Chapter 9. Glass-Rubber Transition Behavior

9.1. Five Regions of Viscoelastic Behavior

- 9.1.1. The glassy region
- 9.1.2. The glass transition region
- 9.1.3. The rubbery plateau region
- 9.1.4. The rubbery flow region
- 9.1.5. The liquid flow region

9.2. Methods of Measuring Transitions in Polymers

9.3. Theories of the Glass Transition

- 9.3.1. The free-volume theory
- 9.3.2. The kinetic theory
- 9.3.3. Thermodynamic theory

9.4. Factors Influencing on T_g

- 9.4.1. Effect of molecular weight
- 9.4.2. Effect of crystallinity
- 9.4.3. Dependence of T_g on chemical structure

Chapter 9. Glass-Rubber Transition Behavior

- The state of a polymer depends on
  i) the temperature
  ii) the time allotted to the experiment.

- At low T, all amorphous polymers : stiff and glassy
  ⇒ the glassy state (=vitreous state)

- On warming,
  the polymers softer in a characteristic temperature range known as the glass-rubber transition region.

- The importance of Tg in polymer science stated by Eisenberg.
  "The glasstransition is perhaps the most important single parameter which one needs to know before, one can on the application of … non-crystalline polymers … "

CNDL

9.1. Five Regions of Viscoelastic Behavior

- Viscoelastic materials simultaneously exhibit a combination of elastic and viscous behavior.
  → generally, refers to both the time and temperature dependence of mechanical behavior.
- In fact many important polymers do not crystallize at all but form glasses at low temperatures.→ At higher temperatures they form viscous liquids.
- The transition the separates the glassy state from the viscous state: glass-rubber transition.

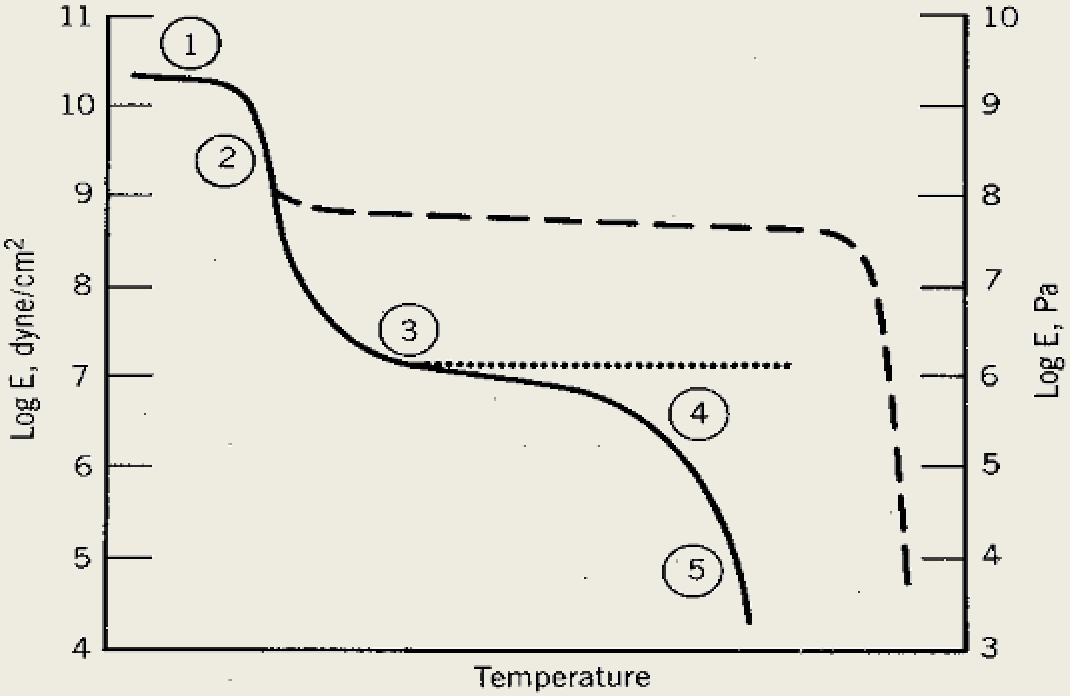


Fig. 9.1 Five regions of viscoelastic behavior for a linear, amorphous polymer, Also illustrated are effects of crystallinity (dashed line) and cross-linking (dotted line)

CNDL

9.1. Five Regions of Viscoelastic Behavior

9.1.1. The glassy region

e.g. PS drinking cups
PMMA (Plexiglas® sheets)

- just below Tg
  - Young's modulus(E) for glassy polymers
    $\simeq 3\times10^{10}$ dynes/cm^2
    $\simeq 3\times10^{9}$ Pa
    (constant over a wide range of polymers)
  - Molecular motions are largely restricted to vibrations and short-range rotational motions
    └→ (1～4 chain atoms are involved)

9.1. Five Regions of Viscoelastic Behavior

9.1.2. The glass transition region

Typically E drops a factor of about 1000 in a 20～30 ℃ range : leathery behavior $E \simeq 10^{10}$dyne/cm^2

T_g → the temp. where the thermal expansion coefficient undergoes a discontinuity.

→ often taken at the max. rate of turndown of the modulus at the elbow.

→ the onset of long-range, coordinated molecular motion.

(10～50chain atoms involved)

→ varies widely with structure and other parameters

9.1. Five Regions of Viscoelastic Behavior

9.1.3. The rubbery plateau region

$E \simeq 2 \times 10^7$ dynes/cm^2 (2×10^6 Pa)

: Polymers exhibit long-range rubber elasticity,

: coordinated molecular motion is governed by reptation and diffusion.

Two cases in this region

1. The polymer is linear : modulus drops off slowly.

   plateau width $\propto$ MW

   (The higher, The longer)

2. The polymer is crosslinked : $E = 3nRT$

   where n is the no. of active chain segments in the network

   : improved rubber elasticity is observed.→ Chapter 10

9.1. Five Regions of Viscoelastic Behavior

The height of the plateau is governed by the degree of crystallinity.

⇒ crystalline regions tend to behave as a filler phase
crystalline regions tend to behave as a type of physical cross-linked, tying the chains together.

: crystalline plateau extends until Tm of the polymer

$$T_g = (\frac{1}{2} \sim \frac{2}{3})T_m$$

9.1. Five Regions of Viscoelastic Behavior

9.1.4. The rubbery flow region

- Rubber elasticity and flow depending on the time scale of the experiment

  For short t, the physical entanglements are not able to relax-the material still behaves rubbery.

  For longer t, the increased molecular motion imparted by the increased T permits assemblies of chains to move in a coordinated manner (depending on MW), and hence to flow.

9.1.5. The liquid flow region

: Polymer flows readily and obeys the Newtonian Law $f = \eta(\frac{ds}{dt})$

: The increased ε allotted to the chains permits them to reptate out through entanglements rapidly and flow as individual molecules.

: For semicrystalline polymers,

$E \propto$ degree of crystallinity $\therefore$ as T↑, E↓

E and viscosity are related through the molecule relaxation time.

9.1. Five Regions of Viscoelastic Behavior

9.1.6. Effect of Plasticizer

: small, non-volatile molecules which dissolve in the polymer.

: separate the chains from each other and hence making reptation easier.

T_g ↓ → rubbery plateau is lowered.

: if the polymer is semicrystalline, the melting point T_m ↓, the extent of crystallinity X_c ↓

: e.g. dioctyl phthalate for PVC

9.1. Five Regions of Viscoelastic Behavior

9.1.7. Melt Viscosity Relationship near T_g

: A criterion sometimes used for T_g for both inorganic and organic polymers is the temperature at which the melt viscosity reaches a value of 1×10^{13} poises on cooling.

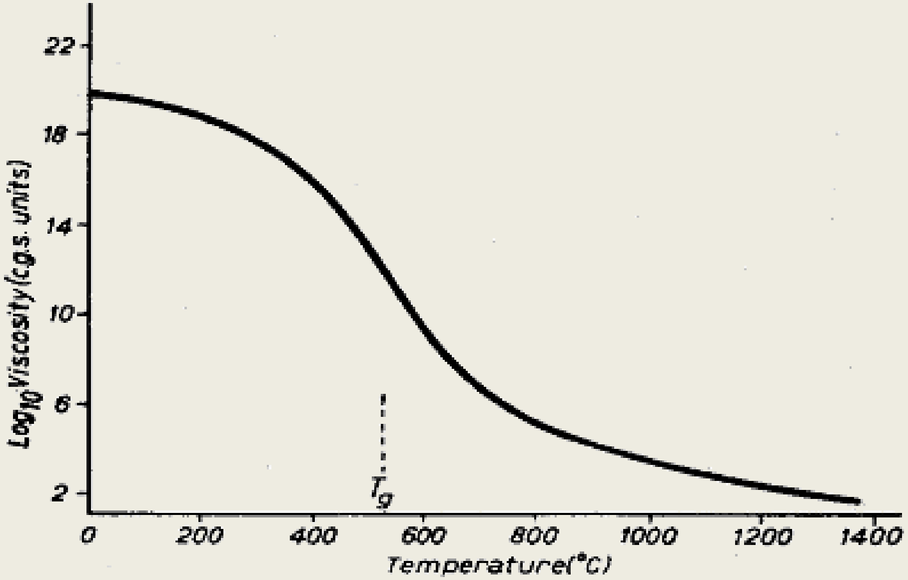


Fig.8.4 Viscosity-temperature relation of a soda-lime-silica glass. Soda-lime-silica glass is one of the commonly used glasses for windows and other items.

