Course: Physical Chemistry of Polymeric Materials

The Glass – Transition T_g

Outline

- Thermodynamic Aspects of Glass and Melting Transition

- Determination of Transitions in Polymers

    Dilatometry
    Differential Scanning Calometry (DSC) see Introduction to solid state (course 6)
    Dynamic Mechanical Analysis (DMA)

- Glass-Transition Theory

    Free Volume Theory – **W**illiams-**L**andel-**F**erry equation-
    Kinetic Theory - Thermodynamic Theory

- Effects on Glass-Transition

    Molecular weight
    Copolymerization
    Crystallinity
    Chemical Structure

Definitions

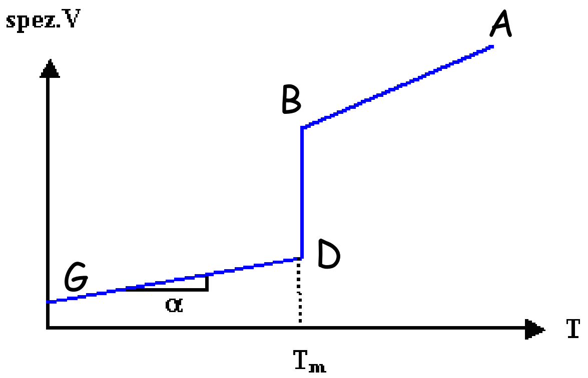
Transition: refers to a change of state induced by changing the temperature or pressure

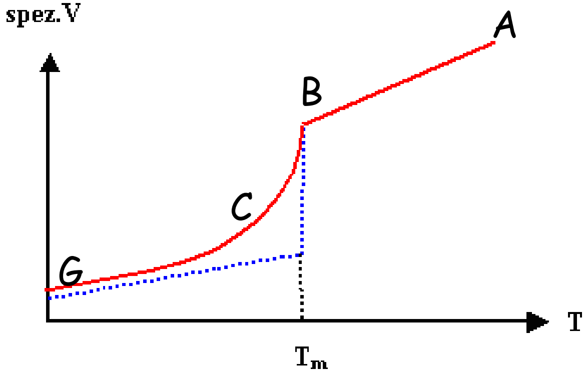
Relaxation: refers to the time required to respond to a change in T or p, measure of the molecular motion

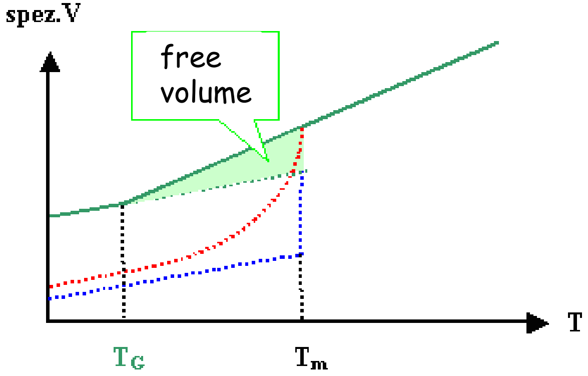
Glass transition = beginning of reptation
(onset of long-range coordinated molecular motion)

= (pseudo) second order transition
(discontinuities in heat capacity and coefficients of expansion)

Thermodynamic: The Glass and Melting Transitions



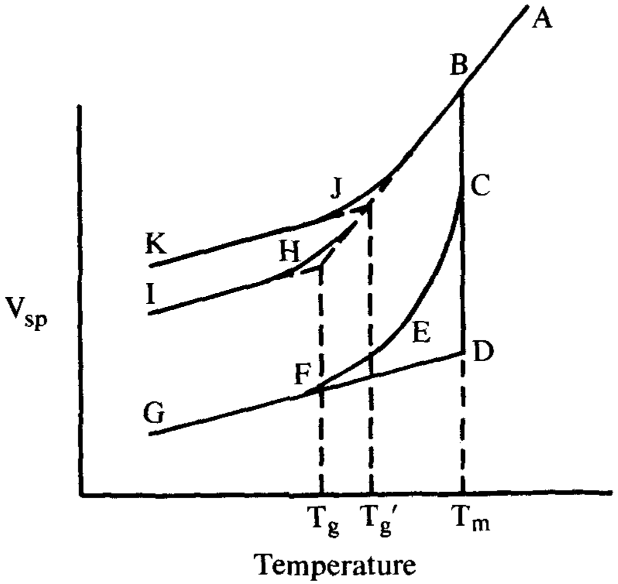




ABDG: freezing/melting of a low molecular weight compound

ABCG: semi-crystalline polymer

ABHI/ABJK: amorphous material at two different cooling rates (cooling rate$_{ABJK}$ > cooling rate$_{ABHI}$)

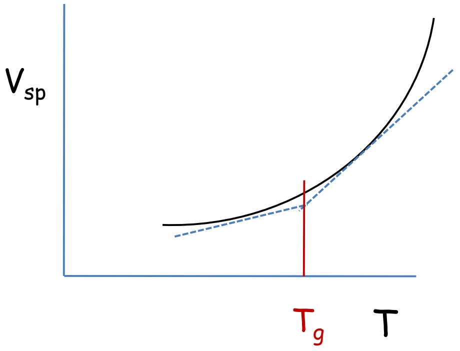


specific volume = volume occupied by a unit of mass of a material (= inverse density)

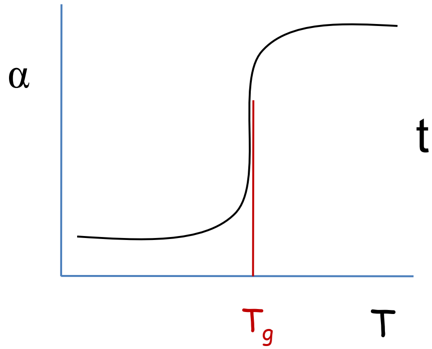
Transitions of some Polymers

Polymer	T_g	T_m	$X_{c\ MAX}$
PET	80ºC	270ºC	>80%
Poly(propylene)	-20ºC	175ºC	>80%
Low-density polyethylene	-20ºC	115ºC	50-60%
High-density polyethylene	-20ºC	135ºC	>90%

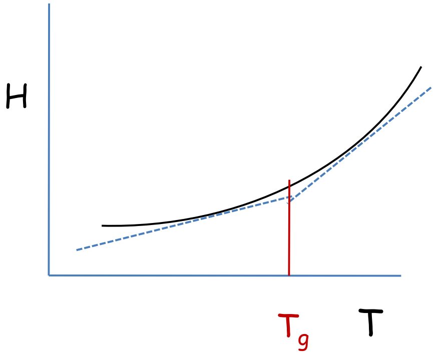
Thermodynamic Aspects of the Glass Transition



