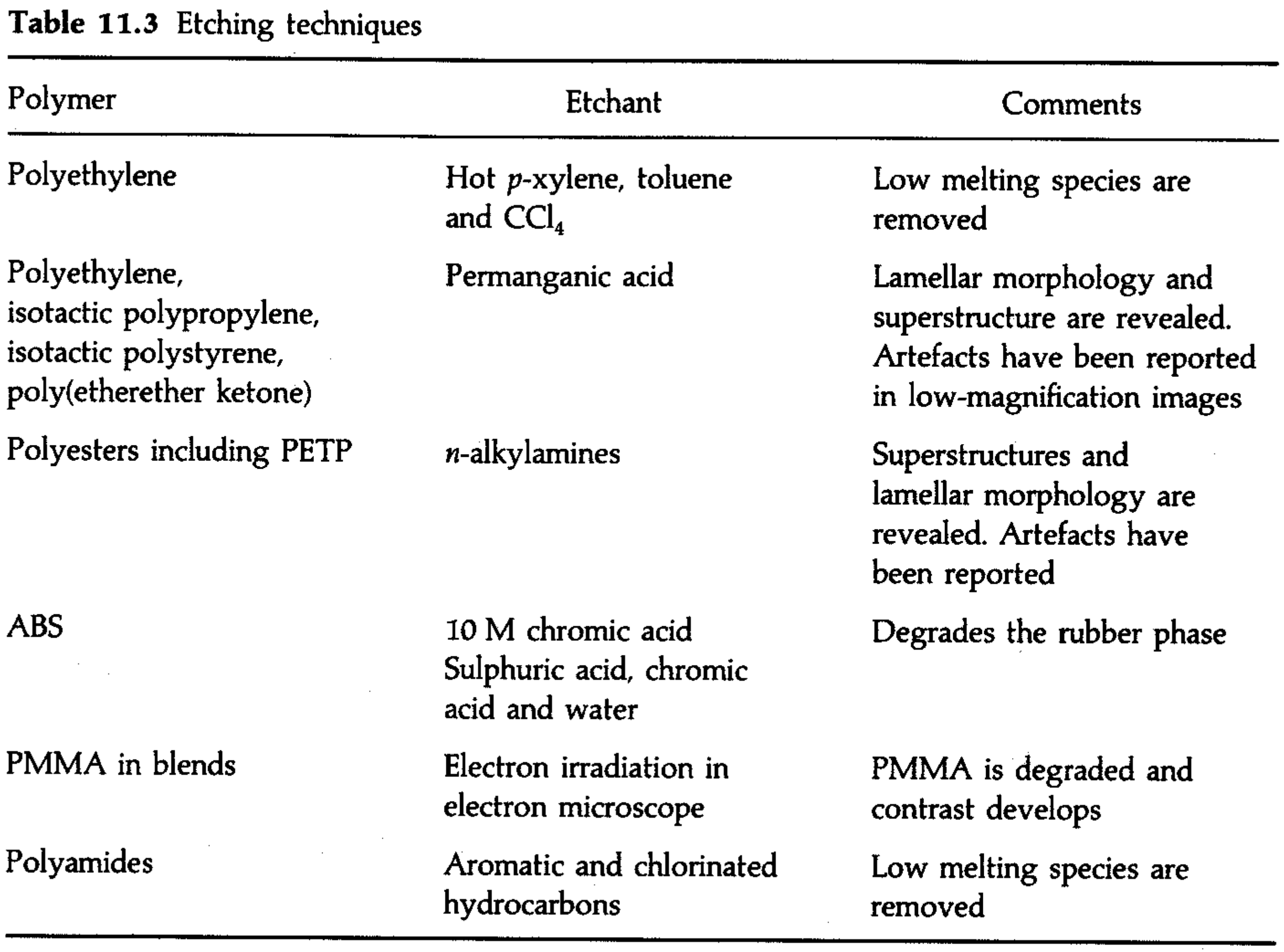


Table 11.3 Etching techniques

Polymer	Etchant	Comments
Polyethylene	Hot *p*-xylene, toluene and CCl_4	Low melting species are removed
Polyethylene, isotactic polypropylene, isotactic polystyrene, poly(etherether ketone)	Permanganic acid	Lamellar morphology and superstructure are revealed. Artefacts have been reported in low-magnification images
Polyesters including PETP	*n*-alkylamines	Superstructures and lamellar morphology are revealed. Artefacts have been reported
ABS	10 M chromic acid Sulphuric acid, chromic acid and water	Degrades the rubber phase
PMMA in blends	Electron irradiation in electron microscope	PMMA is degraded and contrast develops
Polyamides	Aromatic and chlorinated hydrocarbons	Low melting species are removed