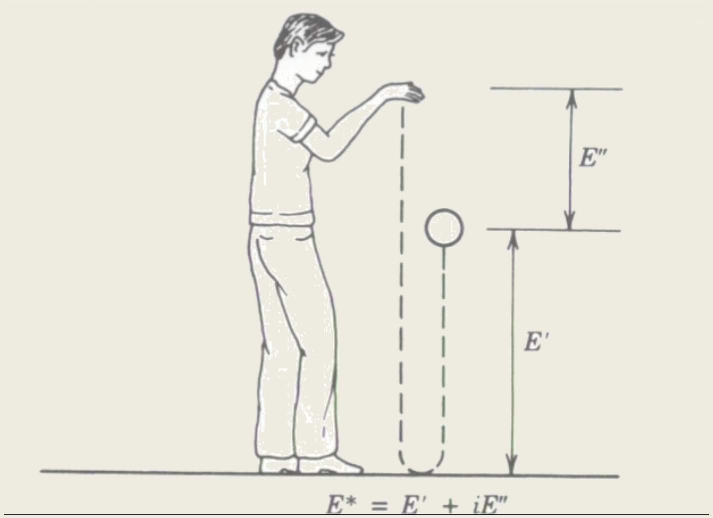
9.1. Five Regions of Viscoelastic Behavior

9.1.8. Dynamic Mechanical Behavior Through Five Regions

E' (Young's storage modulus) : a measure of the energy stored elastically,

E'' (Young's loss modulus) : a measure of the energy lost as heat

→ show similar dependence on temp.



$$\frac{E''}{E'} = \tan\delta$$

= loss tangent

E'' and tanδ are sometimes used as the definition of maxima of T_g

⇒ the portion of the molecule excited may be from 10 to 50 atoms or more (See Table 8.4 in p.358)

9.2. Methods of Measuring Transitions in Polymers

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

: volumetric coefficient of expansion (units : K^{-1})

$\alpha\uparrow$ as $T\uparrow$ (〉 T_g)

1st order transition (melting and boiling): discontinuity in V-T plot.

2nd order transition (glass transition): a change in slope

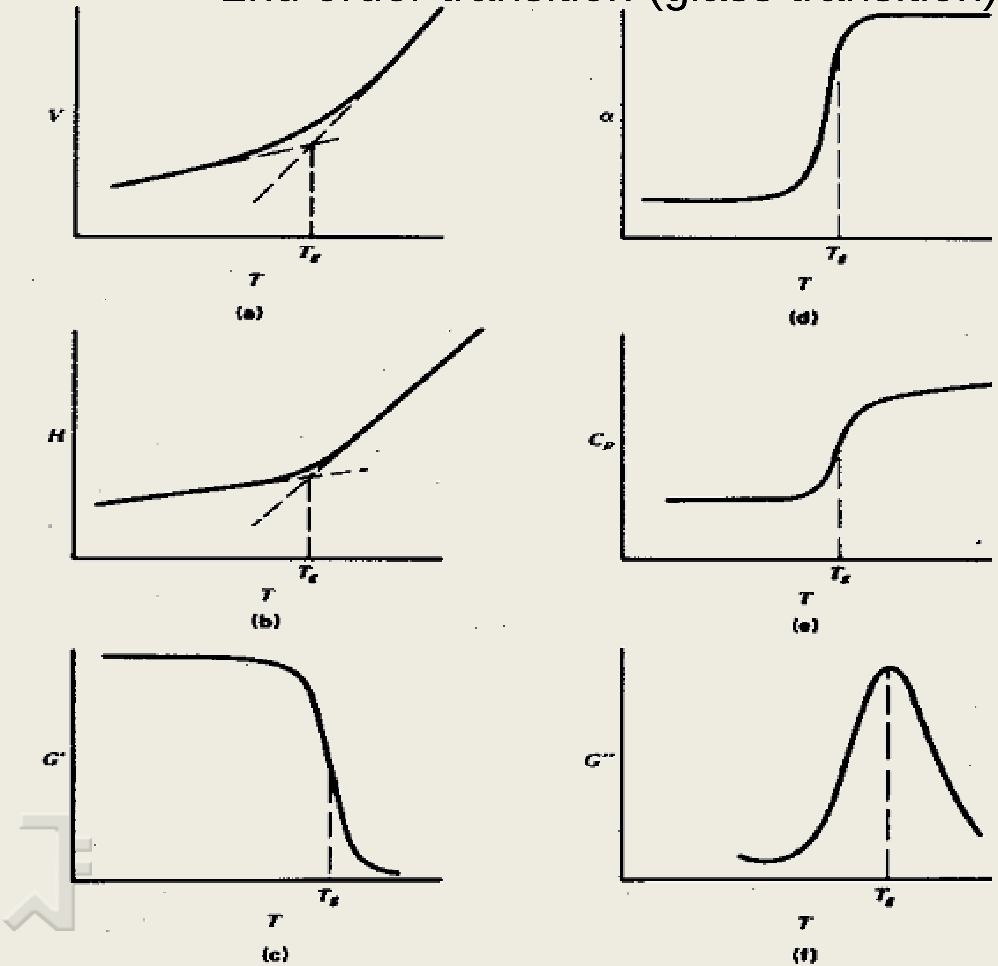


Fig.9.2 Idealized variations in volume, V, enthalpy, H and storage shear modulus, G' as a function of temperature.
Also shown are α, the volume coefficient of expansion, and Cp, the heat capacity, which are, respectively, the first derivatives of V and H with respect to temperature, and the loss shear modulus, G''.

9.2. Methods of Measuring Transitions in Polymers

9.2.1. Dilatometry Studies

: two ways of characterizing polymers via dilatometry.

1) V-T measurement

(E-T measurement) 1℃/min ≃10sec. mechanical measurement.

2) Linear expansivity measurement

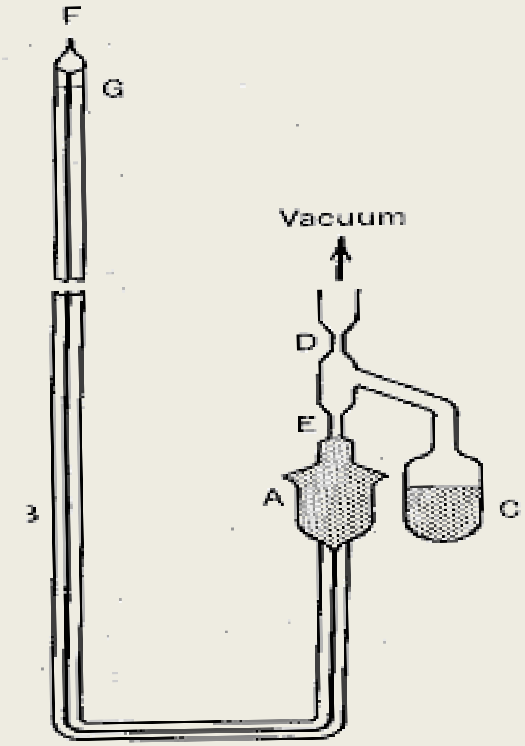


Fig.9.3 A mercury-based dilatometer. Bulb A contains the polymer (about 1g), capillary B is for recording volume changes (Hg+polymer), G is a capillary for calibration, sealed at point F. After packing bulb A, the inlet is constricted at E, C contains weighed mercury to fill all dead space, and D is a second constriction.

9.2. Methods of Measuring Transitions in Polymers

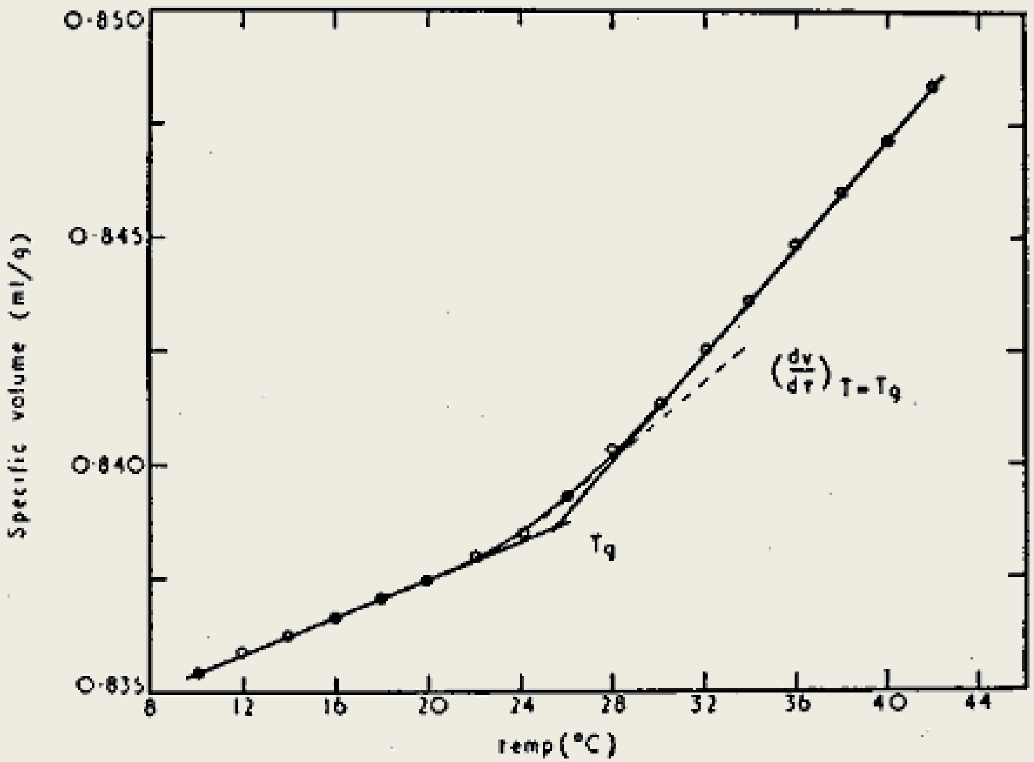


Fig. 9.4 Dilatometric studies on branched poly(vinyl acetate)

9.2. Methods of Measuring Transitions in Polymers

9.2.2. Thermal Methods

⇒ DTA (Differential Thermal Analysis) (older method)

; show changes in heat

DSC (Differential Scanning Calorimetry) (newer method)

; capacity enthalpic changes in the polymer

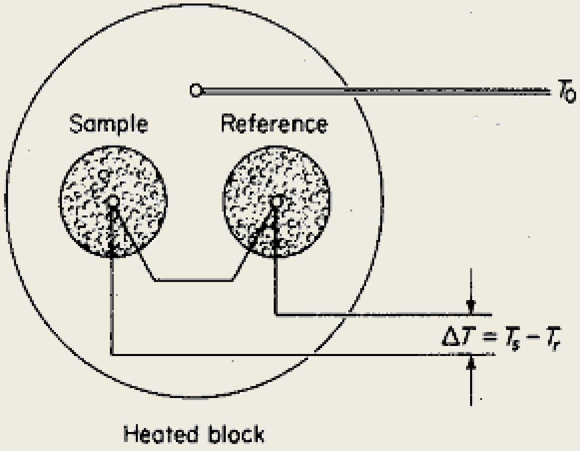


Fig.9.5 Schematic of differential thermal analysis(DTA) apparatus. Heated block is programmed so that T0 increases linearly with time. The difference between the sample temperature(T_s) and the reference temperature(T_r), ΔT, is recorded as a function of T0.

