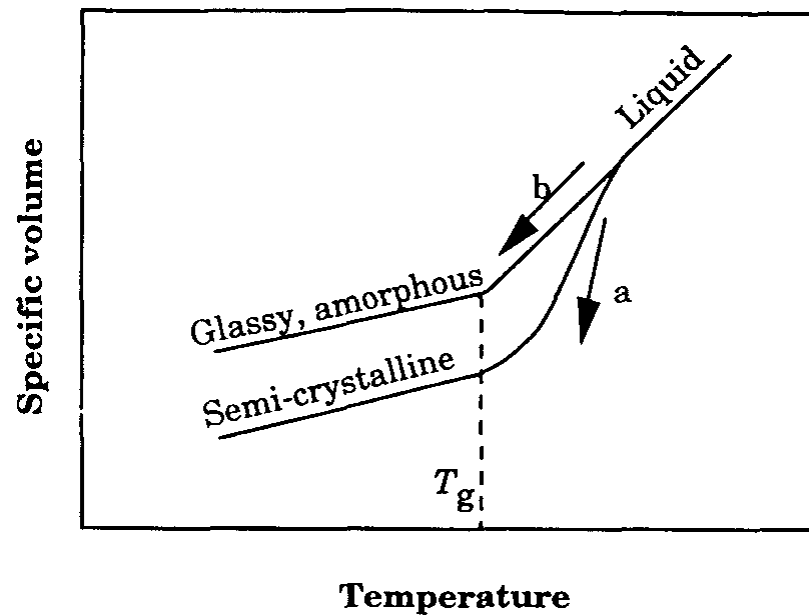


Chapter 5. Glassy Amorphous State

5.1 Introduction

Molten polymer --> (cooling) --> glassy, amorphous
semi-crystalline



a: slow cooling
b: fast cooling

- *Key factor* of crystallizing a polymer : regularity of the polymer

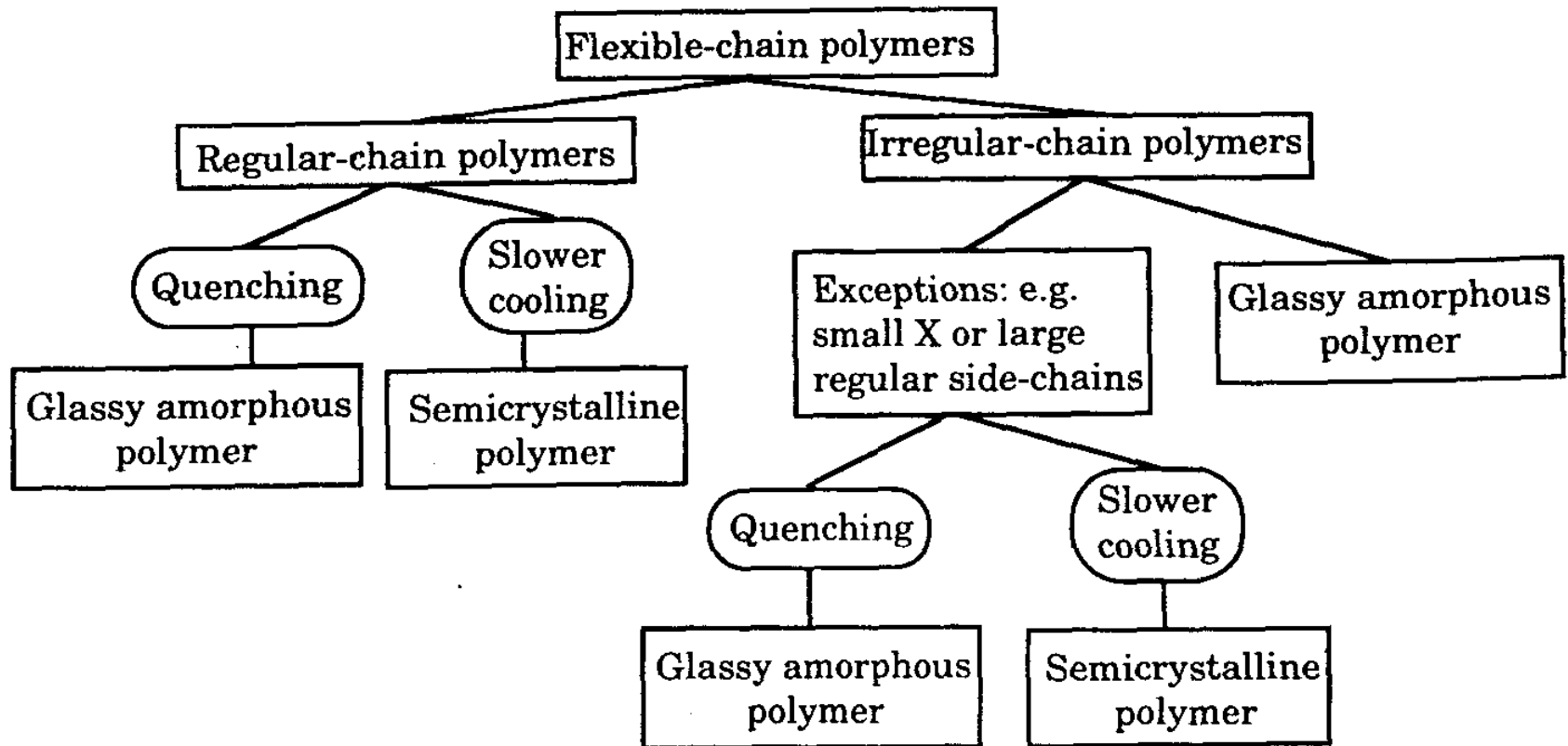
Atactic polymers : do not crystallize