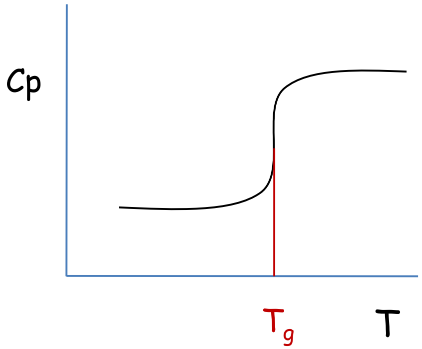
spec. volume



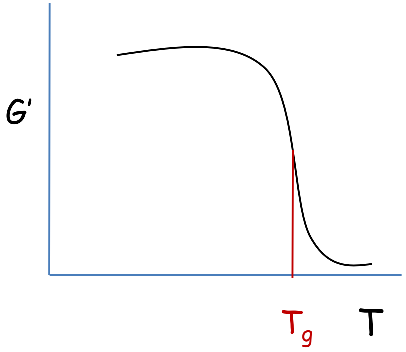
thermal expansion



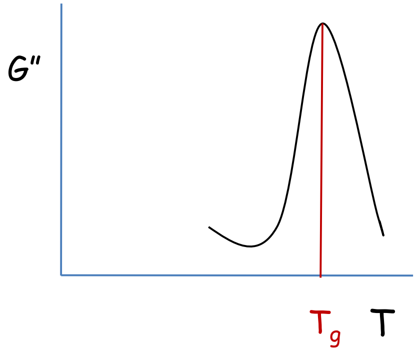
enthalpy



heat capacity



storage modulus



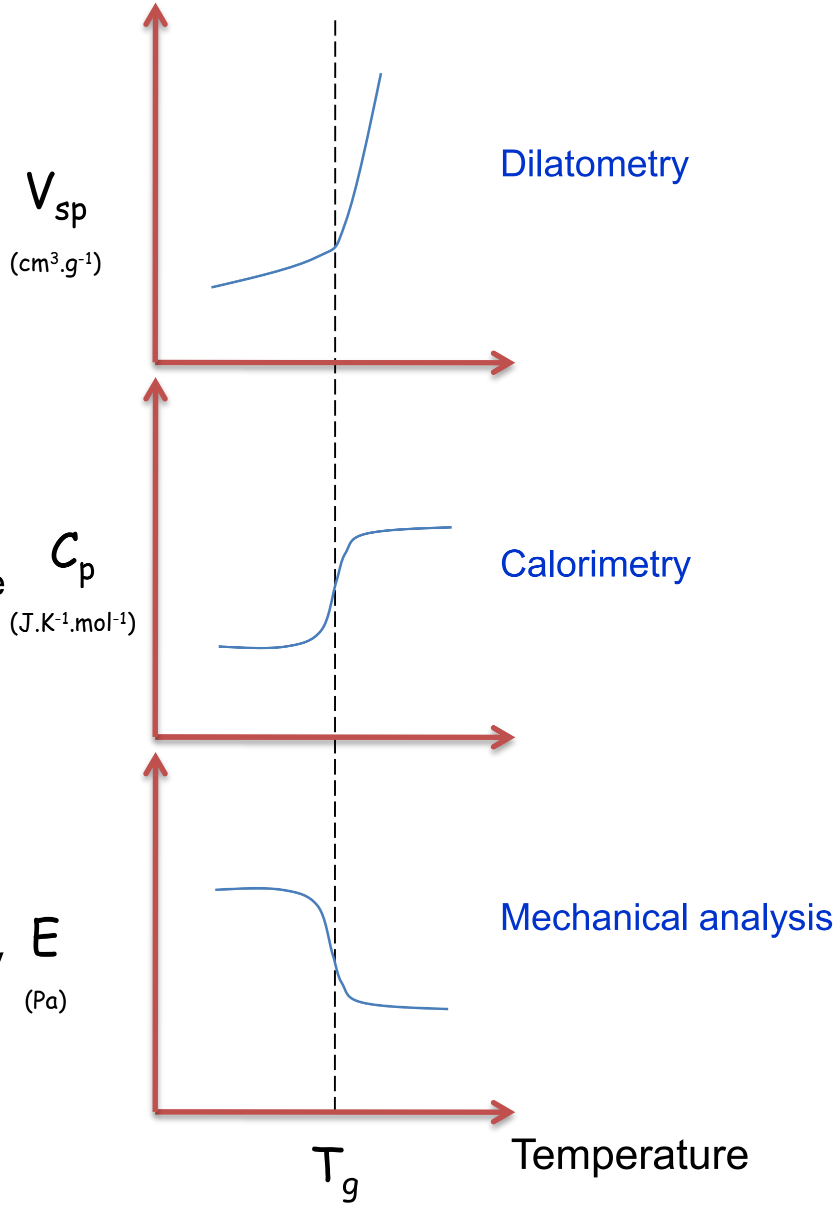
loss modulus

Methods of Measuring Transitions in Polymers

The specific volume.
The volume occupied by the polymer.
Above T_g, the increased mobility of the chains increases the space the chains occupy.
Macroscopically, the polymer can dilate.

Heat capacity.
The energy required to heat one mole by one degree
Above T_g, the chains have more freedom to move and therefore are able to absorb more energy.

The modulus.
A representation of the resistance of a polymer to deformation.
Above T_g, since the chains move more freely, they are more easily deformed



Dilatometry

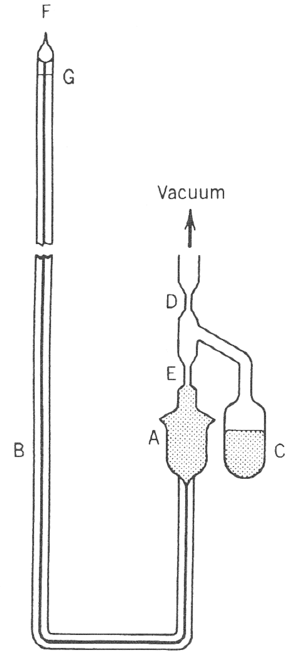


Figure 8.8 A mercury-based dilatometer (24). Bulb *A* contains the polymer (about 1 g), capillary *B* is for recording volume changes (Hg + polymer), *G* is a capillary for calibration, sealed at point *F*. After packing bulb *A*, the inlet is constricted at *E*, *C* contains weighed mercury to fill all dead space, and *D* is a second constriction.

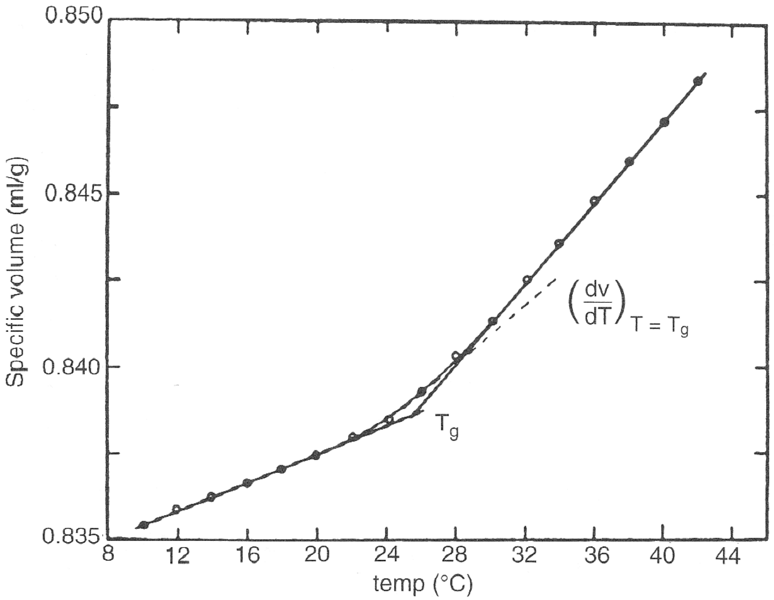


Figure 8.9 Dilatometric studies on branched poly(vinyl acetate) (24).

Volume – Temperature Measurements: polymer is confined by a liquid and the change in volume is recorded as the temperature is raised. Confining liquid is mercury, it does not swell organic polymers and has no transition of its own trough the interesting temp. range.

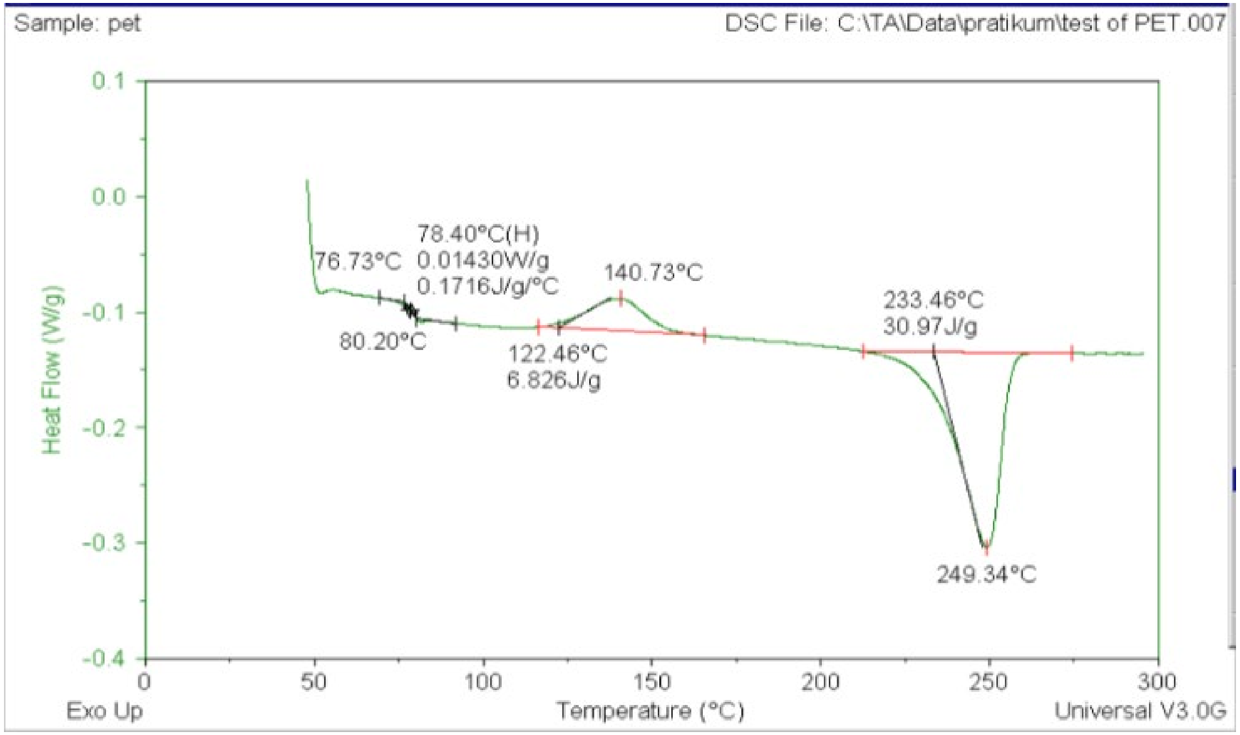
the volumetric coefficient of expansion α, is defined as:

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_p$$

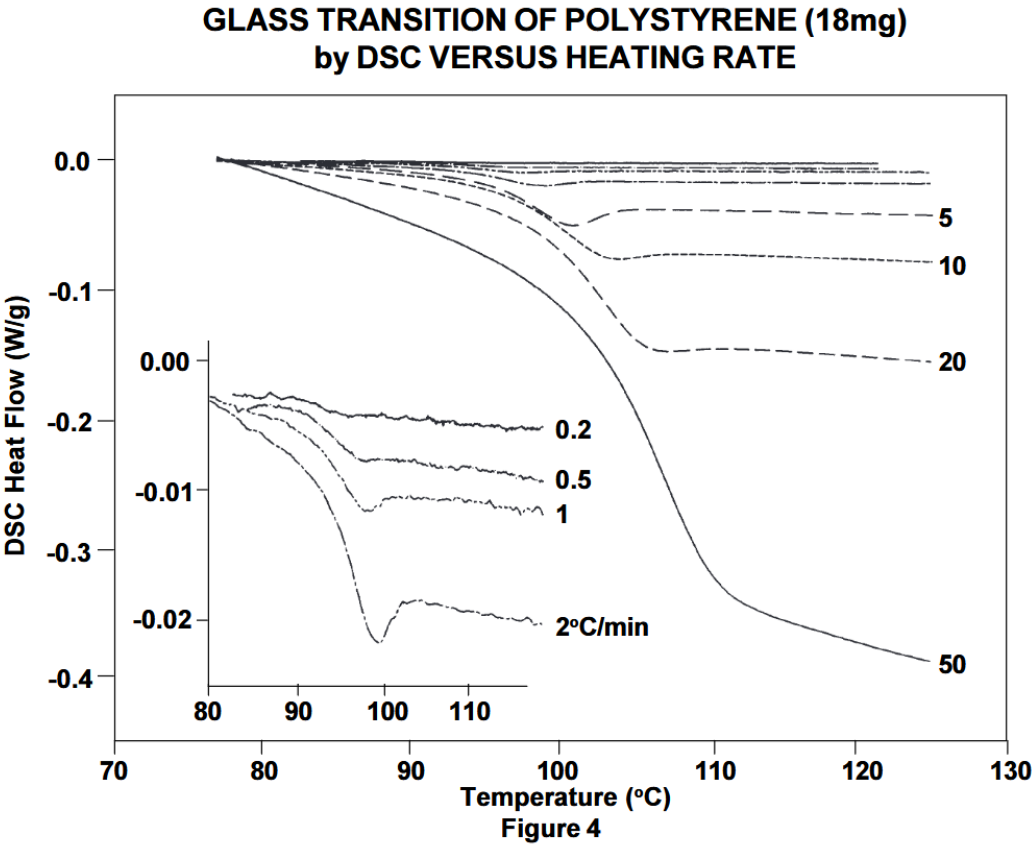
besides T_g, free volume information are obtained.

Revision: DSC - Scan

$$Heat\ Flow = \left(\frac{dq}{dt}\right)_p = C_p \frac{dT}{dt}$$



DSC: influence of heating rate on glass transition



T_g shifts to higher temperatures and the transition broadens as the heating rate is increased

Viscosity ←→ Elasticity

Newton's law of Viscosity:

$$\tau = \eta \frac{d\gamma}{dt}$$

t: time
τ: shear stress
γ: shear strain

Perfect Elasticity: application of Hook's Law to different types of deformation

1: Stretching along a single axis

$$\sigma = E\,\varepsilon$$

Hook's Law

σ: tensile stress
E: Young Modulus
ε: strain

2: Shearing

$$\sigma = G\,\gamma$$

G: shear Modulus

3: Compression

$$V = -B\left(\frac{dV}{dp}\right)_T$$

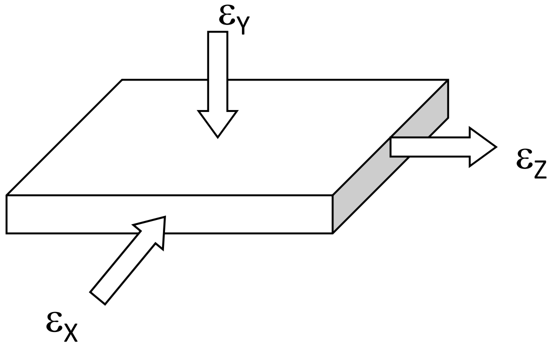
B: Bulk Modulus
V: volume
p: pressure

The Poisson coefficient/ Poisson's ratio

Deformation of a material induces changes in volume. The Poisson coefficient ν takes into account changes in the dimensions of a material along the axis other than those directly involved in the deformation.

$$-\frac{\Delta d}{d} = -\frac{\Delta h}{h} = \nu\frac{\Delta L}{L_0} = \nu\varepsilon$$

$$\boxed{\nu = \frac{1}{2}\left(1 - \frac{1}{V}\frac{dV}{d\varepsilon}\right)}$$



When ν has a value of 0.5, the material undergoes no change in volume.

Generally, ν takes values between 0.2 and 0.5. It is determined by measuring the volume change concurrent with applied strain.

Value	**Interpretation**
0.5	No volume change during stretching
0.0	No lateral contraction
0.49 – 0.499	Typical values for elastomers
0.20 – 0.40	Typical values for plastics

Some Examples of Young Modulus

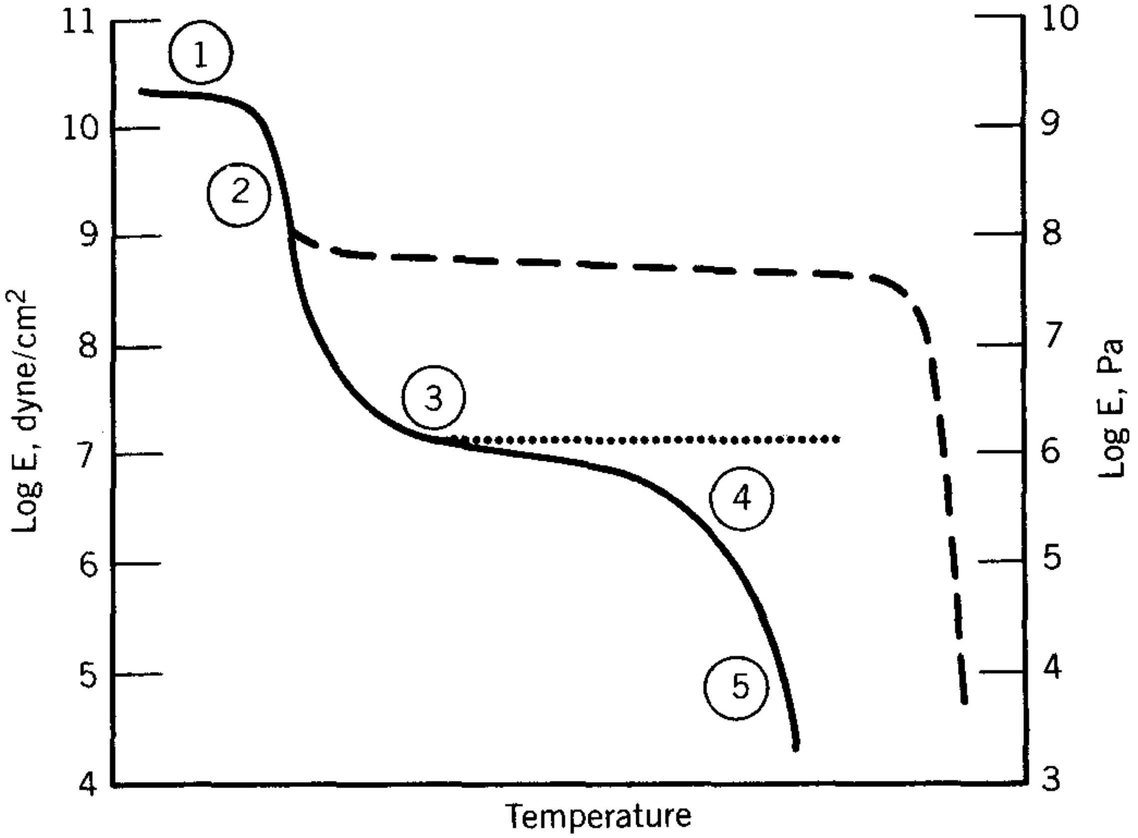
Material	E (kg/m^2)	ν
Tungsten	40 000	0.27
Steel	20 000	0.33
Copper	12 000	0.33
Aluminum	10 000	0.31
Glass	6 000	0.23
Plexiglass	370	0.33
PS	340	0.33
Low density PE	270	0.38
Nylon-6,6	200	0.48
Natural Rubber	0.20	0.50