9.2. Methods of Measuring Transitions in Polymers

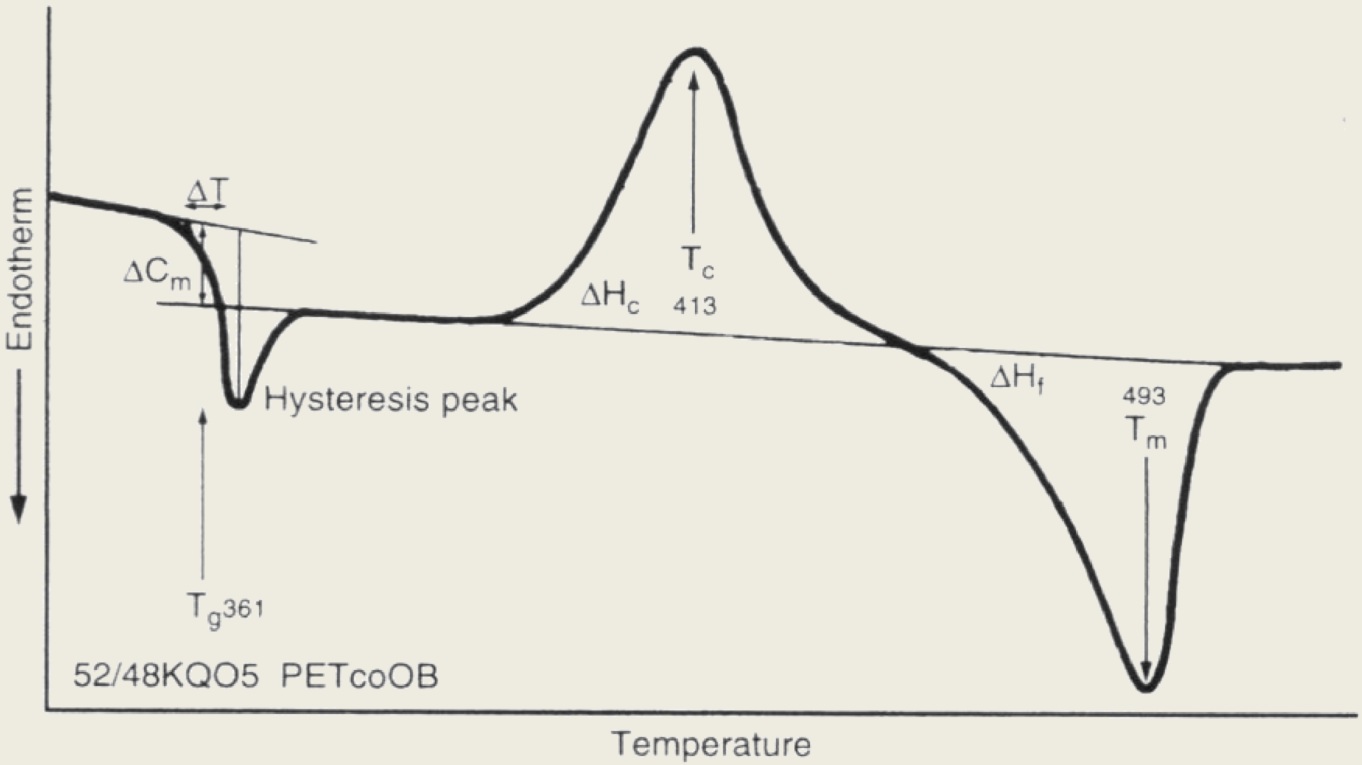


Fig.9.6 Example of a differential scanning calorimetry trace of poly(ethylene terephthalate), quenched, reheated, cooled at 0.5K/min through the glass transition, and reheated for measurement at 10K/min. Tg is taken at the temperature at which half the increase in heat capacity has occurred. The width of the transition is indicated by ΔT.

CNDL

9.2. Methods of Measuring Transitions in Polymers

9.2.3. Mechanical Methods

├ static or quasi - static methods
└ dynamic methods - DMA, Rheovibron

Rheovibron ┬ requires a sample that is self-supporting
(size of a paper match stick)
├ yield absolute values of the storage modulus and tanδ.
└ 110Hz is most of ten used.

Torsional Braid Analysis(TBA)- For not self-supporting sample
└→ monomer, prepolymer, polymer solution, or melt is dipped onto a glass braid which in then set into a torsional motion.
→ sinusoidal decay of the twisting action is recorded as a function of t as T is changed. (see Fig8.13 p325)

9.2. Methods of Measuring Transitions in Polymers

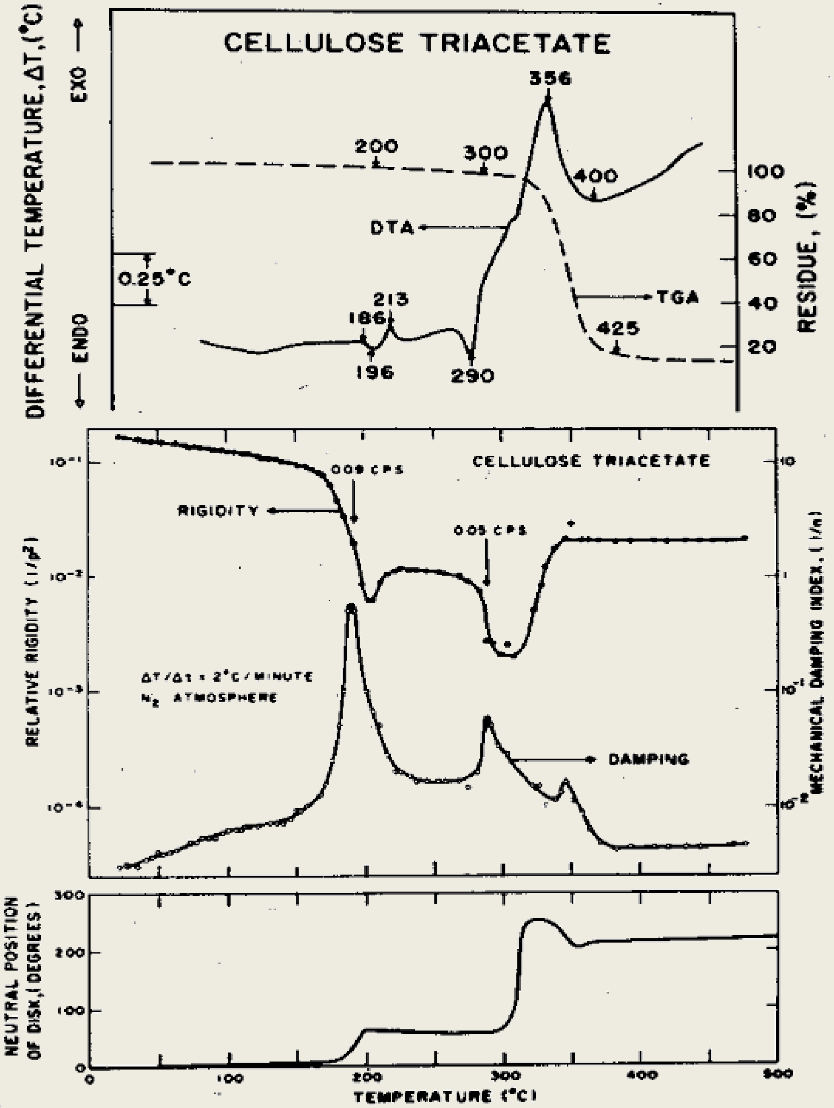


Fig.9.7 Comparison of torsional braid analysis, differential thermal analysis, and thermogravimetric analysis data for cellulose triacetate. The bottom figure shows the twisting of the sample in the absence of oscillations as a result of expansion or contraction of the sample at Tg and Tf.

9.2. Methods of Measuring Transitions in Polymers

9.2.4. Dielectric and Magnetic Methods

⇒ dielectric loss and broad-line NMR

· dielectric loss constant ε", or its associated tanδ

→ measured by placing the sample between parallel plate capacitors and alternating the electric field.

└→ polar groups on the polymer chain respond to the alternating field.

└→ if the average v of molecular motion = the electric field frequency v, absorption maxima will occur.

·Broad line NMR

- depends on the fact that H nuclei moment and therefore process about an imposed alternating magnetic field, especially at radio frequencies

→ Stronger interactions exist between the magnetic dipoles of different H nuclei in polymers below Tg

→ result in a broad signal.

→ As T↑ through Tg, proton orientations become increasingly random, and the signal sharpens.

