Glass-Rubber Transition

A Second order Transition Important in Polymeric Systems

Change in Specific Volume

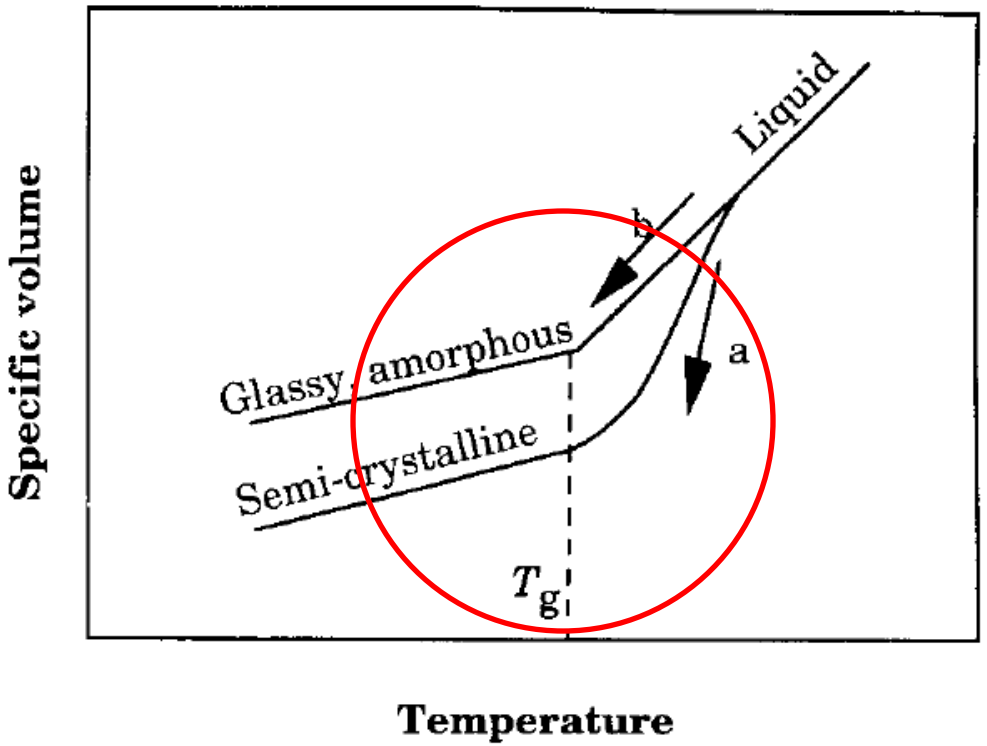


Figure 5.1 Cooling of a liquid following routes a (crystallization) or b (forming a glassy amorphous structure).