ex) IPP : crystallize

atactic PP : not

Exceptions) 1. X group in $\text{---}\left(\text{CH}_2\text{CHX}\right)_n\text{---}$ is very small. ex.) PVAL

2. X group of a long regular side chain (side chain crystallization)

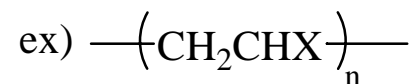


Effect of molecular and thermal factors of the structure of solidified polymer

$\therefore T_g$ values depend on experimental conditions.

5.2 Glass transition temperature

* Effect of repeating unit structure



- relatively inflexible X group: $T_g \uparrow$ with size of the group \uparrow

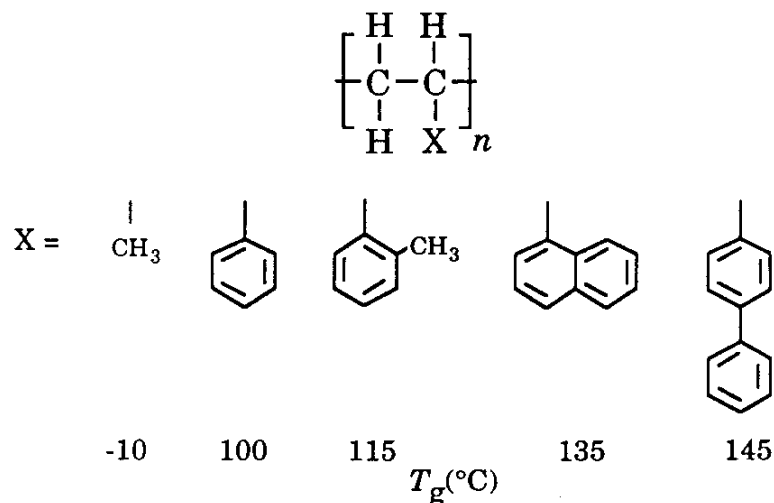
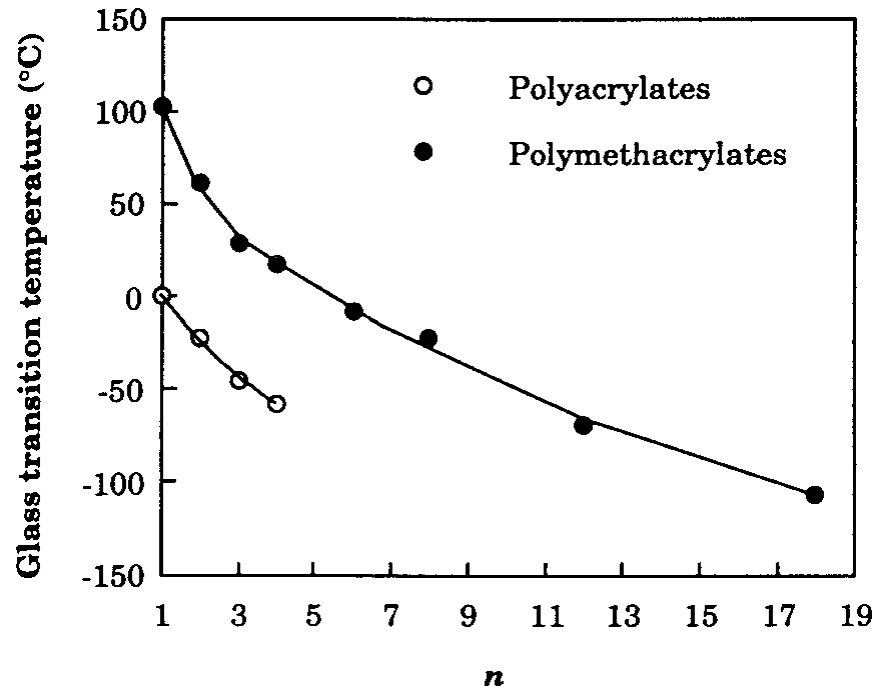