9.2. Methods of Measuring Transitions in Polymers

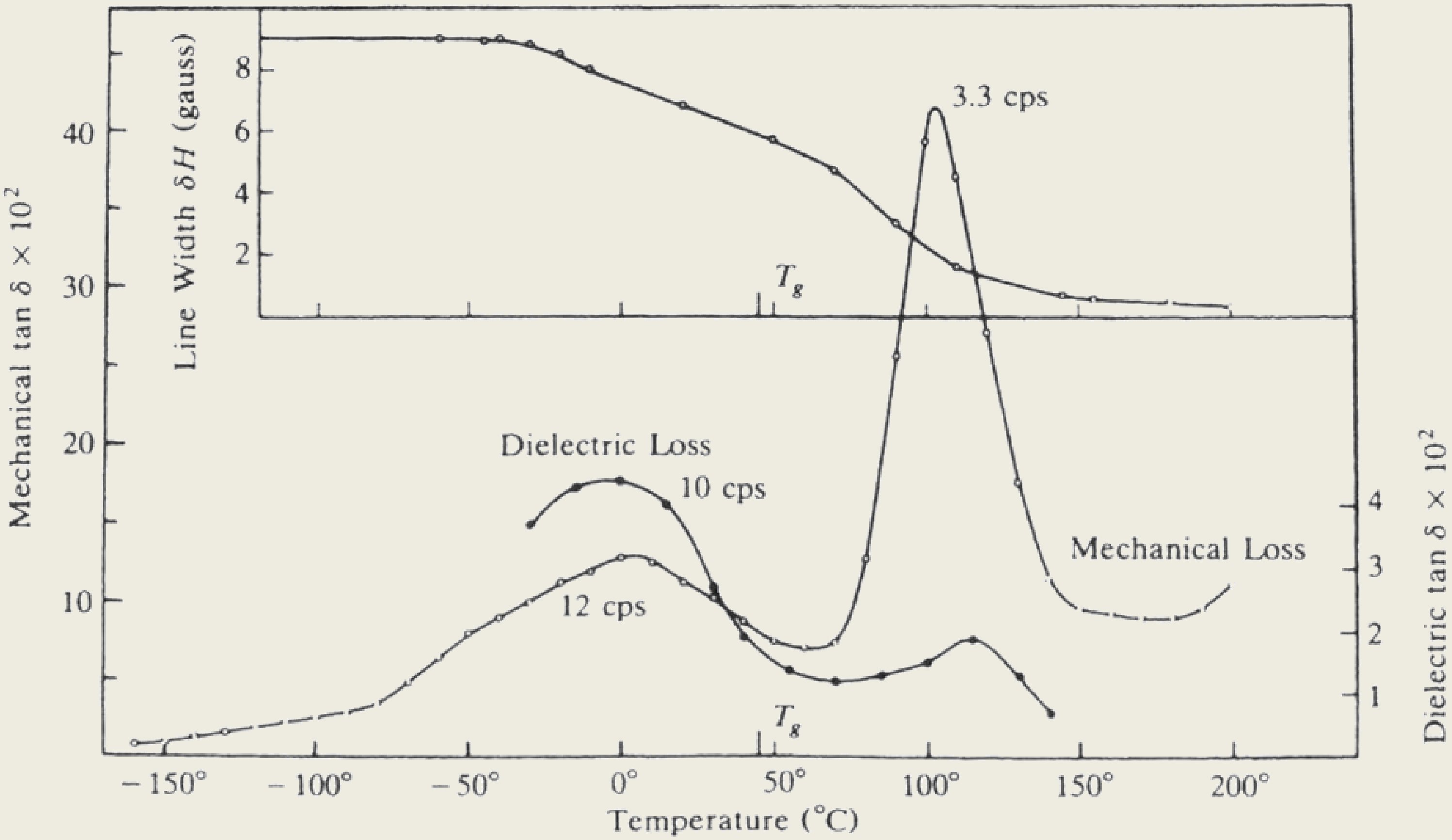


Fig.9.8 Mechanical and dielectric loss tangent tanδ and NMR absorption line width δH(maximum slope, in gauss) of polytrifluorochloroethylene (Kel-F).

9.2. Methods of Measuring Transitions in Polymers

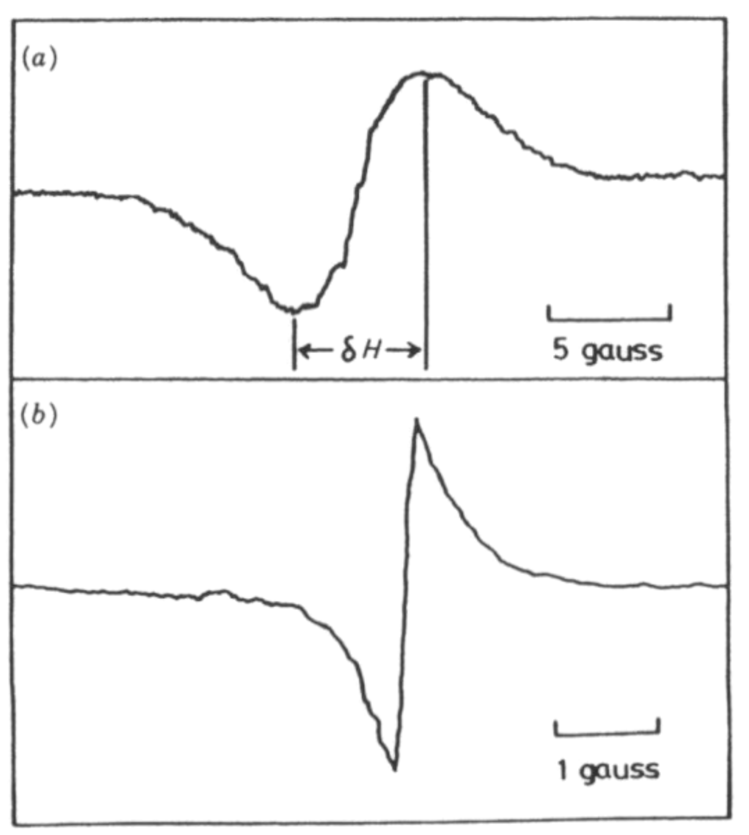
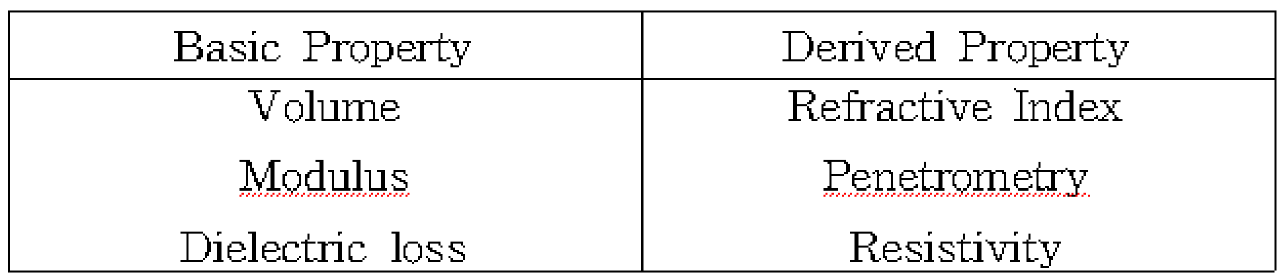


Fig.9.10 Broad-line NMR spectra of a cured epoxy resin. (a) Broad line at 291K ; (b) motionally narrowed line at 449K (Tg+39K)

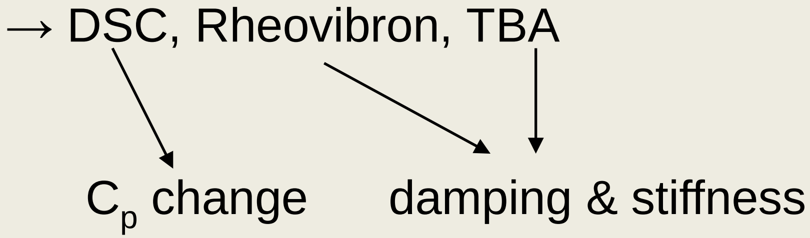
9.2. Methods of Measuring Transitions in Polymers

9.2.5. A Comparison of the Methods.



Basic Property	Derived Property
Volume	Refractive Index
Modulus	Penetrometry
Dielectric loss	Resistivity

· the derived property is frequently measured from a practical point of view.



→ DSC, Rheovibron, TBA

C_p change　　damping & stiffness

※ Other Transitions and Relaxations

The Schatzki Crankshaft Mechanism

1. Main-chain Motions (see Fig. 8.16 p375)

For PE, T_{tran} = -120℃ due to the Schatzki mechanism.

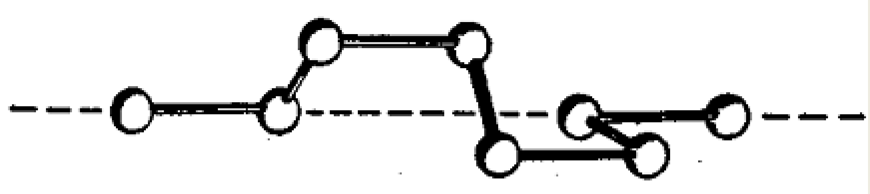


Fig.8.16 Schatzki's crankshaft motion requires at least 4 -CH2- groups in succession. As illustrated, for eight -CH2- groups, bonds 1 and 7 are colinear and intervening -CH2- units can rotate in the manner of a crankshaft.

2. Side-Chain Motions

·Major difference between main-chain and side-chain motions

= the toughness imparted to the polymer

→ Low T main-chain motions act to absorb ε much better than the equivalent side-chain motions, in the face of impact belows.

└→tend to prevent main-chain rupture.

※ Other Transitions and Relaxations

The T_{ll} Transition

→ thought to represent the onset of the ability of the entire polymer molecule to move as a unit.

→ above Tll, physical entanglements play a much smaller role, as the molecule becomes able to translate as a whole unit.