Effect of structure, side chain effect

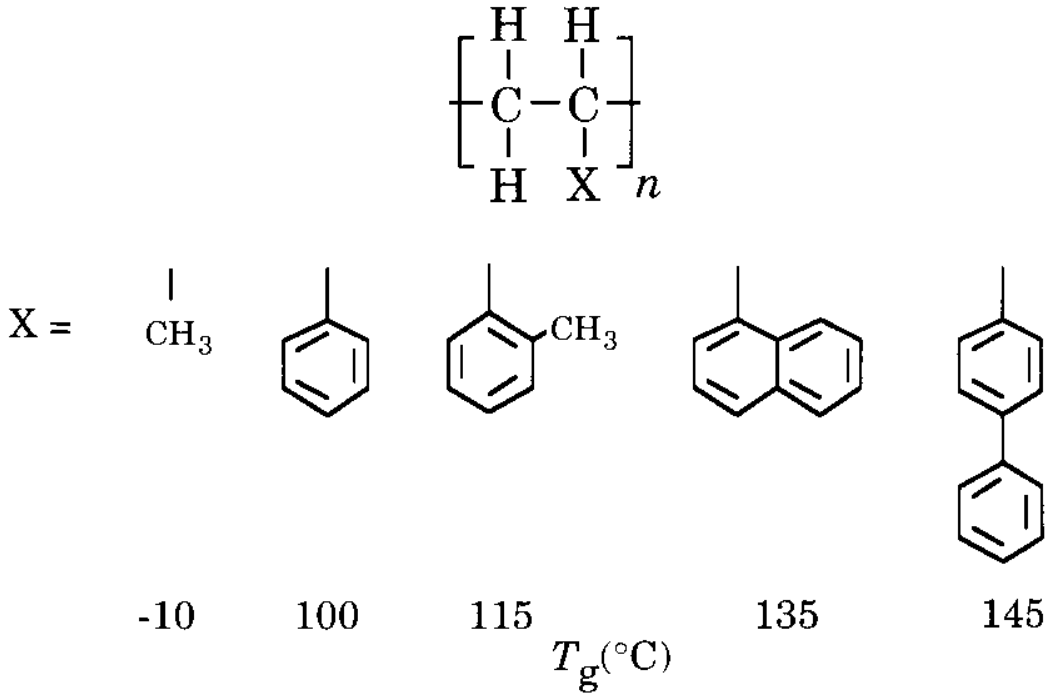


Figure 5.3 Glass transition temperatures of different vinyl polymers showing the influence of the size of the pendant group. Data from Eisenberger (1984).

Effect of structure, flexible side chains

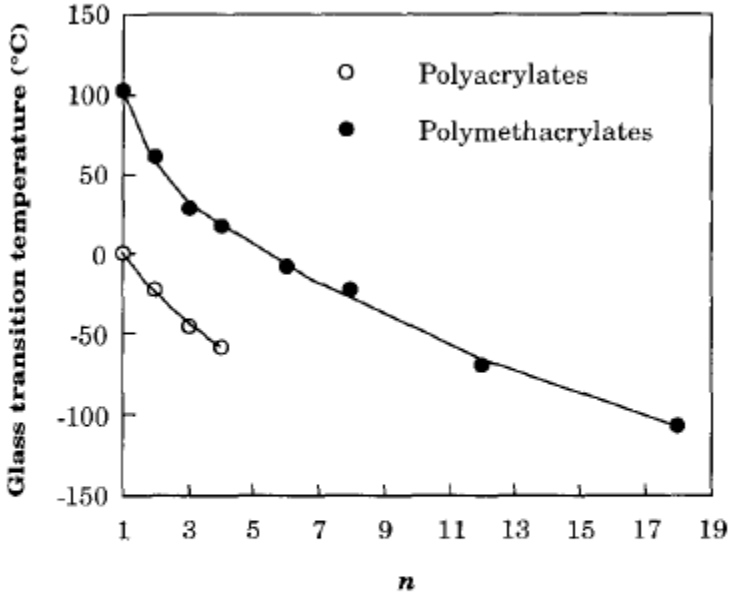


Figure 5.4 Glass transition temperature of polyacrylates and polymethacrylates as a function of number of carbons (n) in the oligo-methylene (R) group. Drawn after data from Rogers and Mandelkern (1957) (polymethacrylates) and Shetter (1963) (polyacrylates).

Effect of structure, chlorine effect

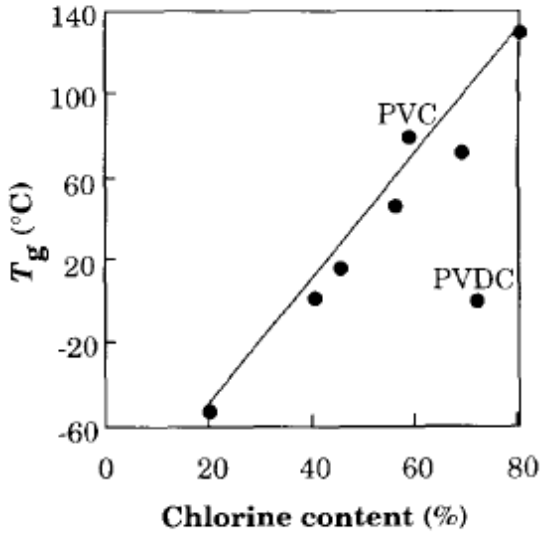


Figure 5.5 Effect of chlorine content on the glass transition temperature of chlorinated polyethylene. Data for polyvinylchloride (PVC) and polyvinylidene chloride (PVDC) are shown for comparison. Drawn after data from Schmieder and Wolf (1953).

