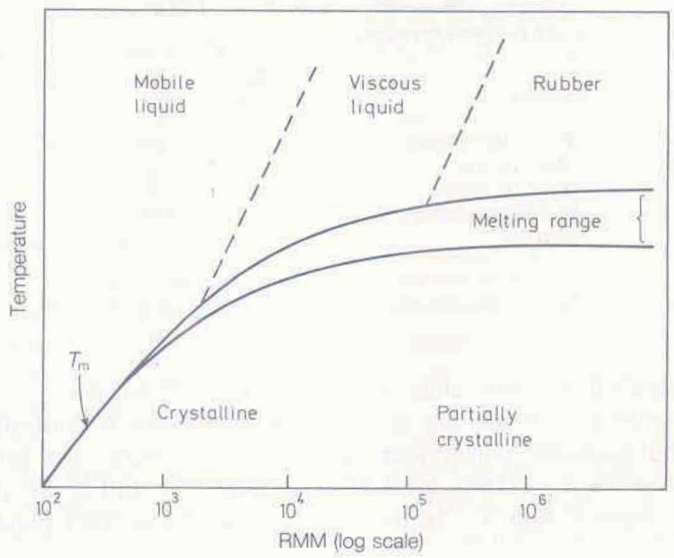
2.5 Crystallization and melting (Continued)

Mw vs Tm (Figure 2.9)



2.9 Dependence of melting temperatures T_m on relative molecular mass (RMM). At low RMM there is one T_m; at higher RMM there is a band of melting temperatures, which is due to the existence of a range of crystal thicknesses in the solid polymer.

For Mw < 10^3

►A sharp single melting peak.

►Tm increases with Mw.

For Mw>10^3

►Tm levels off (asymptotic) with melting range (Due to the MWD)

►Tm ∝ lamella thickness

►Large molecule, high structural regularity, crystallization at high temperature gives thick lamella.

►Tm is defined for the thickest, largest and most perfect crystal obtainable. (See a melting endotherm from DSC measurements)

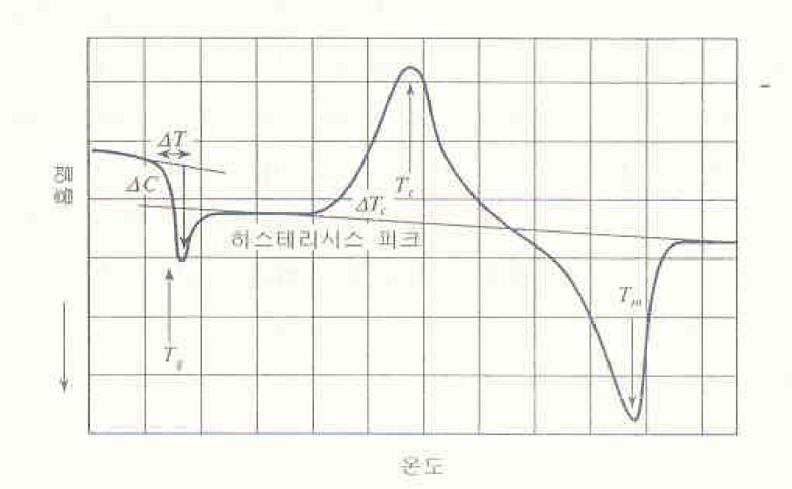


Figure Typical DSC measurements.