→ in controversy for the existence.

9.3. Theories of the Glass Transition

How can the transition be explained on a molecular level?

9.3.1. The Free Volume Theory

- first developed by Eyring and others
- molecular motion in the bulk state depends on the presence of holes or places where there are vacancies or voids.

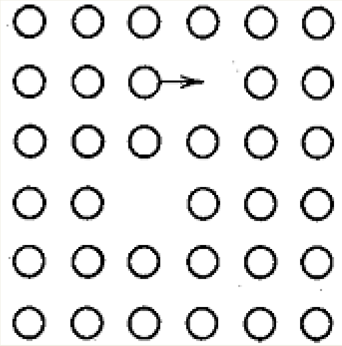


Fig.9.11 A quasicrystalline lattice exhibiting vacancies, or holes. Circles represent molecules; arrow indicates molecular motion.

- for a polymeric segment to move from its present position to an adjacent site, a critical void volume must first exist before the segment can jump.

  → molecular motion cannot take place without the presence of holes (≃free volume)

- One of the most important consideration: quantitative development of the exact free-volume fraction in a polymeric system

CNDL

9.3. Theories of the Glass Transition

① T_g as an iso-Free-Volume State

For MW=∞, $v_f = K + (\alpha_R - \alpha_G)T$: Fox and Flory

v_f : specific free volume

α_R, α_G : cubic expansion coefficient in the rubbery and glassy states.

- $T < T_g$ local conformational arrangement of the polymer segment = independent of MW and T
- at $T = T_g$ iso-free-volume state

$v - (v_{0,R} + \alpha_G T) = v_f$: by Simha and Boyer

$v = v_{0,R} + \alpha_R T$

$\therefore \quad (\alpha_R - \alpha_G)T_g = K_1$

v : specific volume

$v_{0,G}$, $v_{0,R}$: volumes extrapolated to 0K using

9.3. Theories of the Glass Transition

$K_1 = (\alpha_R - \alpha_G)T_g = 0.113$: by Simha and Boyer

$\therefore$ theoretical free volume 11.3%

$\alpha_R T_g = K_2 = 0.164$

→ K_1 and K_2 provide a criterion for the glass temperature

$\alpha_G T \propto$ the occupied volume

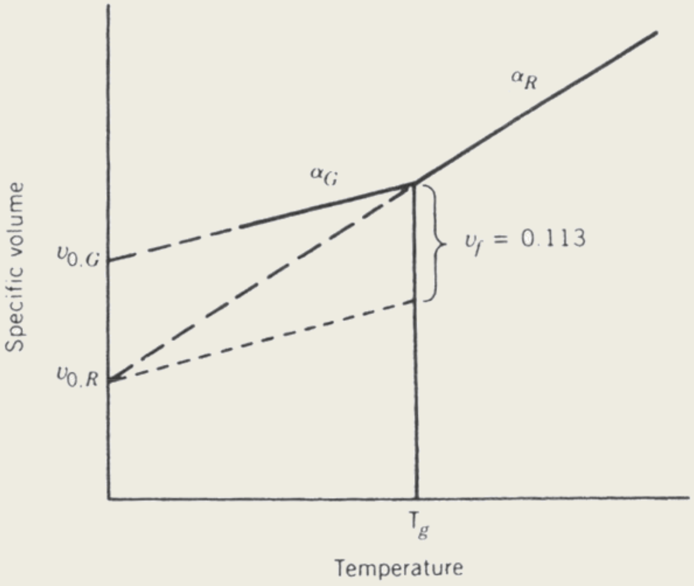


Fig.9.12 A schematic diagram illustrating free volume as calculated by Simha and Boyer.

9.3. Theories of the Glass Transition

② The WLF equation (William-Landel-Ferry)

Flow, a form of molecular motion,

└→ requires a critical amount of free volume.

→ considers the analytic relationships between polymer melt viscosity and free volume

$$\ln \eta = B(\frac{V_0}{V_f}) + \ln A$$: Doolittle equation

A, B : constants

v_0 = occupied volume

v_f = specific free volume

└→ provides a theoretical basis for the WLF eqn.

→ WLF eqn. begins with a consideration of the need of free volume to permit rotation of chain segments, and the hindrance to such rotation caused by neighboring molecules

9.3. Theories of the Glass Transition

Free volume to permit rotation of chain segments

$$P = \exp(-\frac{\Delta E_{act}}{kT})$$

└→ the probability of the barriers to rotation per unit time, cooperative motion, or reptation being surmounted.

└→ increases with T

t : Long times allow for greater probability of the required motion.

for the onset of the motion

$$\ln tP = const. = -\frac{\Delta Eact}{kT} + \ln t$$

$$\therefore \quad \ln t = const. + \frac{\Delta E_{act}}{kT} \qquad \Delta \ln t = -\frac{\Delta E_{act}}{kT^2}\Delta T$$

(: associated with free volume)

$\therefore$ as $\ln t$ ↑ = ↓ in T

9.3. Theories of the Glass Transition

assume $$\frac{\Delta E_{act}}{kT} = \frac{B'}{f}$$

B' : constant

f : fractional free volume

$$\therefore \quad P = \exp(-\frac{B}{f})$$

For the particular set of properties to be observed

$$\ln tP = const. = -\frac{B}{f} + \ln t$$

$$\Delta \ln t = B\Delta(\frac{1}{f})$$

∴ a change in the fractional free volume is equivalent to a change in the logarithm of the time scale of the event.

9.3. Theories of the Glass Transition

Setting α_f = expansion coefficient of the free volume
f_0 = fractional free volume at T_g

Then, the dependence of the fractional free vol. on T

$$f = f_0 + \alpha_f (T - T_0)$$

with T_0 : generalized transition T

$$\Delta \ln t = B(\frac{1}{f} - \frac{1}{f_0})$$

$$\Delta \ln t = B\left[\frac{1}{f_0 + \alpha_f (T - T_0)} - \frac{1}{f_0}\right]$$

$$= B\left[\frac{f0 - [f_0 + \alpha_f (T - T_0)]}{f_0[f_0 + \alpha_f (T - T_0)]}\right]$$

$$= -\frac{B\alpha_f (T - T_0)/f_0}{f_0 + \alpha_f (T - T_0)}$$

$$\Delta \ln t = -\frac{(B/f_0)(T - T_0)}{(f_0/\alpha_f) + (T - T_0)}$$

9.3. Theories of the Glass Transition

meaning of $\Delta \ln t$

$$\Delta \ln t = \ln t - \ln t_0 = \ln \frac{t}{t_0} = \ln A_T$$

└→shift factor

A_T : relates not only to the time for a transition with another time but also to many other time-dependent quantities at the transition T and another T.

$$\ln A_T = -\frac{(B/f_0)(T-T_0)}{(f_0/\alpha_f)+(T-T_0)}$$

$$\log A_T = -\frac{B}{2.303 f_0}\left[\frac{(T-T_0)}{(f_0/\alpha_f)+(T-T_0)}\right]$$

9.3. Theories of the Glass Transition

For small v_f

since $\frac{v_f}{v_0} \cong \frac{v_f}{\underline{v_0 + v_f}} \cong f$

specific volume

$$\therefore \quad \ln \eta = \ln A + \frac{B}{f}$$

(from Doolittle eqn.)

$$\ln \eta - \ln \eta_0 = \ln A - \ln A + \frac{B}{f} - \frac{B}{f_0}$$

$$\therefore \quad \ln \frac{\eta}{\eta_0} = B(\frac{1}{f} - \frac{1}{f_0})$$

$$\boxed{\ln \frac{\eta}{\eta_0} = \ln \frac{t}{t_0} = \ln A_T}$$

($\because$ viscosity is a time (shear rate) - dependent quantity)

9.3. Theories of the Glass Transition

Experimental evaluation,

$$\log\frac{\eta}{\eta_s} = -\frac{8.86(T-T_s)}{51.6+(T-T_s)}$$

(T_0 =T_s=T_g+50℃)

$$\log\frac{\eta}{\eta_g} = -\frac{17.44(T-T_g)}{51.6+(T-T_g)}$$

$$\log A_T = -\frac{B}{2.303 f_0}\left[\frac{(T-T_0)}{(f_0/\alpha_f)+(T-T_0)}\right]$$

$$\frac{B}{2.303 f_0} = 17.44 \qquad \frac{f_0}{\alpha_f} = 51.6$$

if B=1 them $f_0 = 0.025$ $\quad \alpha_f = 4.8\times10^{-4}\deg^{-1}$

∴ free volume at $T_g \simeq 2.5$ % (2.35% based on more recent thermodynamic data.)