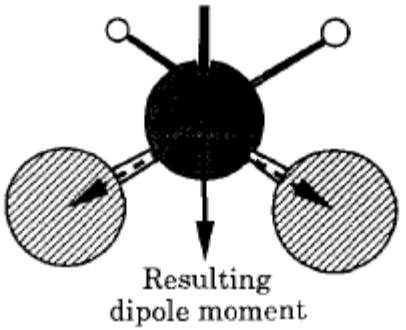


Figure 5.6 Repeating unit of polyvinylidene chloride and schematic representation of the resulting dipole moment.

Effect of structure, cohesive energy density

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

where δ^2 is the CED, m is a parameter which describes the internal mobility of the groups in a single chain, R is the gas constant and C_1 is a constant. The CED provides an integrated measure of the strength of the secondary bonds in a compound. Materials with strong secondary bonds show high CED values.

Effect of structure, cohesive energy density

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

Beaman (1953) and Boyer (1954) noticed in the early 1950s that both T_g and the melting point (T_m) of crystallizable polymers increased with decreasing chain flexibility and increasing CED. They established the following empirical correlations:

$$\frac{T_g}{T_m} = \frac{1}{2} \qquad \text{(symmetrical molecules)} \qquad (5.2)$$

$$\frac{T_g}{T_m} = \frac{2}{3} \qquad \text{(asymmetrical molecules)} \qquad (5.3)$$

According to more recent data, about 80% of the data for symmetrical and asymmetrical polymers are within the T_g/T_m limits 0.5–0.8.