Figure 5.3 Glass transition temperatures of different vinyl polymers showing the influence of the size of the pendant group. Data from Eisenberger (1984).

- relatively flexible side chain : $T_g \downarrow$ with length of the side chain \uparrow



n : the number of carbons in the oligo-methylene (R) group

- longer pendant groups $\rightarrow T_g \uparrow$

· $T_g \uparrow$ with increasing *polarity* ($T_g \uparrow$ with Cl content \uparrow), C-Cl : polar

→ generally,
$$T_g = \frac{2\delta^2}{mR} + C_1$$

δ^2 : CED (cohesive energy density)

m : internal mobility of the groups in a single chain

T_g & $T_m \uparrow$ with chain flexibility \downarrow

T_g & $T_m \uparrow$ with CED \uparrow

$$\frac{T_g}{T_m} = \frac{1}{2} \quad (\text{symmetrical molecules})$$

$$\frac{T_g}{T_m} = \frac{2}{3} \quad (\text{asymmetrical molecules})$$

$$\frac{T_g}{T_m} = 0.5 \sim 0.8$$

*** Free volume**

volume { free volume
occupied volume

$$f(\text{fractional free volume}) = \frac{\text{free volume}}{\text{total volume}}$$

Ideal crystal : $f \approx 0$

Glassy, amorphous polymer : relatively small f

Amorphous, rubber polymer : relatively large f

Estimation of the size of empty volume \Rightarrow X-ray scattering

* **Effect of molecular architecture** on T_g

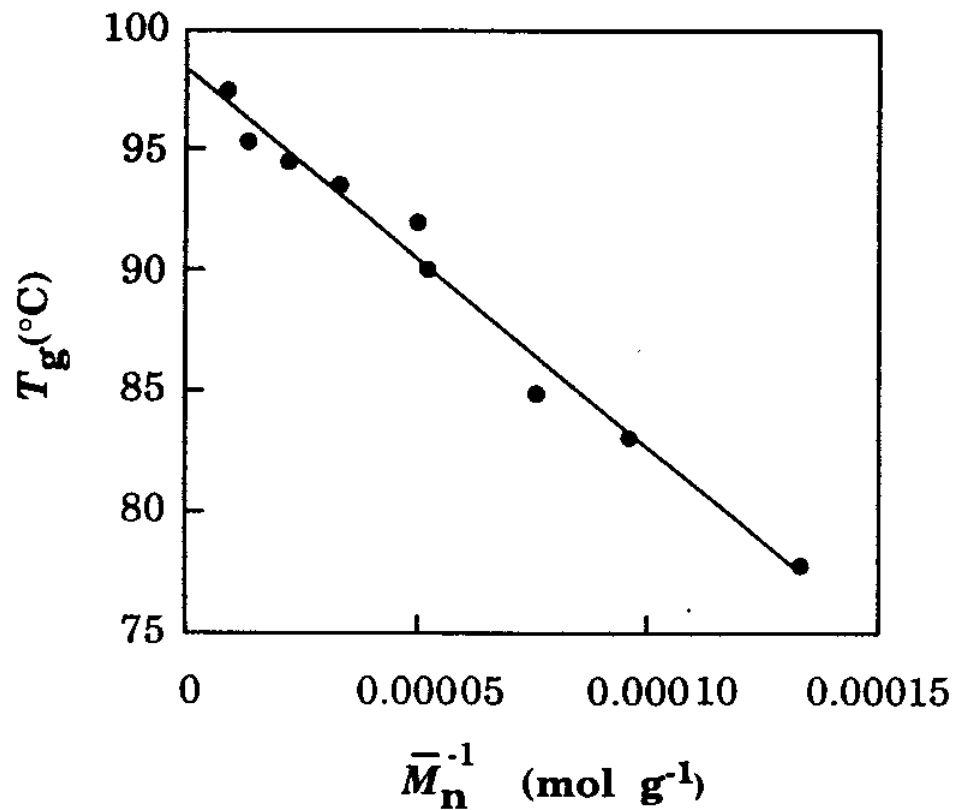
: Molar mass, degree of crosslinking, chain branching

$$\cdot f = f^0 + \frac{C_2}{M} \quad f^0 \rightarrow f \text{ of the polymer of infinite molar mass}$$

$$\approx (C_3 + C_4 T) + \frac{C_2}{M} \quad (\text{temperature dependence})$$

$$\Rightarrow T_g \approx \frac{f_g - C_3}{C_4} - \frac{C_2}{C_4 M} = C_5 - \frac{C_6}{M}$$

f_g : (universal fractional free volume) \rightarrow fractional free volume at T_g



Dependence of T_g on molar mass for narrow fractions of atactic polystyrene

- Crosslinks reduce f

$$f \approx f^0 - n_c C_7 = f^0 - \frac{C_8}{M_c}$$

n_c : # of crosslinks

$\overline{M_c}$: number average MW of the chains between crosslinks

$$T_g \approx C_9 + \frac{C_{10}}{M_c} \text{ by analogy with } M \text{ dependence}$$