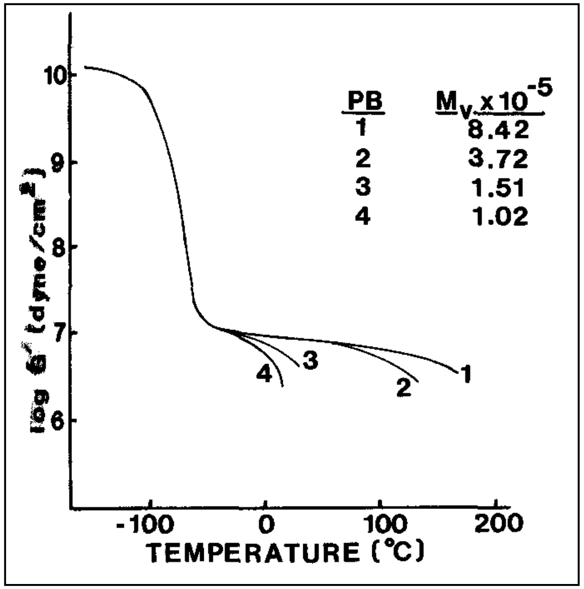
The SI units for moduli are N/m^2 = Pa (Pascal).

Other units are also commonly used:
dynes/cm^2 (1 Pa = 10 dynes/cm^2) and kg/mm^2 (1 kg/mm^2 = 9.81 Pa).

Temperature Dependence of the E-Modulus

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





Effect of molecular weight on length of plateau

① glassy region

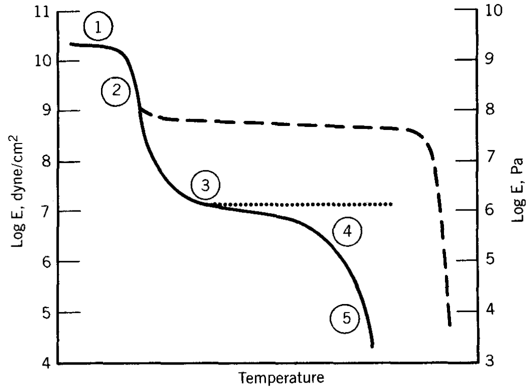
② transition region

③ rubbery plateau

④ rubbery flow

⑤ liquid flow

Properties of Polymers in their Different States

Region	Property of the polymer	E (dynes/cm²)	Types of molecular movements
1. The glassy region	Glassy and brittle	3×10^{10}	Molecular motions are restricted to vibrations and short range rotational motions
2. Glass transition region	Leathery	$3\times10^{10} \rightarrow 3\times10^{7}$ ⇘ Drops by ~10^{3}	T_g marks the onset of longe range coordinated motion. Below T_g, motion is restricted to 1-4 chain atoms. In T_g region, 10-50 chain atoms can move in coordinated fashion
3. Rubbery plateau region	Polymer exhibits long range rubber elasticity	2×10^{7}	Movement over the entire main-chain
Linear polymers	E gradually drops with T in this region		 Five regions of viscoelastic behavior for a linear, amorphous polymer. Also illustrated are effects of crystallinity (dashed line) and cross-linking (dotted line).
Crosslinked polymers	E does not change. $E = 3\,n\,R\,T$; n = number of active network segments/unit volume (= ρ/M_c)		
Semi-crystalline polymers	Height of the plateau is increased. The crystalline domains act as a filler phase and as physical crosslinks		
4. Rubbery flow region	The polymer is characterized by rubber elasticity and flow properties. For short time experiments: the entanglements are not able to relax: rubbery behaviour Longer times: coordinated movement becomes possible: flow This region does not occur for crosslinked polymers	$10^{7} \rightarrow 10^{4}$	Depends on frequency of sampling: Fast = elastic; Slow= viscous
5. Liquid flow region	Polymer flows readily	For semi-crystalline polymers: E depends on the crystallinity. The measured modulus is a composite of the modulus of the amorphous and crystalline parts.	Movement of individual polymer molecules

Dynamic Mechanical Analysis (DMA)

DMA can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force

Modes of deformation:

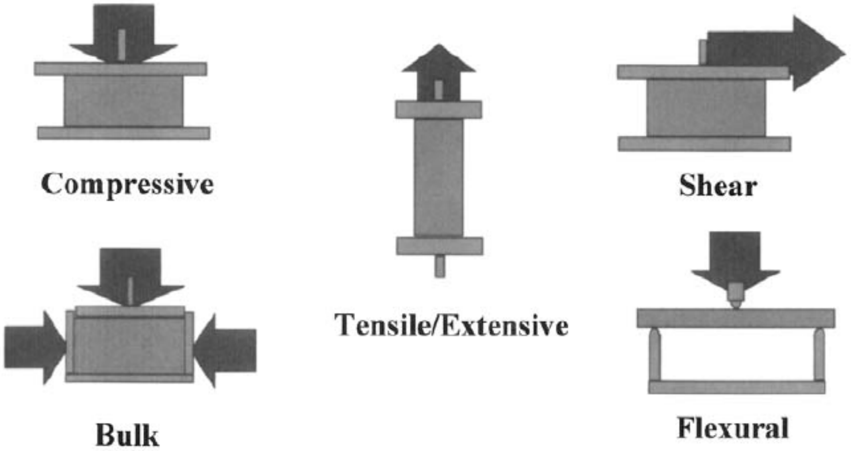


FIGURE 2.5 Modes of deformation. Geometric arrangements or methods of applying stress are shown. All of bottom fixtures are stationary. Bulk is 3-D compression, where sides are restrained from moving.

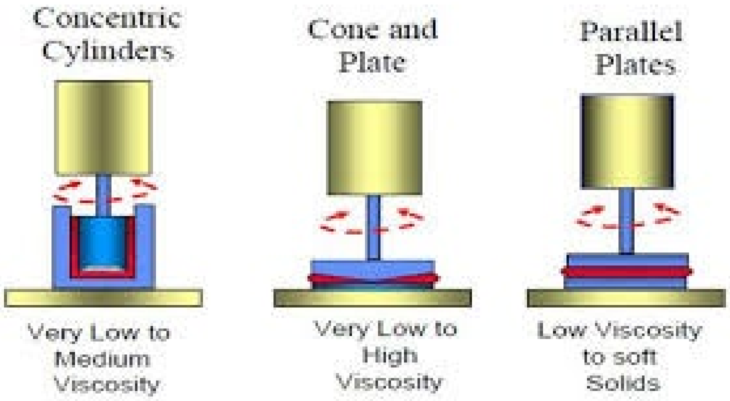
The letter used to designate the modulus changes depending on the geometry of the deformation:

E : Tensile/Extensive

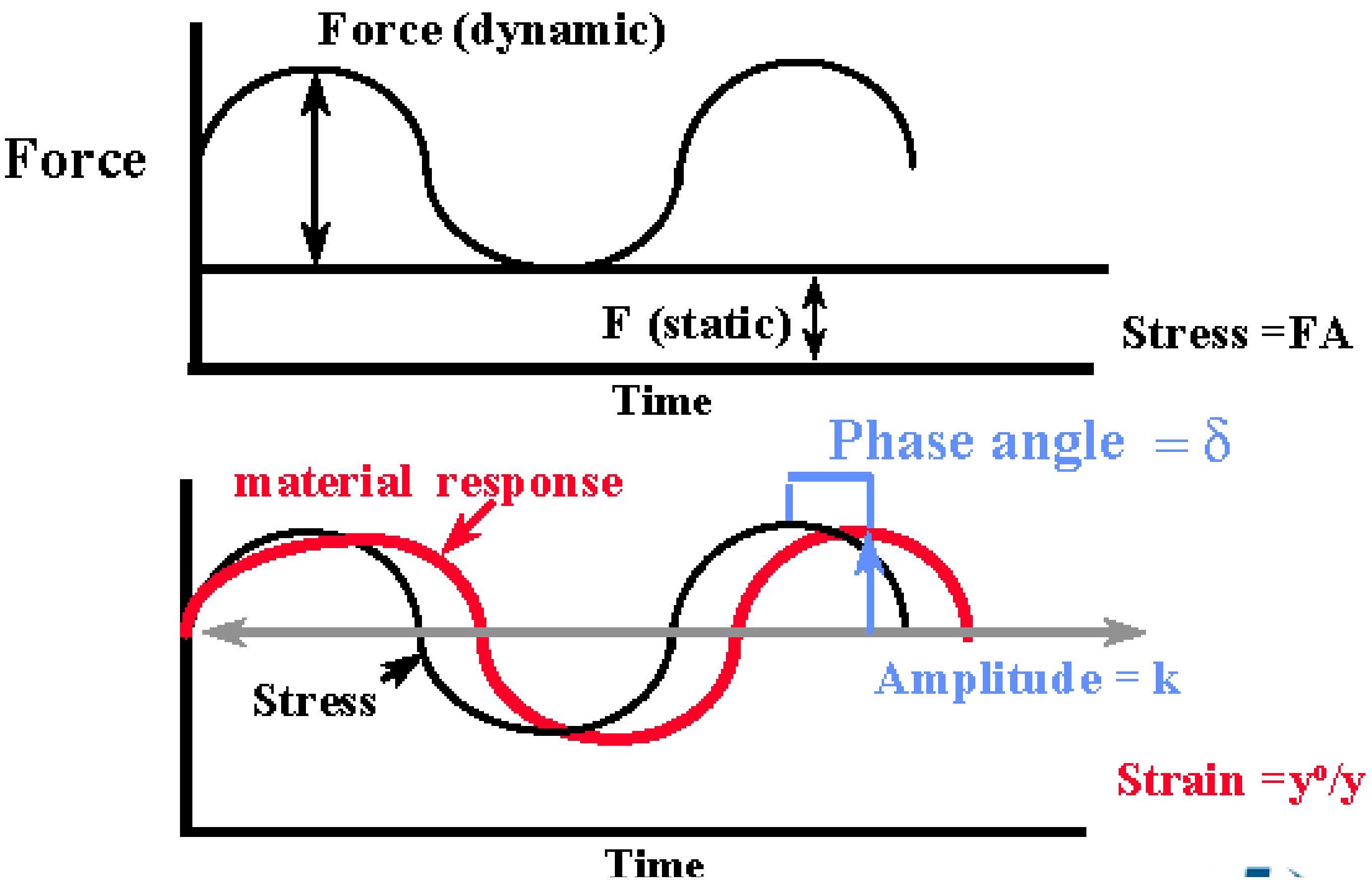
G: Shear and Flexural

K: Compressive and Bulk

Principle of DMA Instrument



Dynamic Stress and Strain

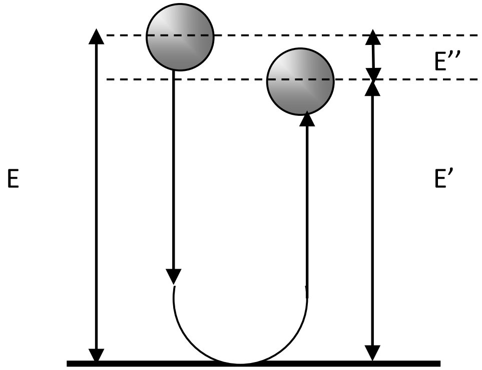


Dynamic Mechanical Behavior: Storage and Loss Moduli

E refer to quasistatic measurements (slow constant deformation).
When cyclical or repetitive motions of stress and strain are involved (sinusoidal deformation), the static modulus can therefore be decomposed into two dynamic mechanical moduli.

$$\sigma = E^* \varepsilon$$

Complex Young's modulus $E^* = E' + iE''$



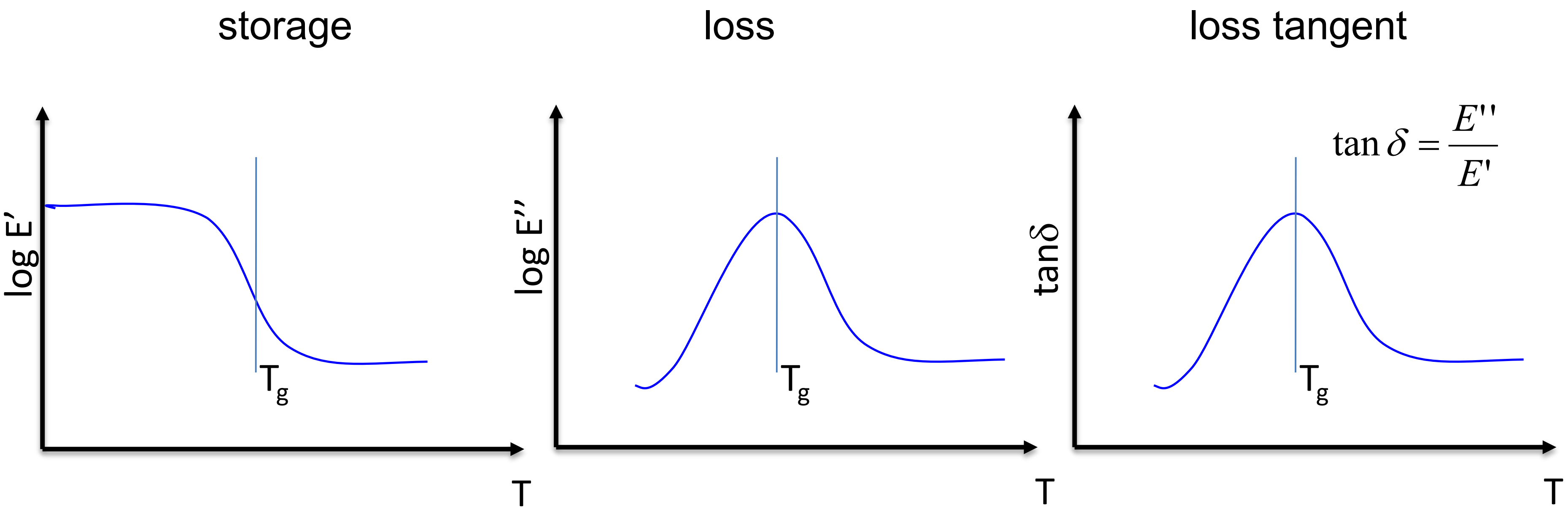
E' = storage modulus
measure of energy stored elastically during deformation

E" = loss modulus
measure of the energy lost to thermal transitions, movements of molecules, etc.…

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

Definitions of G*, D* and J* are similar

Transitions observed by DMA

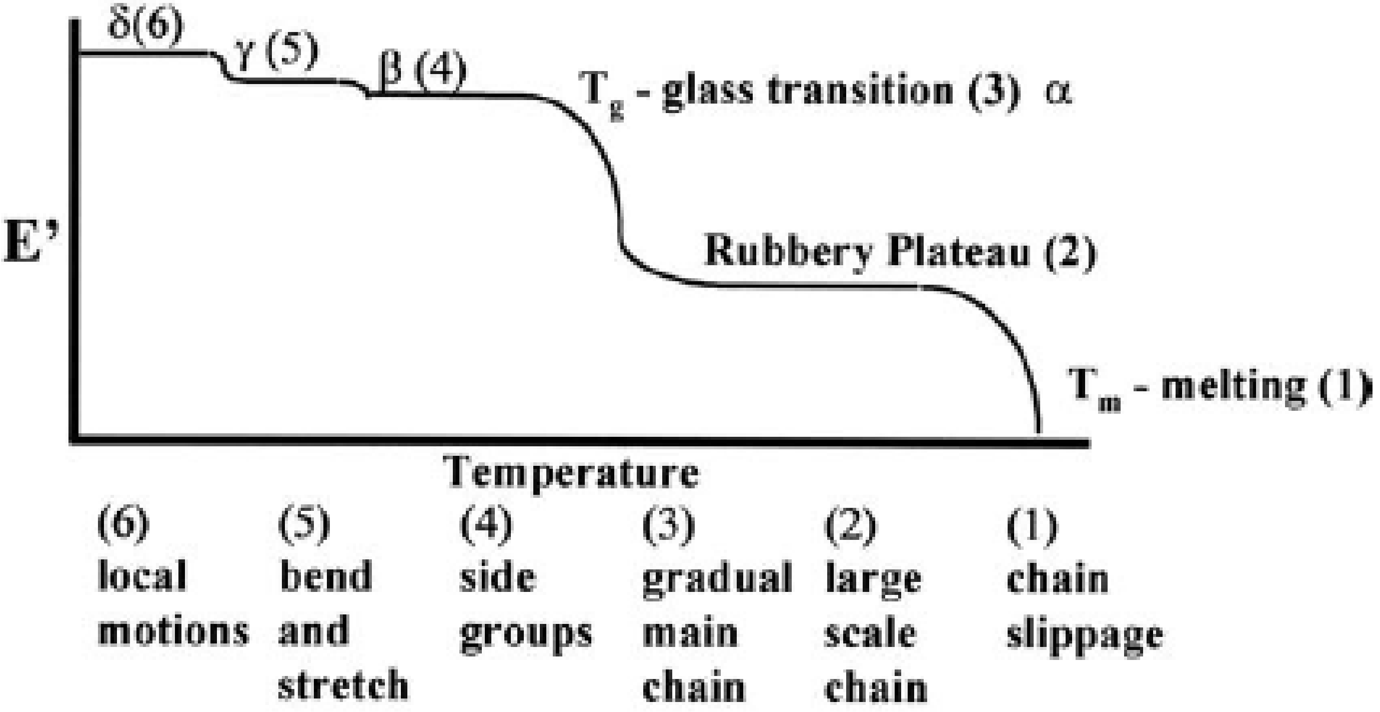


$$\tan\delta = \frac{E''}{E'}$$

As the temperature increases, a material becomes softer because the chains are more free to move.