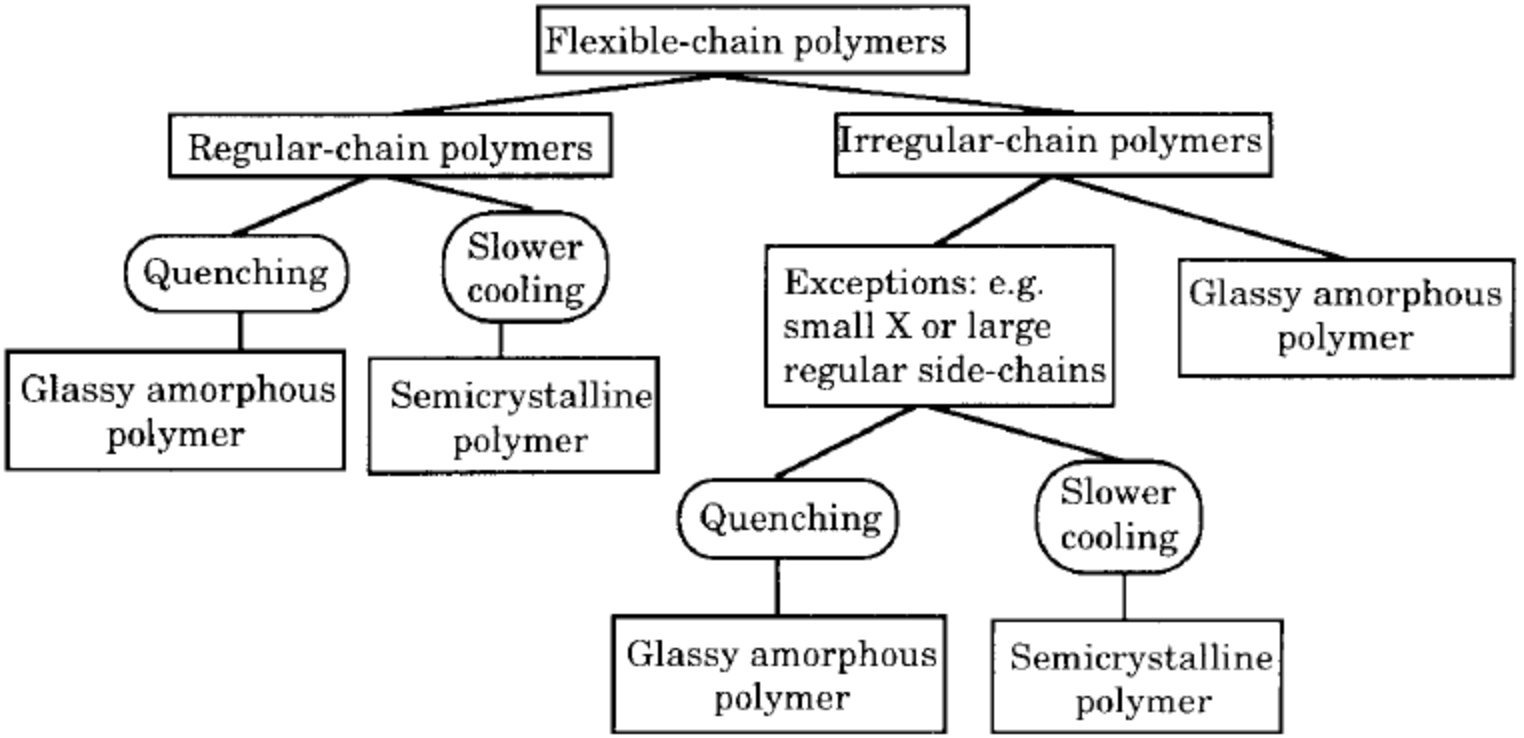
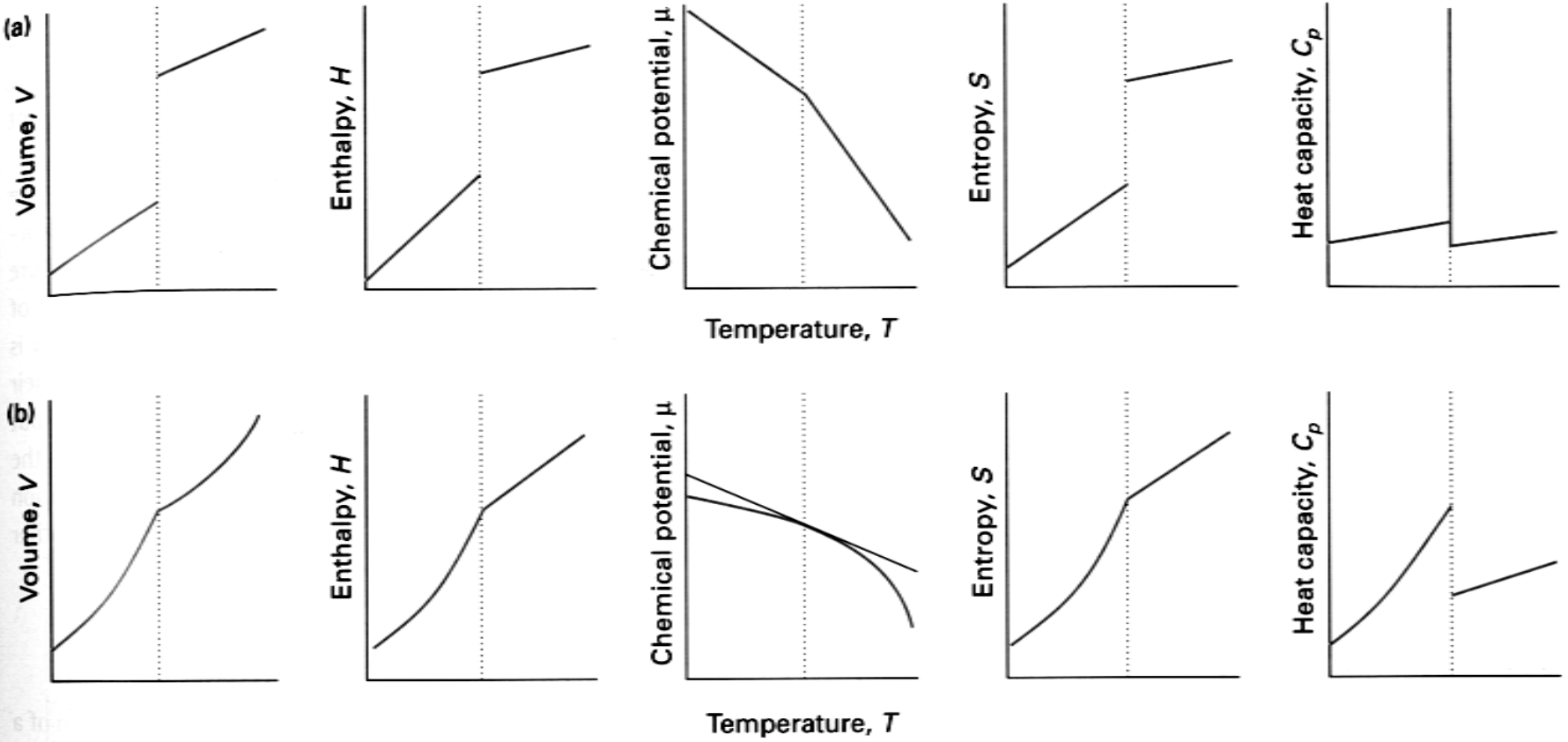


Figure 5.2 The effect of molecular and thermal factors on the structure of the solidified polymer.