In a polymer of M & $\overline{M_c}$,

$$T_g \approx C - \frac{C'}{M} + \frac{C''}{M_c}$$

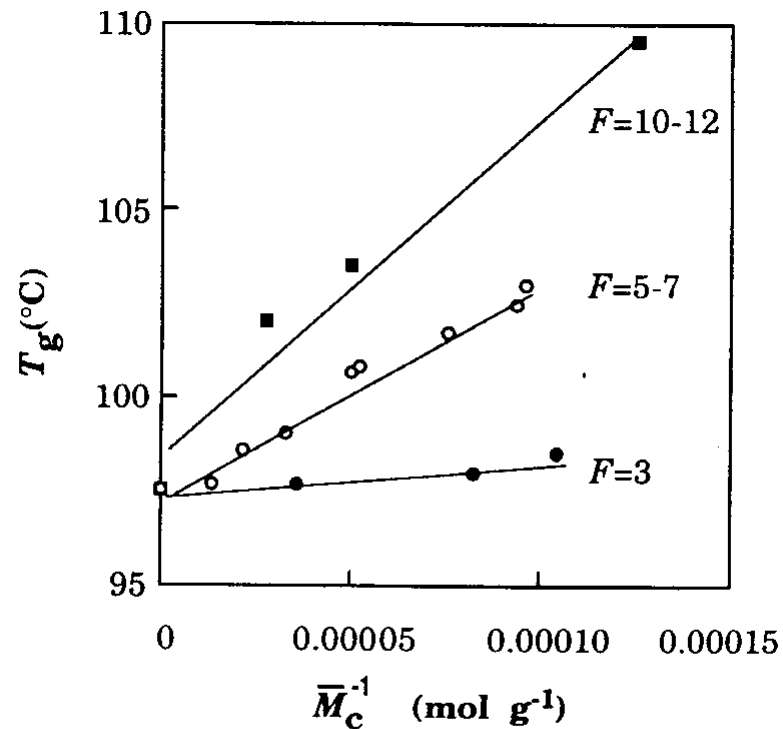


Figure 5.9 Effect of crosslinking on T_g of branched poly(styrene-co-divinyl benzene). The crosslink functionality (F) is shown adjacent to each regression line. Drawn after data from Rietsch, Daveloose and Froelich (1976).

* T_g of **blends & copolymers**

: highly dependent on the morphology

Immiscible polymer blend \rightarrow two T_g 's

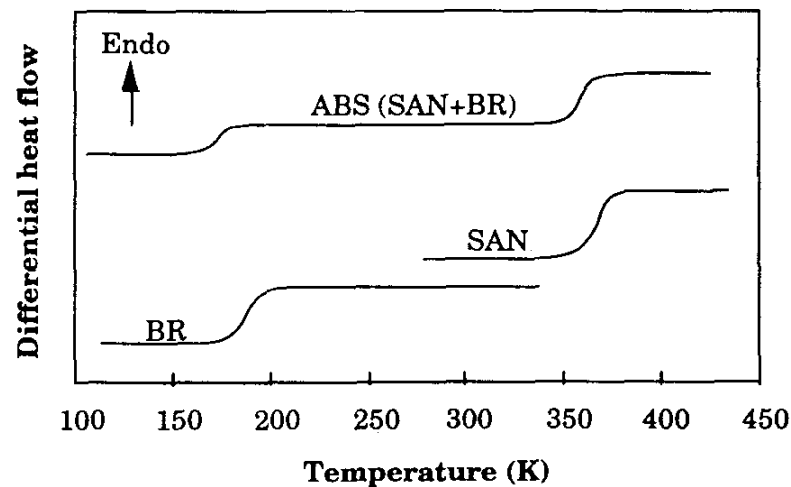


Figure 5.10 DSC traces of ABS and of its constituents poly(butadiene) (BR) and poly(styrene-*co*-acrylonitrile) (SAN). Schematic after data from Bair (1970).

Miscible polymer blend \rightarrow one T_g

: Fox equation,

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$
$$\Downarrow$$
$$\frac{1}{T_g} = \sum \frac{w_i}{T_{gi}}$$

w_i : wt. fraction of polymer i

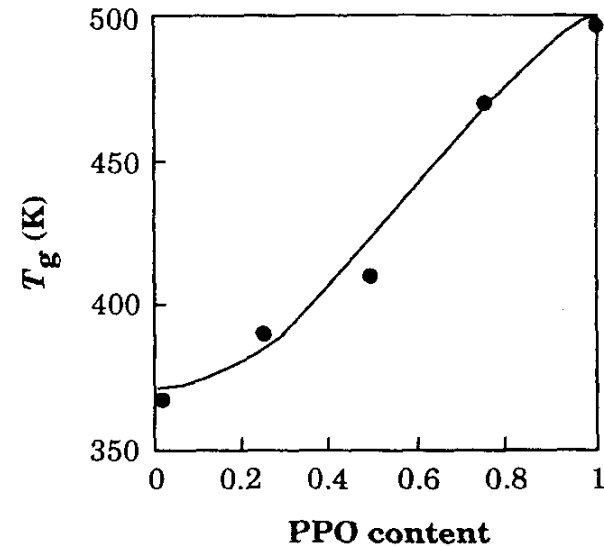


Figure 5.11 Glass transition temperature of compatible blends of polystyrene and polyphenylene oxide (PPO) as a function of PPO content. Drawn after data from Bair (1970).