At a transition, the energy required to make these molecules move causes a peak in the E'' and the tanδ spectrum.

Idealized DMA Scan



An idealized scan showing the effect of various molecular relaxations of the storage modulus, E'. In some materials like PET, the β-transition occurs as a broad slope, while in other it exhibits a relatively sharp drop.

Other Transitions and Relaxations

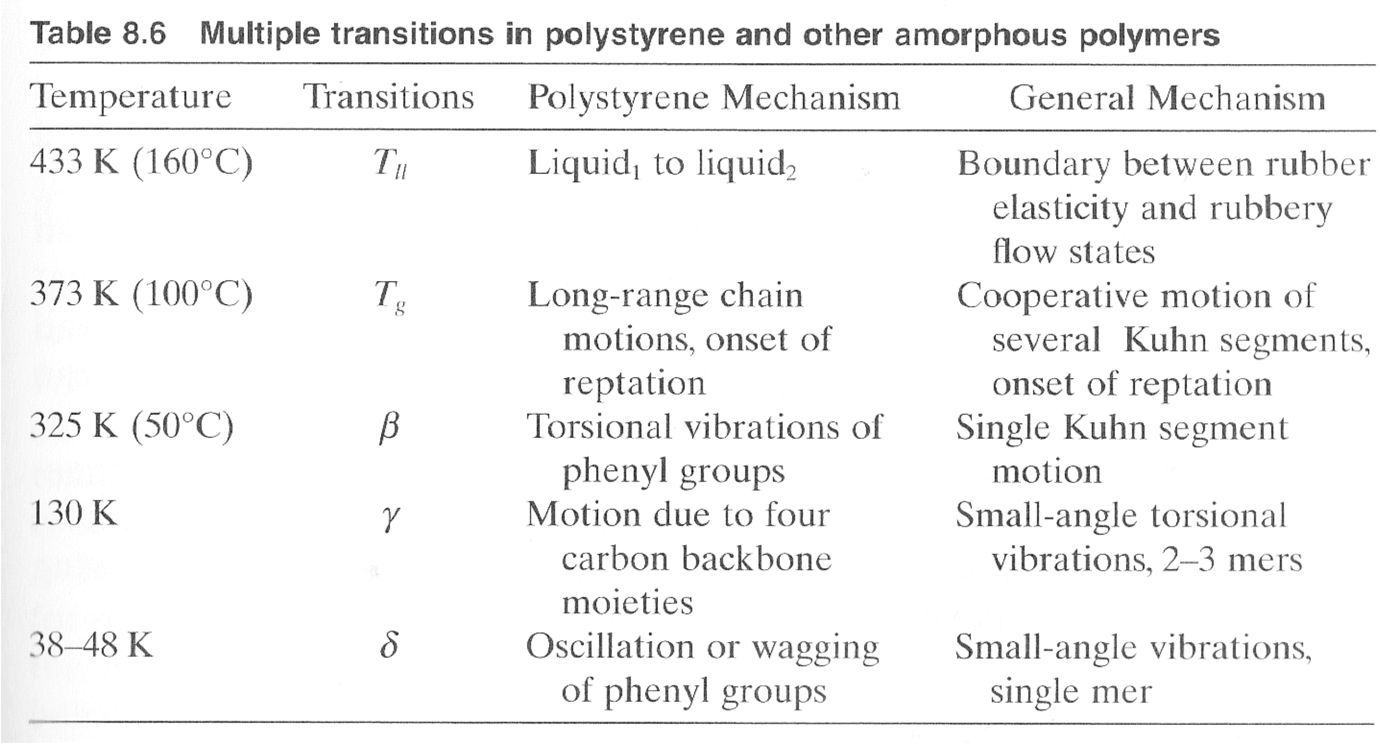


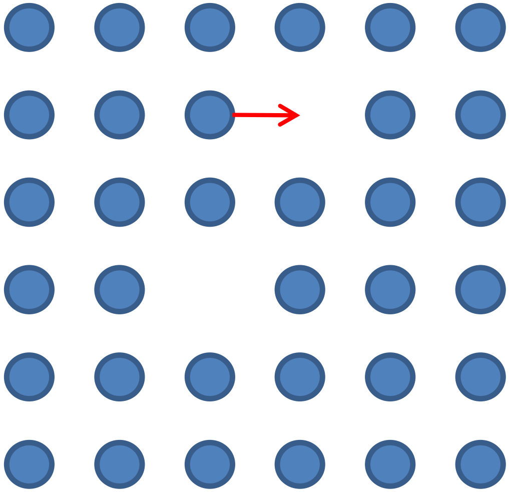
Table 8.6 Multiple transitions in polystyrene and other amorphous polymers

Temperature	Transitions	Polystyrene Mechanism	General Mechanism
433 K (160°C)	T_{ll}	Liquid_1 to liquid_2	Boundary between rubber elasticity and rubbery flow states
373 K (100°C)	T_g	Long-range chain motions, onset of reptation	Cooperative motion of several Kuhn segments, onset of reptation
325 K (50°C)	β	Torsional vibrations of phenyl groups	Single Kuhn segment motion
130 K	γ	Motion due to four carbon backbone moieties	Small-angle torsional vibrations, 2–3 mers
38–48 K	δ	Oscillation or wagging of phenyl groups	Small-angle vibrations, single mer

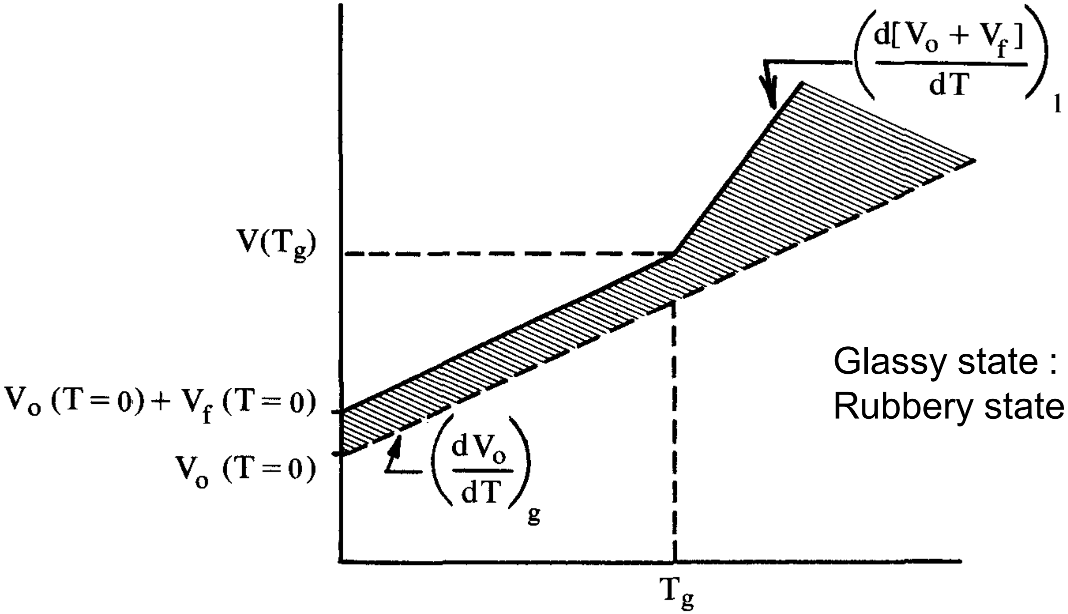
Glass Transition Theories

How can the glass transition be explained on a molecular level?

The Free-Volume Theory



Free Volume Theory



Glassy state : V_{Free} ~ 2.5 %
Rubbery state: V_{Free} ~ 5-6 %

Figure 4.15 Geometrical representation of the temperature variation of the actual volume (solid line) and the "occupied" volume (broken line). The shaded difference indicates the free volume which decreases to a critical value at T_g.

V (T) = observed volume of a sample = $V_0(T) + V_f(T)$

V_0 = occupied volume: increases with T due to changes in the amplitude of molecular vibrations with T, which affect the excluded volume of the molecules

V_f = free volume: refers to the „elbow room“ that molecules require to undergo rotation and translation motion, i.e. related to T_g !!