1.Types of Transitions Ehrenfest Classification

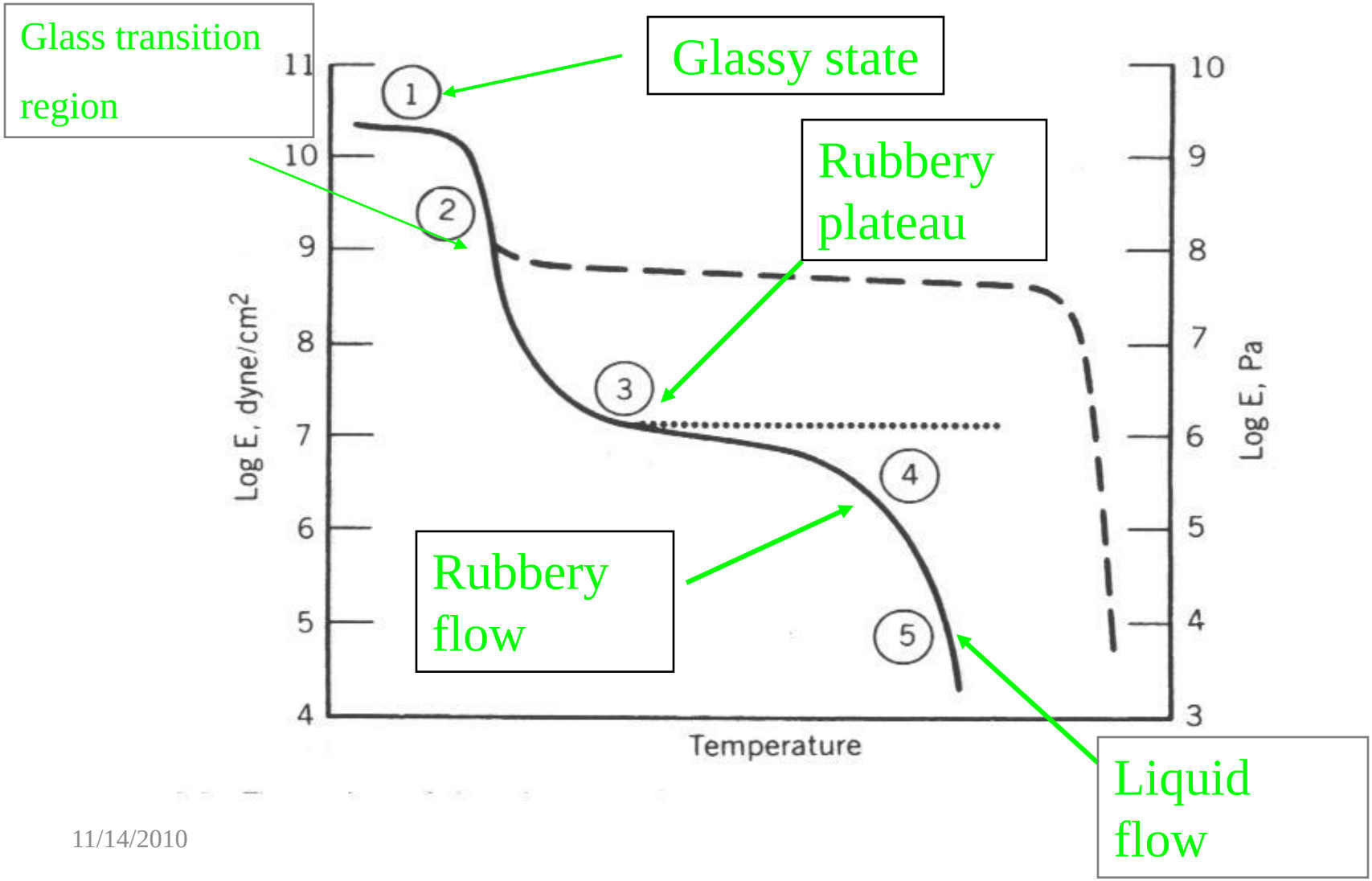
- **Classification of Transitions into :**
  - **First-order, first derivative of chemical potential with respect to T is discontinuous during the transition.**
  - **Second-order first derivative of chemical potential with respect to T remain continuous during the transition.**