Table 2.1 for Tm and T1

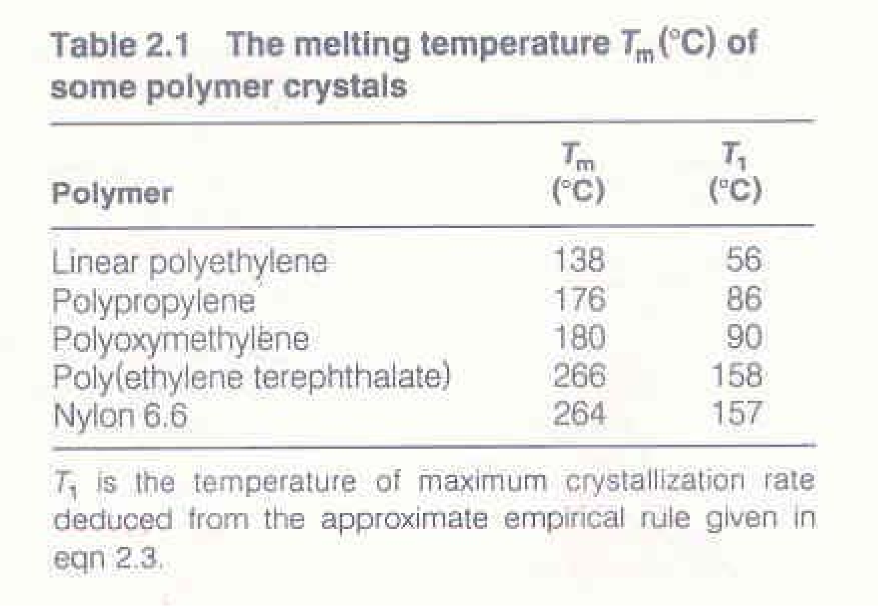
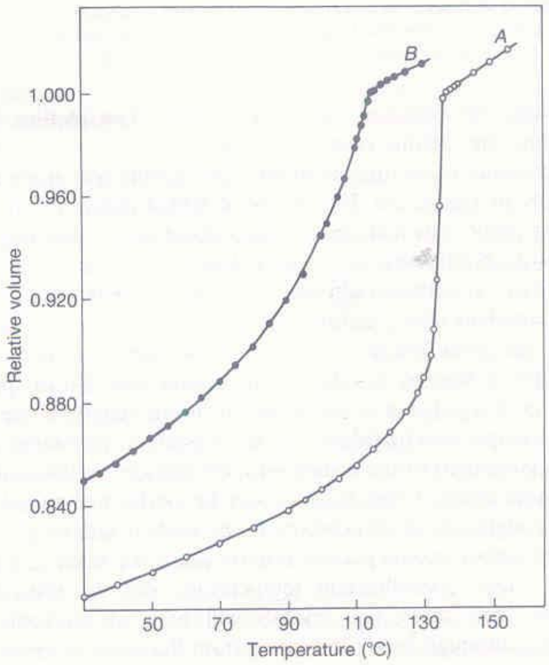


Table 2.1 The melting temperature T_m (°C) of some polymer crystals

Polymer	T_m (°C)	T_1 (°C)
Linear polyethylene	138	56
Polypropylene	176	86
Polyoxymethylene	180	90
Poly(ethylene terephthalate)	266	158
Nylon 6.6	264	157

T_1 is the temperature of maximum crystallization rate deduced from the approximate empirical rule given in eqn 2.3.

Figure 2.10 Relative volume (1/density) during heating for BPE (B) and LPE (A)



2.10 Plot of relative volume during heating against temperature *T*. The relative volume is the ratio of the specific volumes at *T* and T_m. Curve A is for linear polyethylene; curve B is for branched polyethylene (after Mandelkern).

LPE= sharp melting

BPE= broad melting

In molten state, there is no difference between LPE and BPE.

►Two steps in melt crystallization = Nucleation + Growth

▻At high temperature: slow nucleation + rapid growth (low viscosity) → thick crystal → high Tm

▻At low temperature: fast nucleation + slow growth (high viscosity) →thin crystal → low Tm

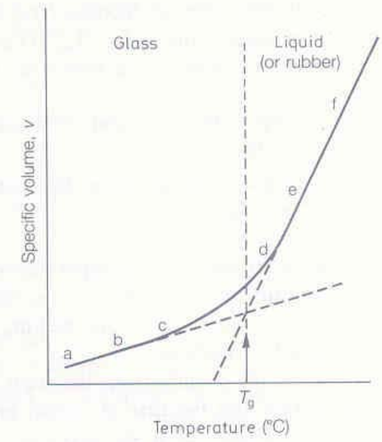
►Maximum rate of crystallization occurs at a degree of supercooling of approximately

$$\triangle T = T_m - T_c = 0.2\ T_m\ \text{(K) or}$$

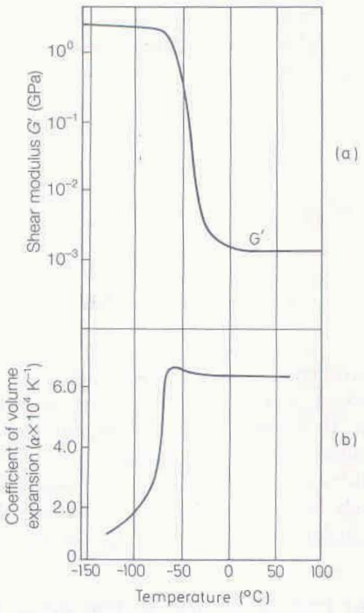
$$T_1 = 0.8\ T_m \qquad (2.8)$$

2.6 Glass Transition Temperature

See Figures 2.11 and 2.12 for Specific volume-Temperature and Modulus-Temperature.