Williams-Landel-Ferry (WLF) Equation

The WLF equation is based upon the realization that free volume is needed to permit rotation of chain segments and that such rotations are hindered by neighboring chains. The WLF equation takes into account the time scale (t) of the experiment. Long times t (as well as higher T and lower η !) allow for greater probability of the required motion.

$$\log A_T = -\frac{B}{2.303 f_o} \times \frac{T - T_o}{\frac{f_o}{\alpha_f} + T - T_o}$$

with f_0 = fractional free volume
α_f = expansion coefficient of the free volume
$\ln A_T = \ln (t/t_0) = \ln (\eta/\eta_0)$

For many linear, amorphous polymers, the WLF equation can be simplified to:

$$\boxed{\log A_T = -\frac{C_1 (T - T_g)}{C_2 + (T - T_g)}}$$

where C_1 and C_2 are constants which are universal for most polymers. At T_g, $C_1 = 17.4$ and $C_2 = 51.6$

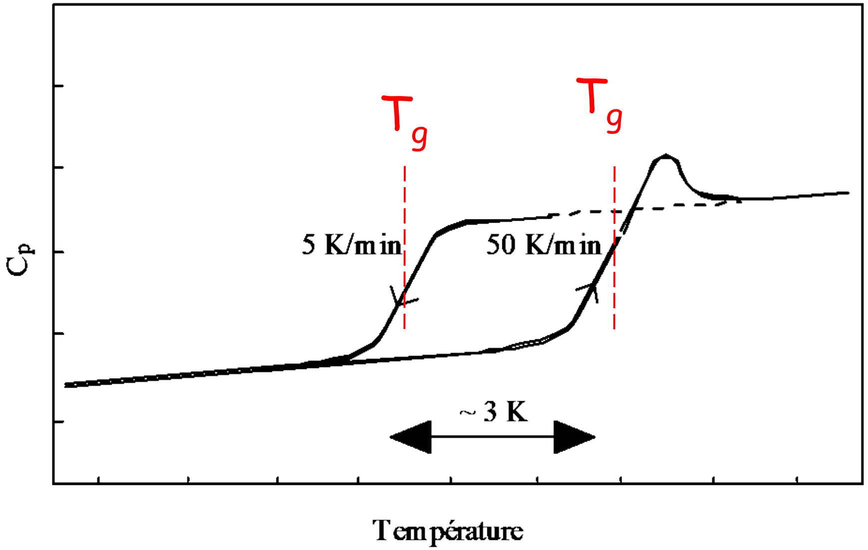
Williams-Landel-Ferry (WLF) Equation

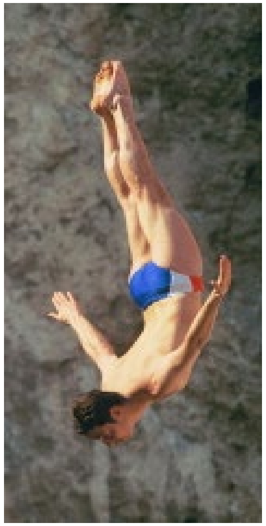
$$\log A_T = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

A shift in the log time scale will produce the same change in molecular motion as will the corresponding change in T

This is referred to as the time-temperature equivalence

This implies that the speed with which we measure the T_g will affect its value





The water "feels" harder when diving

Glass Transition Theories

TABLE 6.10 Glass Transition Theory Box Scores

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

1. The free-volume theory introduces free volume in the form of segment-size voids as a requirement for the onset of coordinated molecular motion. This theory provides relationships between coefficients of expansion below and above T_g and yields equations relating viscoelastic motion to the variables of time and temperature.

2. The kinetic theory defines T_g as the temperature at which the relaxation time for the segmental motions in the main polymer chain is of the same order of magnitude as the time scale of the experiment. The kinetic theory is concerned with the rate of approach to equilibrium of the system, taking the respective motions of the holes and molecules into account. The kinetic theory provides quantitative information about the heat capacities below and above the glass transition temperature and explains the 6–7°C shift in the glass transition per decade of time scale of the experiment.

3. The thermodynamic theory introduces the notion of equilibrium and the requirements for a true second-order transition, albeit at infinitely long time scales. The theory postulates the existence of a true second-order transition, which the glass transition approaches as a limit when measurements are carried out more and more slowly. It successfully predicts the variation of T_g with molecular weight and cross-link density (see Section 6.7), diluent content, and other variables.

The Effect of Molecular Weight on T_g

General:

$$T_g = T_{g,\infty} - \frac{K}{(\alpha_R - \alpha_G)M}$$

The increase in T_g with increasing molecular weight is due to the decrease in free volume caused by the decreased number of end groups

PS, slow heating rate

$$T_g = 106°\mathrm{C} - \frac{2.1 \times 10^5}{M_n}$$

PS, normal heating rate

$$T_g = 100°\mathrm{C} - \frac{1.8 \times 10^5}{M_n}$$

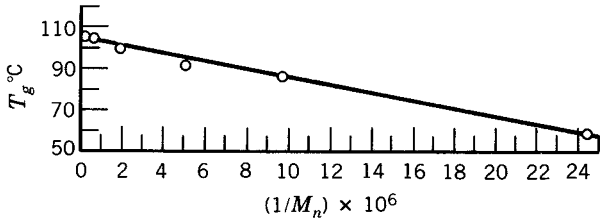


FIGURE 6.26 The glass transition temperature of polystyrene as a function of $1/M_n$ (27b).

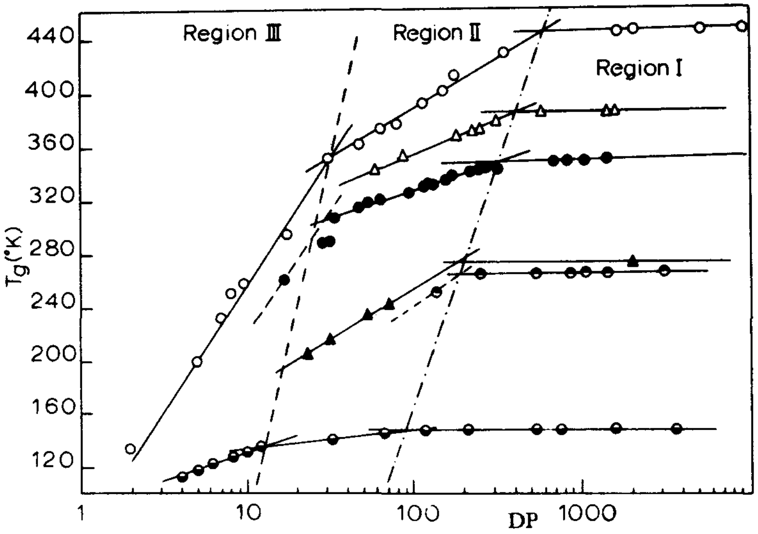


FIGURE 6.27 Plot of T_g (°K) as a function of log DP, the number of backbone chain atoms/bonds, for poly(α-methyl-styrene) (open circles); poly(methylmethacrylate) (open triangles); poly(vinyl chloride) (solid circles); isotactic polypropylene (solid triangles); atactic polypropylene (circles, top half solid); and poly(dimethylsiloxane) (circles, bottom half solid) (84a).

J.M.G. Cowie, Eur. Polym., 11, 297 (1975)

T_g's of Copolymers and Mixtures

1. Random copolymers and miscible polymer blends

Describes the T_g of random copolymers and one-phase mixtures of two polymers (homogeneous blends)

Fox equation:

$$\boxed{\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}}$$

W_1, W_2 = weight fractions

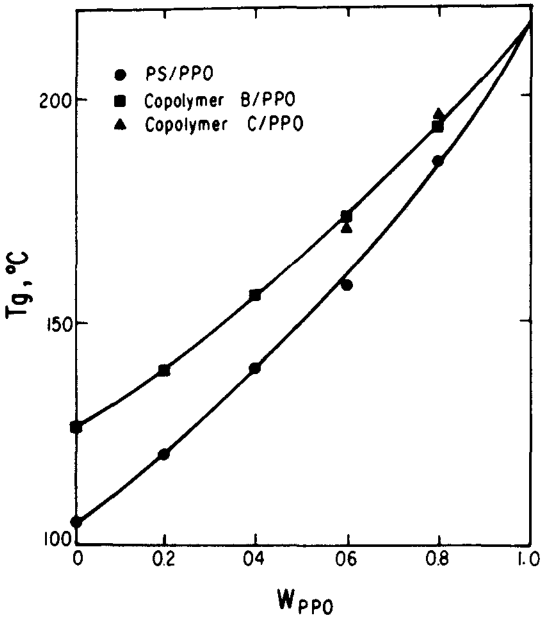


FIGURE 6.29 Glass-transition temperatures, T_g, of poly(2,6-dimethyl-1,4-phenylene oxide)-*blend*-polystyrene (PPO/PS) blends versus mass fraction of PPO, M_{PPO}. The full curve was calculated from equation (6.70) as circles. $\Delta C_{p1} = 0.0671$ cal K^{-1} g^{-1}, $\Delta C_{p2} = 0.0528$ cal K^{-1} g^{-1}; $T_{g1} = 378$ K, $T_{g2} = 489$ K. PPO was designated as component 2 (85, 92).