9.3. Theories of the Glass Transition

9.3.2. The Kinetic Theory of the Glass Transition

- Estimations of the free-volume hole size in polymers

$$V_f = a + bh\,(T/T^*)$$

V_f: free volume, h: hole fraction, T*=T/Ť, Ť: reduced temperature

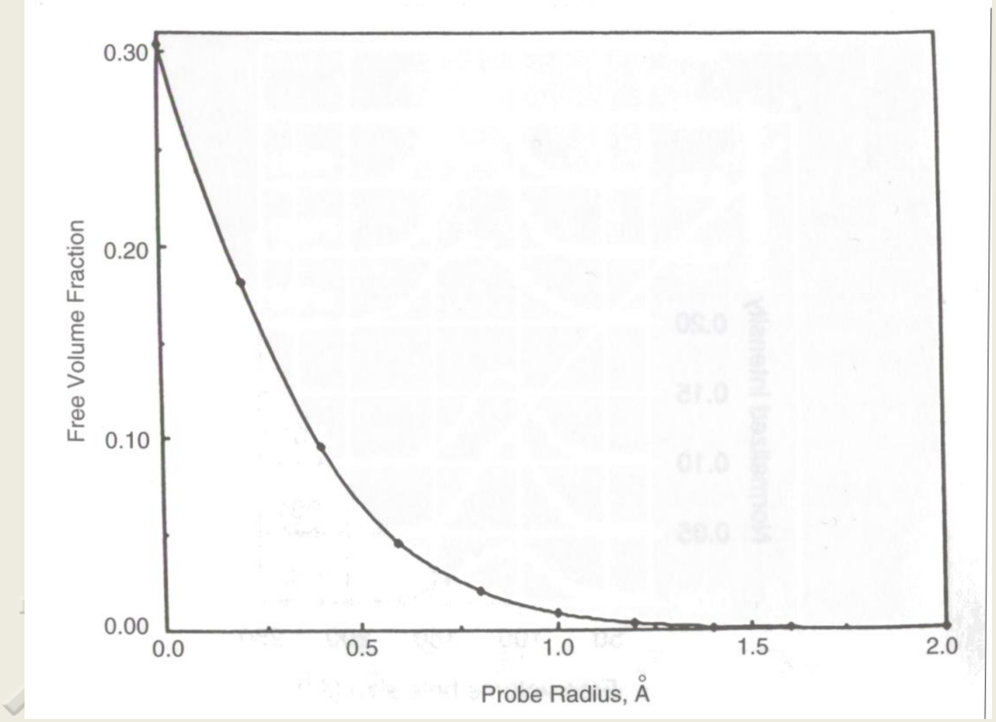


Fig.9.13 Theoretical free volume fraction as a function of the probe sized for polybutadiene.

9.3. Theories of the Glass Transition

9.3.3. Thermodynamic Theory of T_g

·Transition is primarily a kinetic phenomenon because

(a) T_{trans} can be changed by changing the time scale of experiment. The slower cooling rate, the lower T_g's.

(b) The measured relaxation times near T_{trans} approach the time scale of the experiment

└→ kinetic theory

·What equilibrium properties these glass-forming materials have even it is necessary to postulate infinite time scale experiment?

⇒ Gibbs and DiMarzio gave an answer based on a lattice model.

9.3. Theories of the Glass Transition

9.3.3.1. The Gibbs and DiMarzio Theory

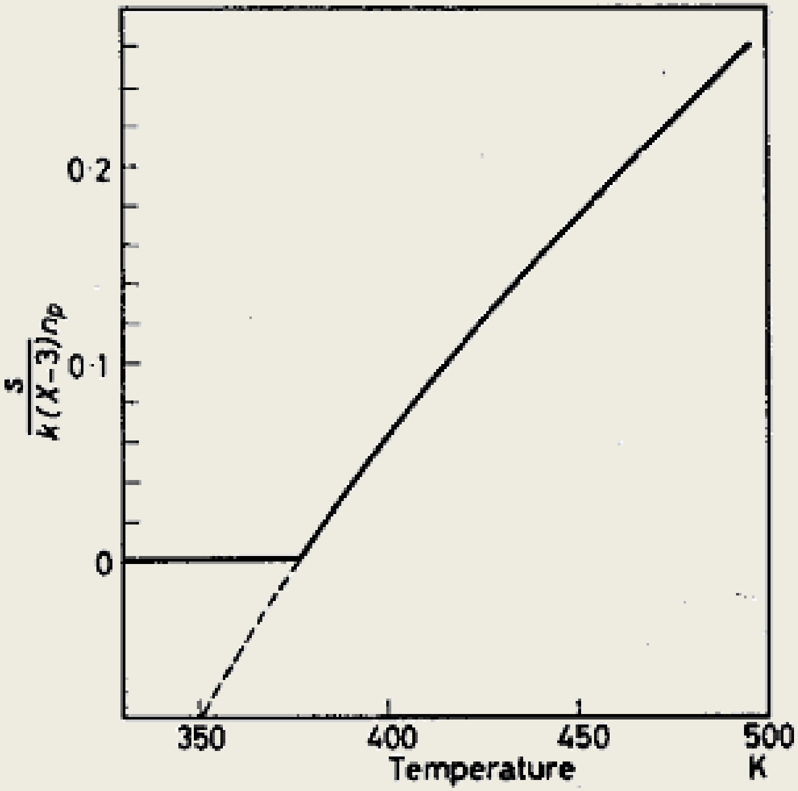


Fig.9.14 Schematic diagram of the conformational entropy of a polymer as a function of temperature according to the Gibbs-DiMarzio theory.

9.3. Theories of the Glass Transition

In infinitely slow experiments,

a glassy phase will eventually emerge whose entropy is negligibly higher than that of the crystal.

└→The central problem is to find the configurational partition function Q, from which the expression for the configurational entropy can be calculated.

└→hindered rotation in polymer chain arising from <u>two energy states</u>

ε_1 is associated with one possible orientation.

ε_2 is associated with all the remaining orientations.

$$\therefore \quad \Delta E = \varepsilon_1 - \varepsilon_2$$

z : coordination no. (=4)

9.3. Theories of the Glass Transition

∴ at equilibrium

$$Q = \sum_{f,n_\chi,n_0} W(f_1 n_x, \cdots, f_i n_x, \cdots, n_0) \times \exp\left[-\frac{E(f_1 n_x, \cdots, f_i n_x, \cdots, n_0)}{kT} \right]$$

where $f_i n_x$ is the no. of molecules packed in conformation *i*

W is the no. of ways that the n_x (χ degree of polymerization) molecules can be packed into sites on the quasi-lattice.

n_0 is the no. of holes.

$$S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,n} + k \ln \Omega$$

→ Appendix 9-2

(from statistical thermodynamics)

⇒ This theory has been applied to the variation of the T_g with

① MW

② random copolymer composition

③ plasticization

④ extension

⑤ cross-linking

CNDL

9.3. Theories of the Glass Transition

9.3.3.2. Effect of Cross-link Density on T_g

·The criterion of the second-order transition temp. is that the dependent conformational entropy, S_c, becomes zero.

$$S_c = S_0 + \Delta S_R = 0$$

where S_0 is the conformational entropy for the uncross-linked system.

$\triangle S_R$ is the change in conformational entropy due to adding cross-links.

9.3. Theories of the Glass Transition

· Since crosslinking decreases the conformational entropy.

the transition temp. is raised.

$$\therefore \frac{T(X')-T(0)}{T(0)} = \frac{KMX'/\gamma}{1-KMX'/\gamma}$$

K : experimentally determined

: independent of the polymer.

where χ' is the no. of X-links per gram.

M is MW of the mer.

γ is the no. of flexible bonds per mer, backbone, and side chain.

or

$\Delta T_{g,c} = ZD$ by Ueberreiter and Kanig

where is the change in the glass temp. with ↑X-linking.

D is X-link density

Z : constant

9.3. Theories of the Glass Transition

9.3.3.3. A Summary of the Glass Transition Theories

① Free Volume Theory

- free-volume in the form of segment-size voids is required for the onset of coordinated molecular motion.
- provides relationships $\alpha_{T<Tg}$ and $\alpha_{T>Tg}$ yields equations relation viscoelastic motion to the variables of time and temperature.

② Kinetic Theory

- defines T_g as the T at which the relaxation time for the segmental motions in the main chain is of the same order of magnitude as the time scale of the experiment.
- concerned with the rate of approach to equil. of the system, taking the respective motions of the holes and molecules into account.
- provides quantitative information about the heat capacities below and above T_g and explains the 6~7℃ shift in T_g per decade of time scale of the experiment.

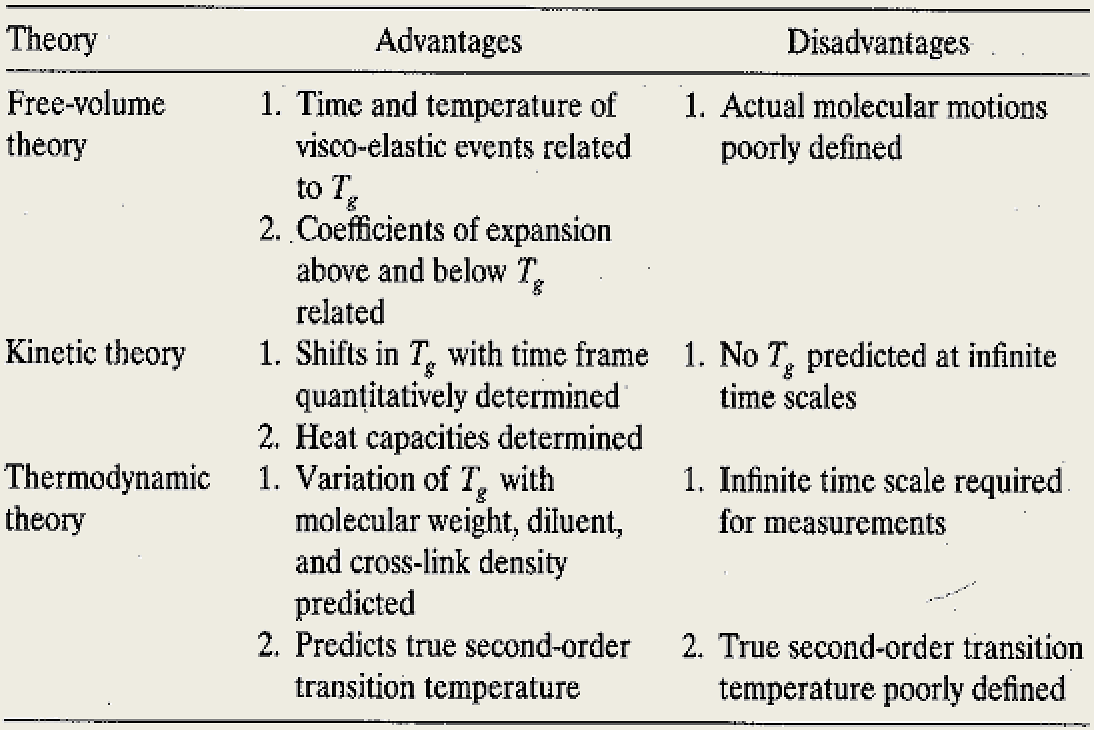
9.3. Theories of the Glass Transition

③ Thermodynamic Theory

- introduces the notion of equilibrium and the requirements for a true second-order transition, albeit at ∞ time scale.
- T_g variation with MW and X-link density, diluent content, and other variables.