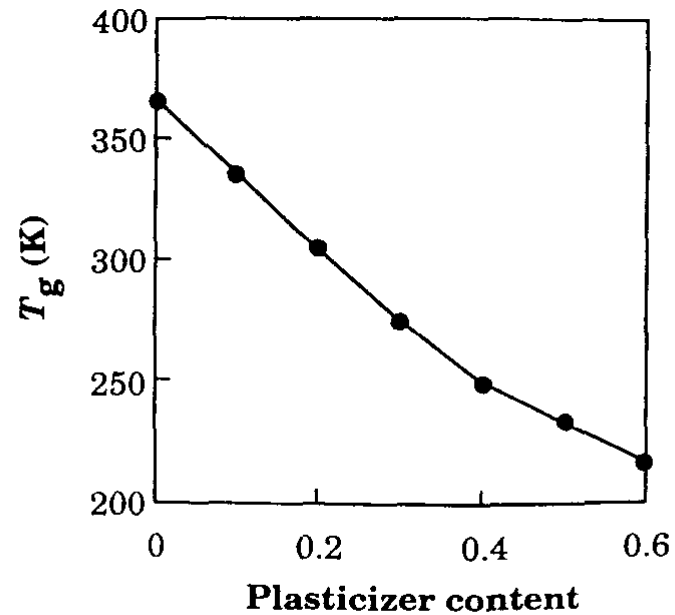


Figure 5.12 Plasticization of PVC: T_g as a function of di(ethylhexyl)-phthalate content. Drawn after data from Wolf (1951).

Plasticizer : low MW liquid having a strong T_g -depressive effect

* **P effect** on T_g

$$\left(\frac{dT_g}{dp} \right) = \frac{\Delta\beta}{\Delta\alpha}$$

α : volume expansion coefficient

$$\equiv \frac{1}{V} \left(\frac{dV}{dT} \right)_p$$

β : compressibility coefficient

$$\equiv -\frac{1}{V} \left(\frac{dV}{dp} \right)_T$$

Typical polymers : 0.2 ~ 0.4K/MPa

5.3 Non-equilibrium feature

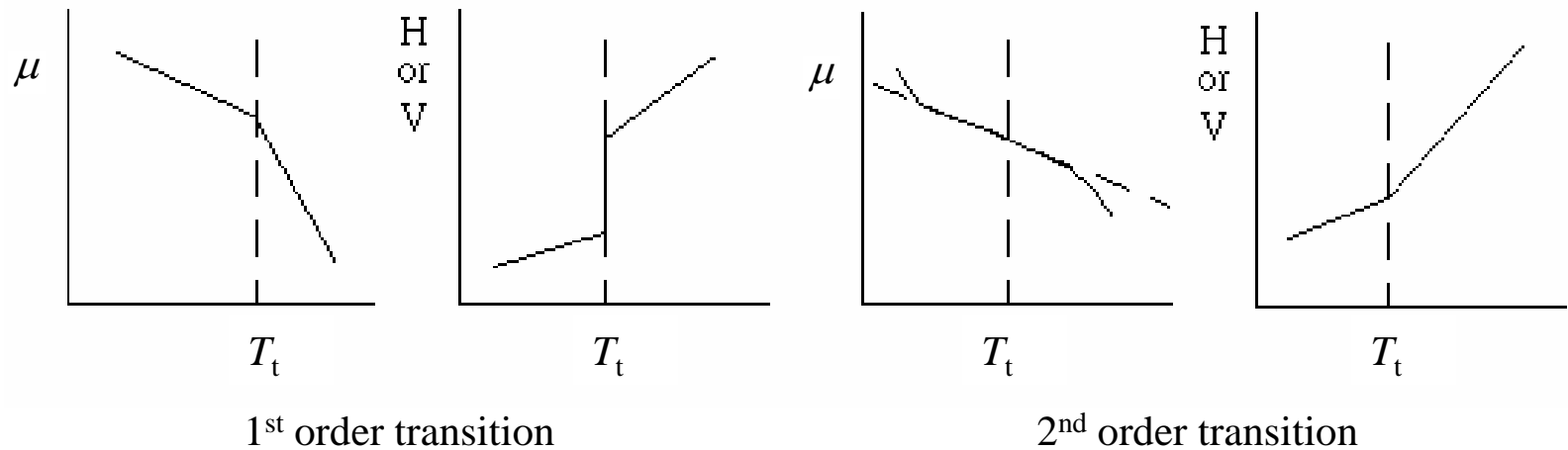
* General aspects

glass transition : second-order transition

정의 : μ 의 T 에 대한 2계 미분이 discontinuous.