2.11 The glass transition temperature T_g is obtained from an experiment in which the specific volume v is measured whilst the specimen is cooled at a fixed rate, usually 1°C per minute. The construction for obtaining T_g from the data is shown. For polymer of low RMM, T_g marks the transition from glass to liquid; for high RMM, T_g marks the transition from glass to rubber.



2.12 The glass–rubber transition in polyisobutylene:

►In glassy state:

▻As T↑ → Secondary force (intermolecular) ↓ → Separation of polymer chains ↑ (Thermal expansion) → Density ↓ (Specific volume ↑) (See secondary force vs thermal energy in Lecture # 187))

--------Note from 187

Chemical Bond

$$\left\{\begin{array}{l}\textit{Primary bond (covalent bond)}\\ \textit{Secondary bond}\end{array}\right.$$

Van der Waals < dipole < H-bond < ionic bond

Table 1.1 Dissociation energy and length of different bonds

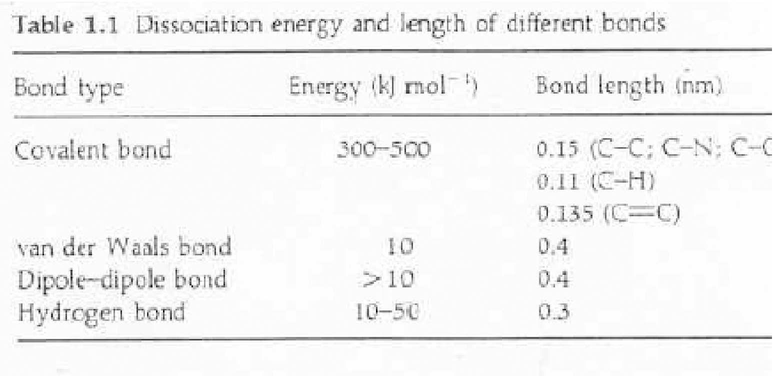


Table 1.1 Dissociation energy and length of different bonds

Bond type	Energy (kJ mol^{-1})	Bond length (nm)
Covalent bond	300–500	0.15 (C–C; C–N; C– 0.11 (C–H) 0.135 (C=C)
van der Waals bond	10	0.4
Dipole–dipole bond	>10	0.4
Hydrogen bond	10–50	0.3

Compare the above bond energy with thermal energy(RT)

RT = 2.5kJ/mole @ 300K

= 4 kJ/mole @ 500K

(R=1.987cal/mole K)

If thermal energy > bond energy ⇒ Bonds tend to dissociate.

At melting

Covalent bondings are preserved.

Rupture & reestablishment of secondarty bonds occur.

------------------------------ End of 187

▻no segmental motion, no conformation change → Thermal expansion coefficient (α, β) is constant and small. (See Figure 2.12)

$\alpha = (1/L)(dL/dT)$, $\beta = (1/V)(dV/dT)$ @ P=constant

▻Only rotation and vibration of elements and groups exist.

►Around Tg, segmental motion (jump) starts → Expansion coefficient increases with T(See increasing slope in Figure 2.11, and a large drop in modulus in Figure 2.12).

►In melt, $>10^6$/s segmental motions!!! (See constant and large slope in Figure 2.11)

(One segment typically consists of 20-30 repeat units.)

Measurement of Tg

i) Specific volume measurement (See Figure 2.11)

ii) DSC (Differential Scanning Calorimeter)

Tg = point of inflection (Second order transition) (Endothermic)
Tm = endothermic peak,
Tc (Exothermic peak) (See a typical DSC curve)

►Tg depends on the rate of cooling.

Slower cooling →lower Tg

(Prolonged process time vs constant relaxation time of polymer chain→Viscous (flow) rather than elastic (recovery) nature is imposed on the polymer. $\gamma = \gamma_o \sin\omega t$

iii) Dynamic mechanical method (DMTA)

►Heat up the sample at a constant frequency strain ($\gamma=\gamma_o \sin\omega t$).

►The temperature at which the external frequency is matched with that of segmental motion, a function of temperature, is Tg.

►At Tg, elastic energy is tremendously damped, dissipated (See the modulus drop and tanδ peak at Tg).