Use of Fox Equation

4.6: Di-n-ethylhexyl phthalate (DEHP) and related compounds are commonly used to plasticize poly(vinyl chloride) (PVC) to produce pliable material generically referred to as "vinyl". A good plasticizer is miscible with the polymer in question, does not crystallize itself, and has a very low vapor pressure. What fraction of DEHP should be added to PVC to bring T g down below room temperature, say 293K, given that Tg for DEHP is about -86°C and for PVC 90°C respectively?

T_g‘s of Copolymers and Mixtures

2. Block copolymers and immiscible polymer blends

Most polymers do not mix and will separate in two phases, each characterized by their own T_g. Block copolymers can also phase separate into different phases, which each shown their own T_g

Characterization of the T_g can provide information about the polymer miscibility and about the occurence of phase separation in block copolymers

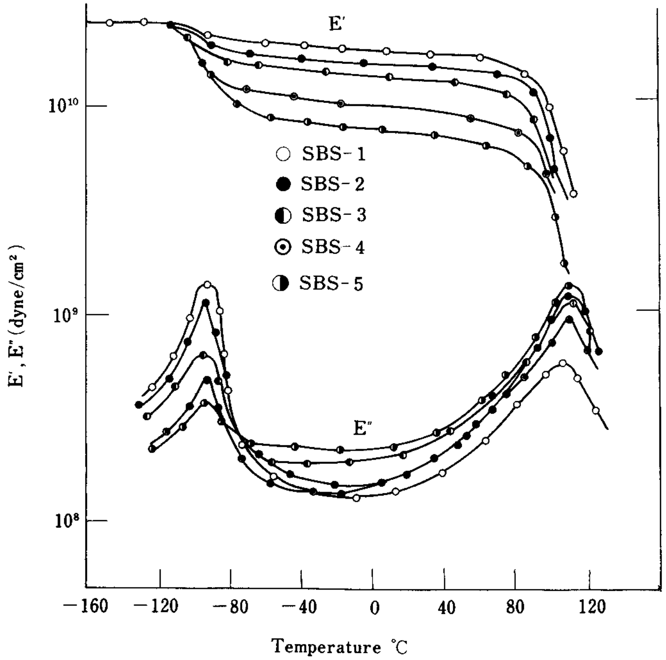


FIGURE 6.30 Dynamic mechanical behavior of polystyrene-*block*-polybutadiene-*block*-polystyrene, a function of the styrene–butadiene mole ratio (95, 96).

The Effect of Chemical Structure on T_g

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	

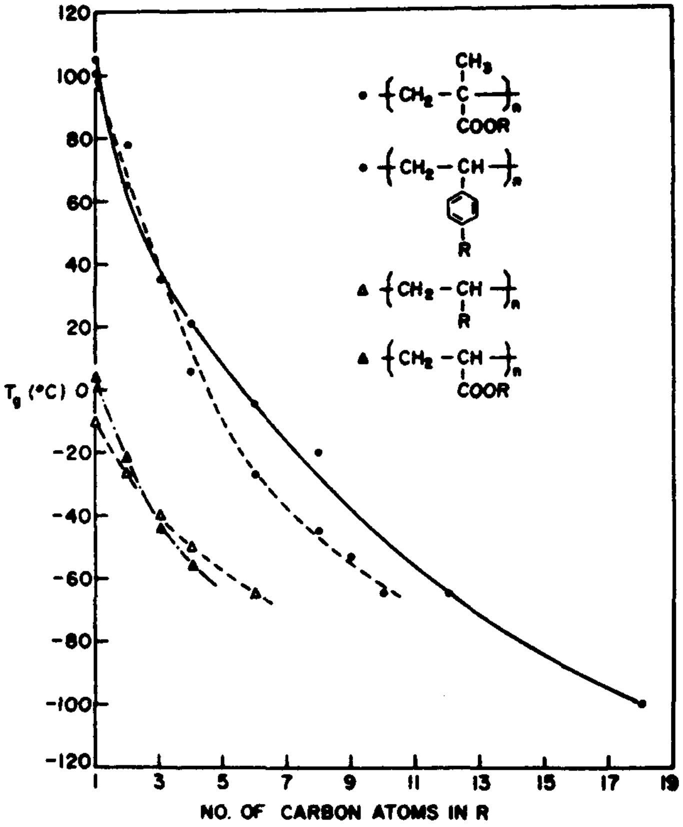


FIGURE 6.33 Effect of side-chain lengths on the glass transition temperatures of polymethacrylates (open circles [S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985, 1957]); poly–p–alkyl styrenes (solid circles [W. G. Barb, *J. Polym. Sci.*, **37**, 515, 1959]); poly–α–olefins (open triangles [M. L. Dannis, *J. Appl. Polym. Sci.*, **1**, 121, 1959; K. R. Dunham, J. Vandenbergh, J. W. H. Farber, and L. E. Contois., *J. Polym. Sci.*, **1A**, 751, 1963]); and polyacrylates (solid triangles [J. A. Shetter, *Polym. Lett.*, **1**, 209, 1963]) (26).

Effect of Crystallinity on T_g

So far studying of amorphous polymers, like atactic polystyrene.
But semicrystalline polymers like polyethylene or polypropylene or the polyamide and – ester types also exhibit glass transitions because of the amorphous portions

Semicrystalline polymers appear to posses 2 T_g’s:

- a lower one that refers to the completely amorphous state
- an upper value that occurs in the semi-crystalline material and varies with extent of crystallinity and morphology

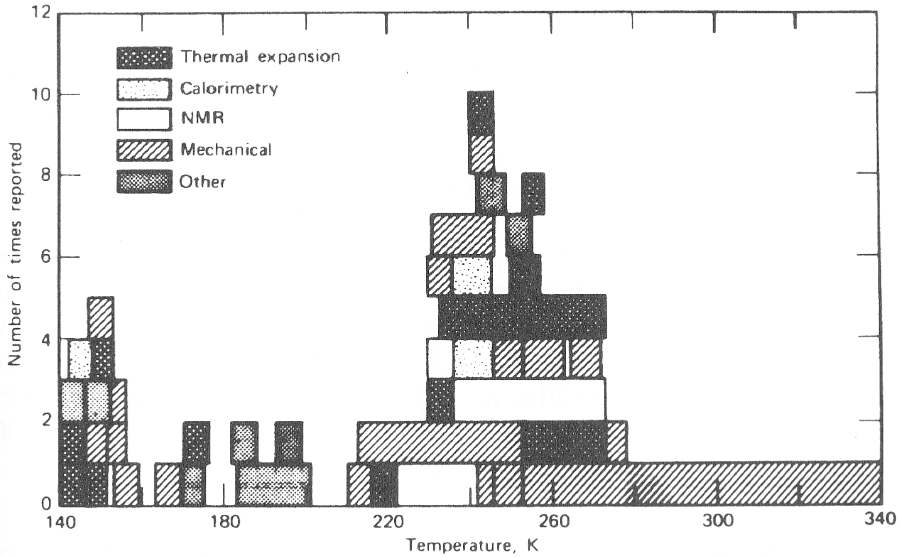


Figure 8.30 Histogram showing number of times a given value of T_g for linear polyethylene has been reported in the literature by various standard methods indicated (126).

Linear polyethylene has a high crystallinity 80% and no side groups. There are found 3 secondary transitions: -30°C, -80°C, -128°C

Summary

1. The glass transition is a kinetic transition, but it approximates a second-order thermodynamic transition.
2. The glass transition temperature may be located in a variety of ways, but the most common tools are DSC and DMA.
3. T_g is the single most important parameter in determining whether a given polymer may be suitable for a certain application. There is no simple way to correlate T_g with a particular structure, although some general rules of thumb exist.
4. The value of T_g may be modified by changing molecular weight or by blending, the molecular weight and composition dependences of T_g are generally straightforward.
5. The concept of free volume is a particularly useful and physically intuitive way to understand the glass transition, and the profound effect that proximity to T_g has on the temperature dependence of any viscoelastic or transport property. The free volume approach provides natural explanation for the widely used WLF-equation, which describes the temperature dependence of viscoelastic properties above T_g.