9.3. Theories of the Glass Transition

Table 9. 1 Glass transition theory box scores



Theory	Advantages	Disadvantages
Free-volume theory	1. Time and temperature of visco-elastic events related to T_g 2. Coefficients of expansion above and below T_g related	1. Actual molecular motions poorly defined
Kinetic theory	1. Shifts in T_g with time frame quantitatively determined 2. Heat capacities determined	1. No T_g predicted at infinite time scales
Thermodynamic theory	1. Variation of T_g with molecular weight, diluent, and cross-link density predicted 2. Predicts true second-order transition temperature	1. Infinite time scale required for measurements 2. True second-order transition temperature poorly defined

9.3. Theories of the Glass Transition

6.6.3.4. A Unifying Treatment

Adam and Gibbs,

'cooperatively rearranging region'

= the smallest region capable of conformational change outside the region.

At T_2, this region = the sample size ($\because$ only one conformation is available)

$$\frac{T_g}{T_2} = 1.30 \pm 8.4\%$$

for a wide range of glass-forming systems, both polymeric and low MW.

9.4. Factors Influencing on Tg

9.4.1. Effect of MW

-Linear Polymers

$$T_g = T_{g,\infty} - \frac{K}{(\alpha_R - \alpha_G)M}$$: by Fox and Flory

where T_g at molecular weight M

$T_{g,\infty}$ at infinite molecular weight

K constant depending on the polymer

with ↑MW, free volume↓, no. of end groups↓.

e.g. For PS under slow heating rates $$T_g = 106°C - \frac{2.1\times10^5}{M_n}$$

under normal heating rate $$T_g = 100°C - \frac{1.8\times10^5}{M_n}$$

By Cowie Tg (∞) = 372.6 $\log DP_c$ – 595

└(infinite MW)

9.4. Factors Influencing on Tg

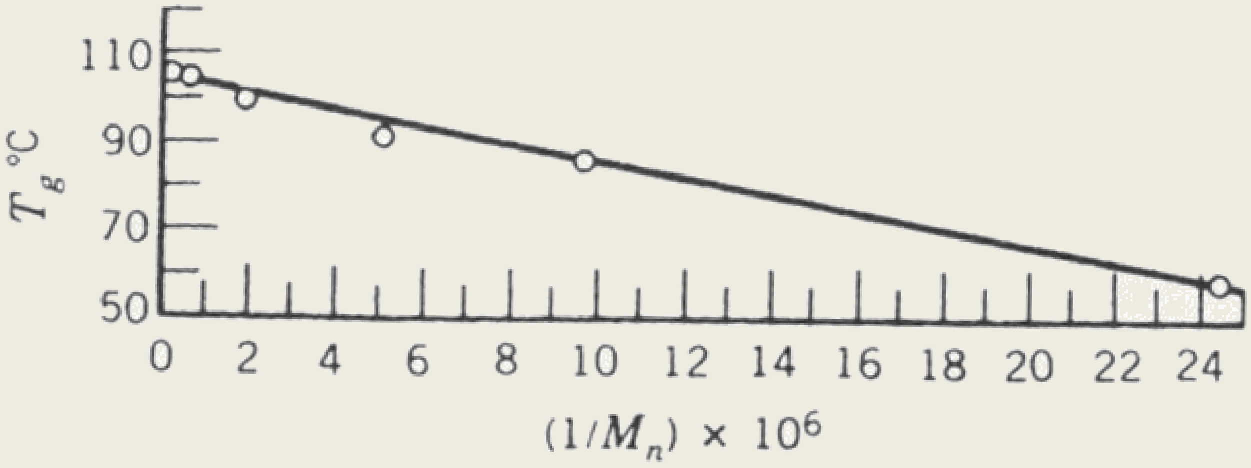


Figure 9.15 The glass transition temperature of poly styrene as a function of 1/M_n.

9.4. Factors Influencing on Tg

- Effect of T_g on polymerization

  (1) during chain polymerization

  ·monomer effectively acts like a plasticizer for the nascent polymer.

  e.g. emulsion polymerization of PS at 80℃

  └→the rxn. will not proceed quite to 100% conversion, because the system vitrifies

  (2) during step polymerization

  ·molecular weight is continuously increasing.

  ├→ gelation sometimes occurs.

  └→ for thermosetting systems, time-temp.-transformation(TTT) diagram developed by Gillham provides an intellectual framework for understanding and comparing the cure and glass transition properties

9.4. Factors Influencing on Tg

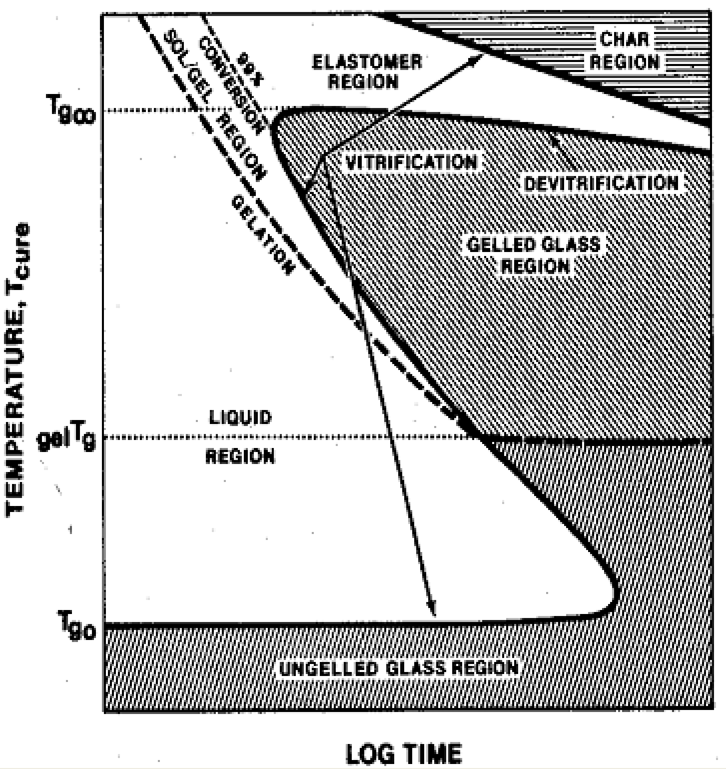


Fig.8.27 The thermosetting process as illustrating by the time-temperature-transformation reaction diagram.

9.4. Factors Influencing on Tg

9.4.2. Effect of Crystallinity on Tg

: Tg is often increased in temp. by the molecular motion restricting crystallites.

: Many semicrystalline polymers appear to possess two glass temperatures.

(a) a lower one, T_g(L), referring to the completely amorphous state and being related to chemical structures

(b) an upper volume, T_g(U), occurring in the semicrystalline material and varying with extent of crystallinity and morphology.

① The glass Transition of Polyethylene

PE : no side chain

high crystallinity (280%)

-30℃, -80℃, or -128℃ transitions were indicated.

9.4. Factors Influencing on Tg

② The Nylon Family Glass Transition

: two subfamilies - i.e. nylon m, n family

nylon m family

Nylon6,12 Tg≃ +40℃, Nylon6 Tg≃ +60℃

└→ Tg depends on the crystallinity of the particular sample.

└→ as m, n↑, Tg↓ : H-bonding effect.

when n>4, characteristic mechanical loss peak at -130℃

└→ suggestive of the Schatzki motion.

9.4. Factors Influencing on Tg

③ Relationships between T_g and T_f.

$\frac{T_g}{T_f} = \frac{1}{2}$ for symmetrical polymers

$\frac{2}{3}$ for non-symmetrical polymers → in older literature

More recently, Boyer reported a cumulative plot of T_g / T_f.