(a)
Volume, V
Enthalpy, H
Chemical potential, μ
Entropy, S
Heat capacity, C_p
Temperature, T
(b)
Volume, V
Enthalpy, H
Chemical potential, μ
Entropy, S
Heat capacity, C_p
Temperature, T

2.Glass-Rubber Transition

- **The state of a polymer depends on temp. and time allotted**
- **At low enough tepms. Amorphous polymers are stiff and brittle(glassy State)**
- **Warming cause the polymer soften in the glass-rubber transition temp.**
- **“the glass transition temp. is perhaps the most important parameter that determines the application of many noncrystaline polymers”, (Eisenburg’s statement)**

2.1The Glassy Region



2.2.Glassy region

- *E,* $3x10^{10}$ dyne/cm^2 ($3x10^9$ Pa) for most polymers
- Molecules have restricted motion and vibration

2.3.Glass Transition Region

- The modulus drops a factor of 1000 over 20-30 °C range
- T_g is often taken at the maximum turndown
- T_g is defined as thermal expansion coefficient undergoes a discontinuity
- The onset of long-range molecular motions
- The glass-transition temp varies with structure and other parameters

Table 8.4 Glass transition parameters (8,14)

Polymer	T_g, °C	Number of Chain Atoms Involved
Poly(dimethyl siloxane)	−127	40
Poly(ethylene glycol)	−41	30
Polystyrene	+100	40–100
Polyisoprene	−73	30–40

2.3.The Rubbery Plateau Region

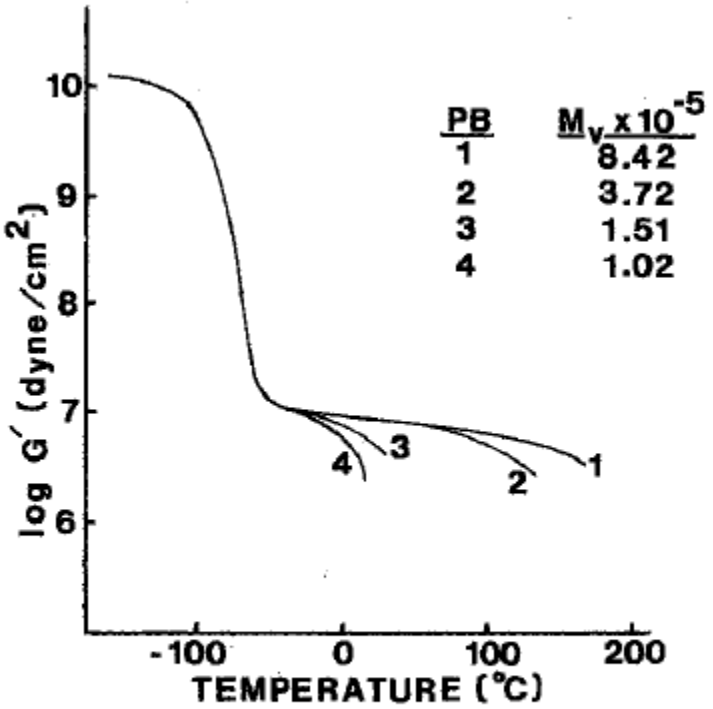


Figure 8.3 Effect of molecular weight on length of plateau (16). PB = polybutadiene.