The 1st derivatives of V & H w.r.t. T are discontinuous.

cf.) μ 의 1계 미분이 불연속 \rightarrow 1st-order transition (V, H 자체가 불연속)



* **Non-equilibrium nature** of a glassy polymer

At constant cooling rate, q

Point B : kinetic glass transition.

V decreases under isothermal condition (C \rightarrow D)

“physical ageing”

or

“isothermal volume recovery”

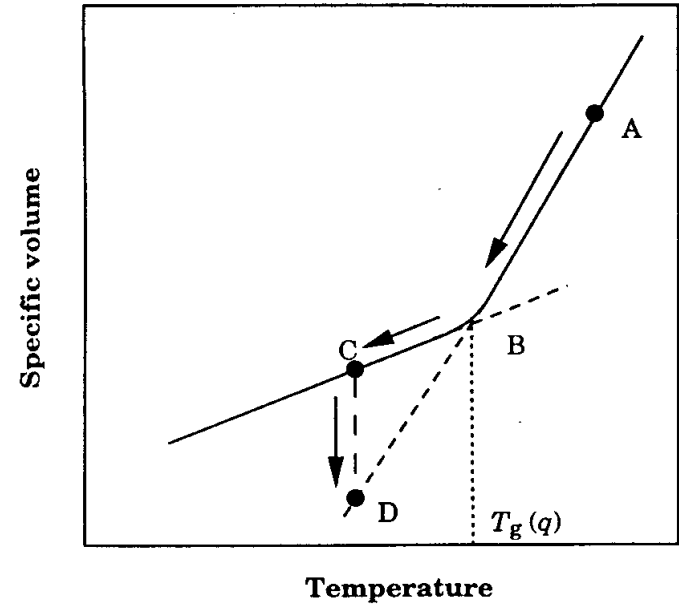


Figure 5.13 Illustration of the non-equilibrium nature of a glassy polymer.

* **Volumetric response** to different cooling rates (See Fig. 5.14)

T_g changes : 3K for a change by a factor of 10 in cooling rate.

- Volume recovery

→ Contraction is more rapid than expansion.

An amorphous polymer which is cooled rapidly through T_g and then held at const. T

⇒ V & H ↓, G (tensile modulus) ↑,
 σ_0 (yield stress) ↑, toughness ↓,
 impact strength ↓, permeability ↓

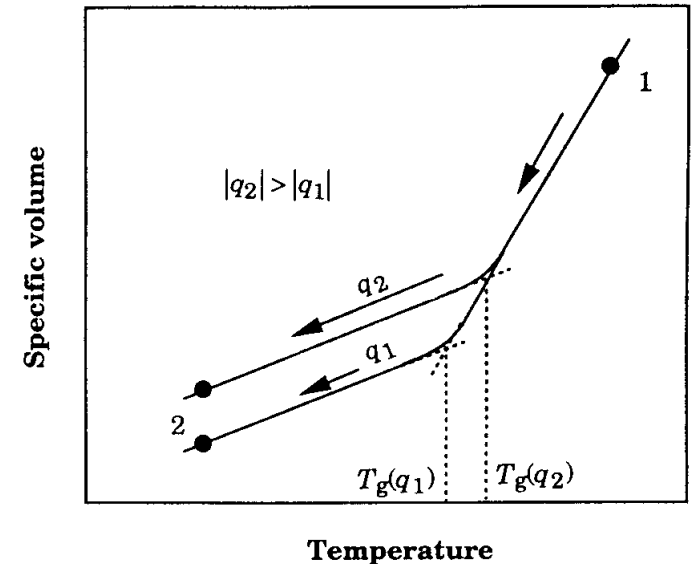


Figure 5.14 Schematic curves showing the cooling rate dependence of the specific volume of a glass-forming wholly amorphous polymer.