Region A $\frac{T_g}{T_f} \cong \frac{1}{2}$ symmetrical polymers

$\frac{T_g}{T_f} \cong 0.667 \pm 0.05$

$\frac{T_g}{T_f} \cong 0.93$

$\therefore$ for an unknown polymer $\frac{T_g}{T_f} \cong \frac{2}{3}$

9.4. Factors Influencing on Tg

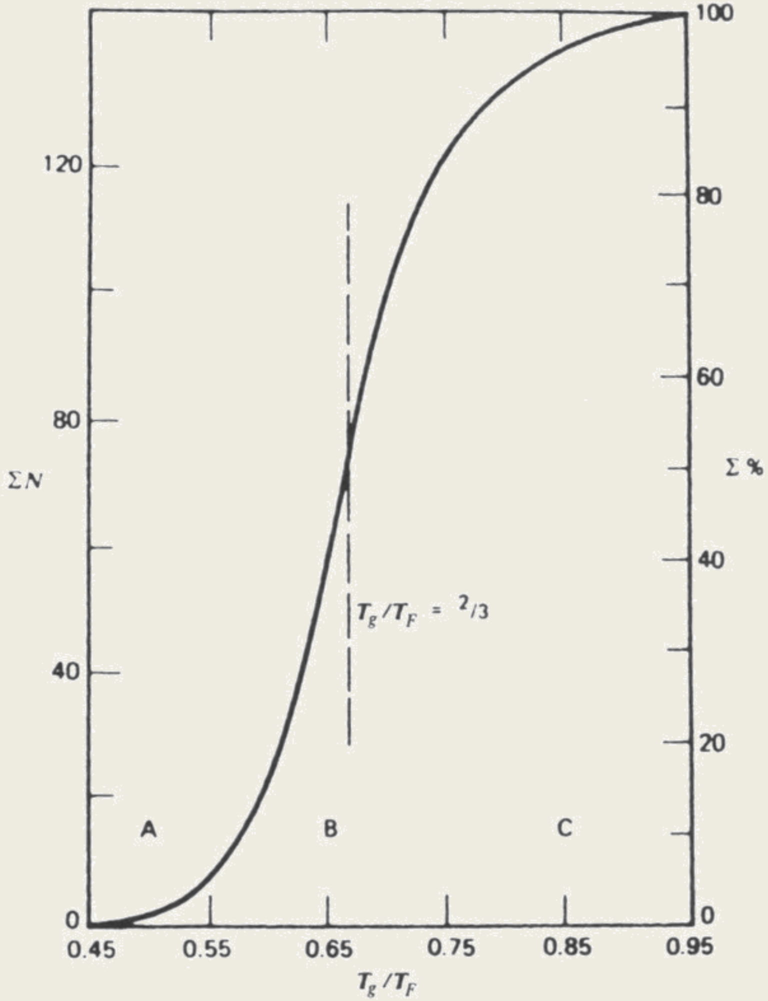
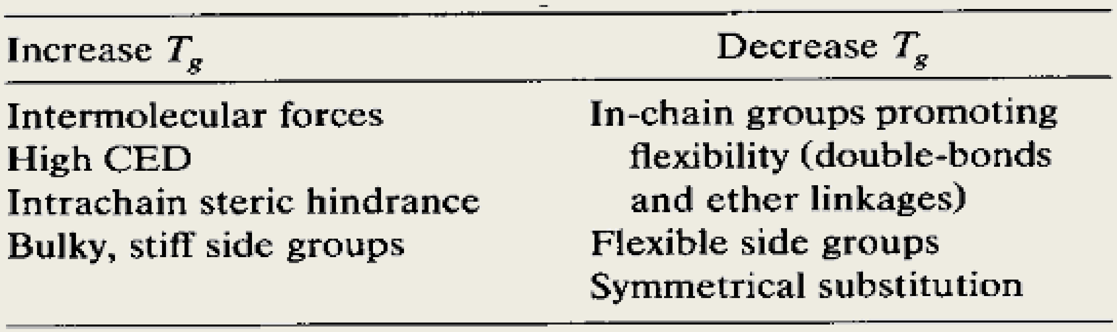


Fig.9.16 Range in T_g/T_f values found in the literature. Region A contains unsubstituted polymers. Region C includes poly(α-olefins) with long side chains. Region B contains the majority of vinyl, vinylidene, and condensation polymers. The left ordinate is cumulative number, N, and the right ordinate is cumulative percentage of all examples reported as having the indicated T_g/T_f values.

9.4. Factors Influencing on Tg

9.4.3. Dependence of T_g on Chemical Structure

Table 9. 2 Factors affecting T_g



Increase T_g	Decrease T_g
Intermolecular forces	In-chain groups promoting flexibility (double-bonds and ether linkages)
High CED	Flexible side groups
Intrachain steric hindrance	Symmetrical substitution
Bulky, stiff side groups	

① Effect of Aliphatic Side Groups on T_g

⇒ flexible pendant group reduces T_g : acting as 'internal diluent'→ lowering the frictional interaction between chains → reduce the rotational ε requirements of the backbone.

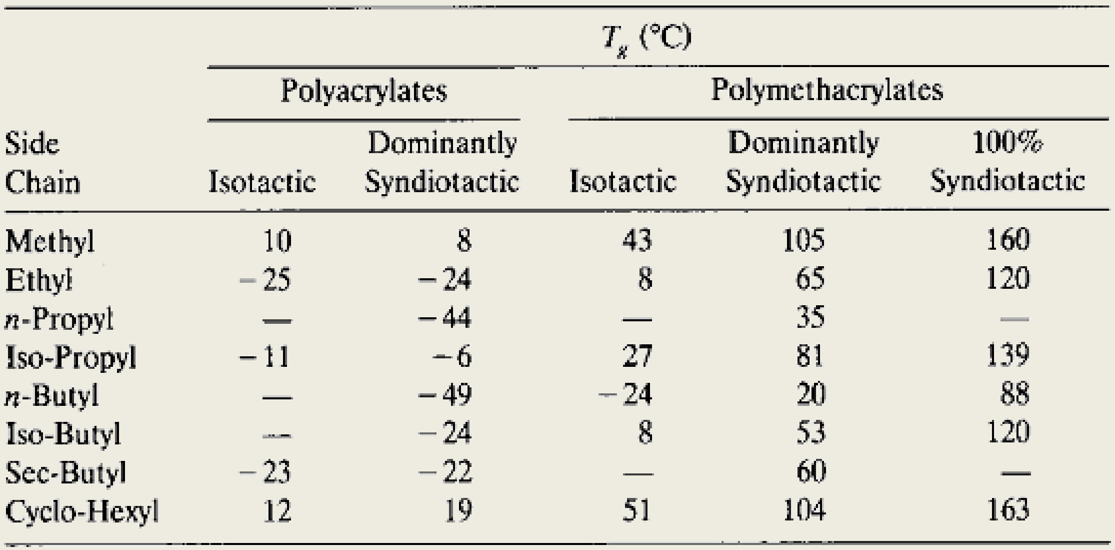
⇒ T_g ↑ as side-chain crystallization sets in.

9.4. Factors Influencing on Tg

② Effect of Tacticity on T_g

syndiotactic > isotactic > atactic

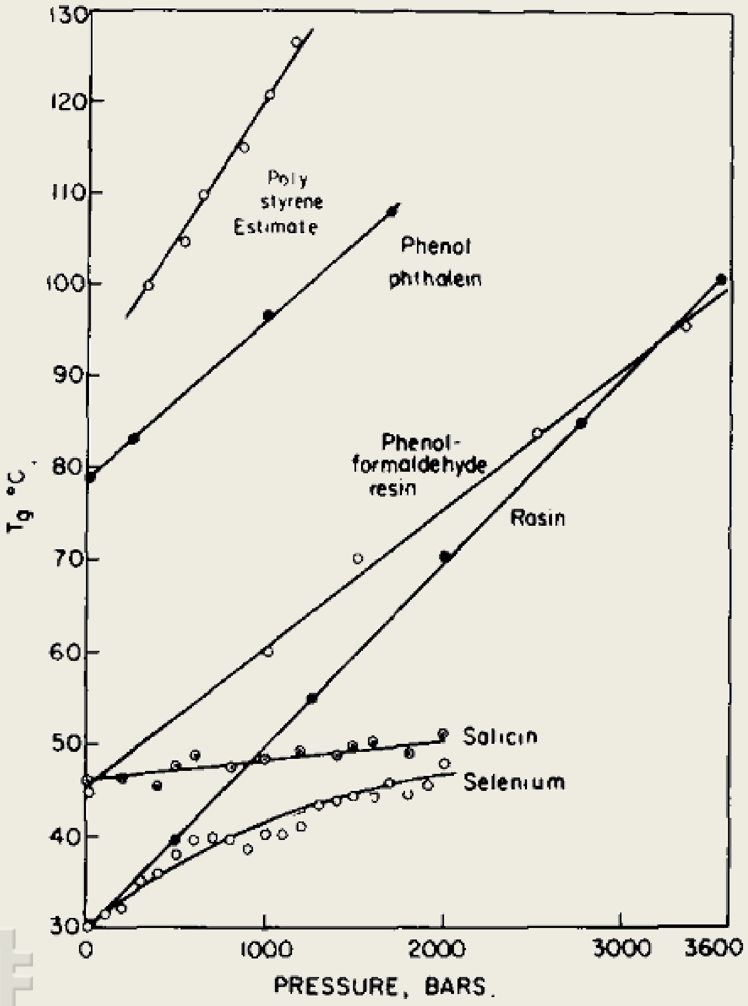
Table 9.3 Effect of tacticity on the glass transition temperatures of polyacrylates and polymethacrylates



	T_g (°C)				
	Polyacrylates		Polymethacrylates		
Side Chain	Isotactic	Dominantly Syndiotactic	Isotactic	Dominantly Syndiotactic	100% Syndiotactic
Methyl	10	8	43	105	160
Ethyl	−25	−24	8	65	120
n-Propyl	—	−44	—	35	—
Iso-Propyl	−11	−6	27	81	139
n-Butyl	—	−49	−24	20	88
Iso-Butyl	—	−24	8	53	120
Sec-Butyl	−23	−22	—	60	—
Cyclo-Hexyl	12	19	51	104	163

9.4. Factors Influencing on Tg

9.4.4. Effect of Pressure on Tg



as P↑, volume ↓ ∴Tg ↑

as T↑ at elevated P, Tg ↑

(see Fig.8.33 p366)

Fig.8.33 Glass transition versus pressure for various substances

9.4. Factors Influencing on Tg

free volume at any T above Tg

$$f = f_0 - \alpha(T - T_g)$$

$$\therefore \quad f_{t,p} = f_0 - \alpha_f (T - T_g(0)) - k_f P$$

where Tg(0) : glass transition at zero pressure

k_f : the free-volume compressibility

under particular Tg and P,

$$f_{t,p} = f_0$$

$$\therefore \quad \alpha_f [Tg - Tg(0)] = k_f P \qquad \qquad \therefore \quad \left(\frac{\partial T_g}{\partial P}\right)_f = \frac{\Delta k_f}{\Delta \alpha_f}$$

⇒ an increase in pressure can bring about vitrification.

c.f. $\dfrac{TV\Delta\alpha}{\Delta C_p} = \dfrac{\Delta k}{\Delta\alpha} = \dfrac{\partial T_g}{\partial P}$: Ehrenfest's relation

Keywords in Chapter 10

-Maxwell Elements, Kelvin Elements, Four-Element, Takayanagi Models

-Relaxation time, Retardation time

-Time-Temperature Superposition Principle

-WLF Equation

-Weissenberg effect

CNDL