2.3.The Rubbery Plateau Region

- The effect of crystallinity:
- If a polymer is semicrystalline, the dashed line in F
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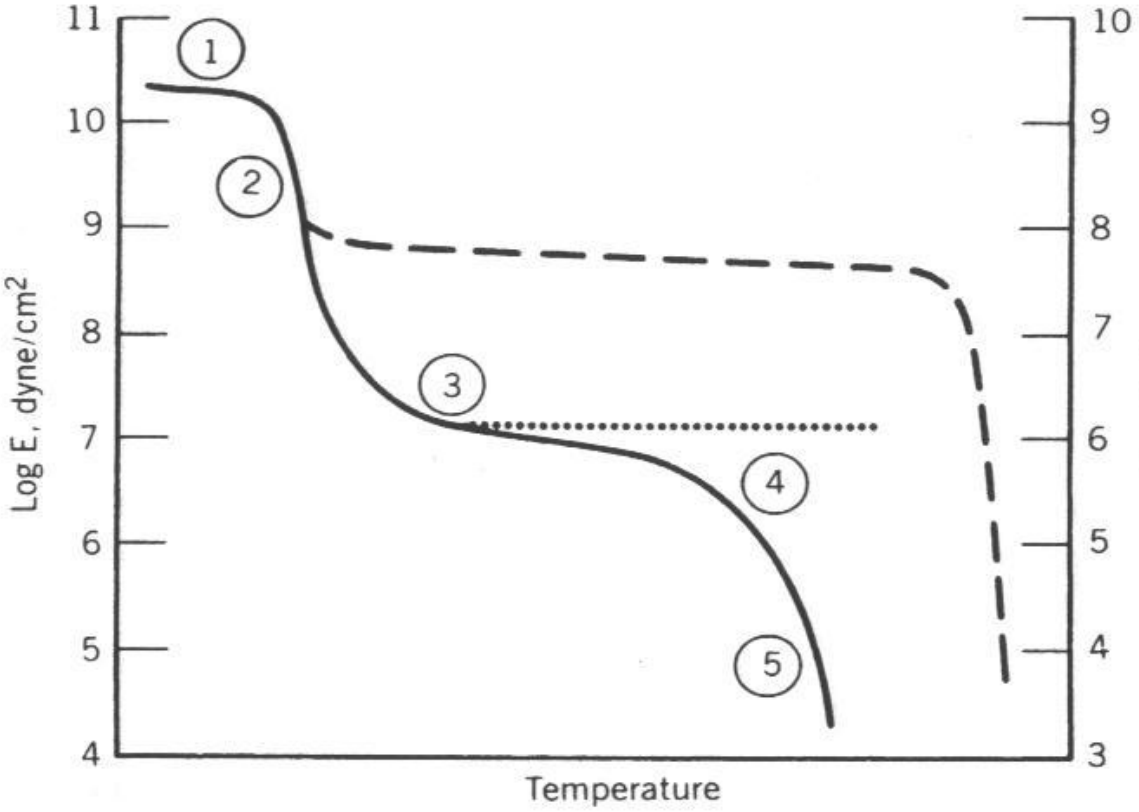
  c
- T talline
  r cond,
  b type
  c

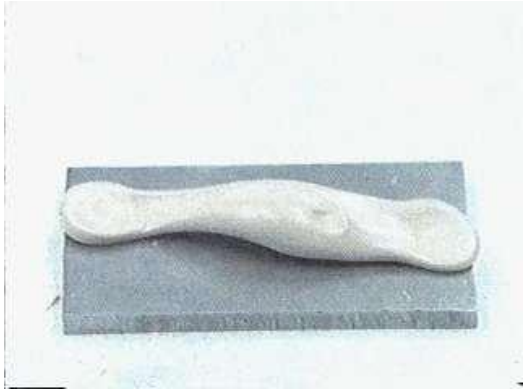


2.4.The Rubbery Flow Region

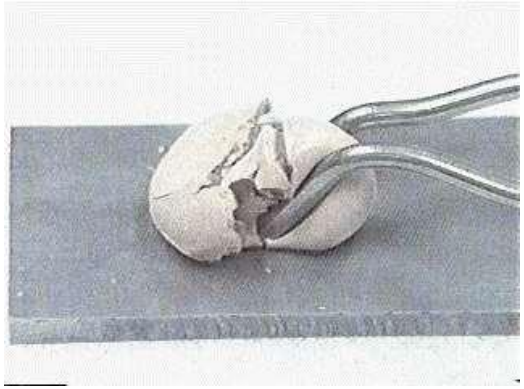
- Rubber elasticity and flow properties.
- Rubber in short time experiments.
- Chain assemblies flow in long term experiments.
- This region does not appear for cross-linked polymers until decomposition temp. is reached.

2.4.The Rubbery Flow Region

A striking example of the rate dependence of these viscoelastic properties is furnished by Silly Putty. Slowly pulling on two parts of the Silly Putty stretches it apart until it very slowly separates. Placing the Silly Putty on a table and hitting it with a hammer will shatter it.

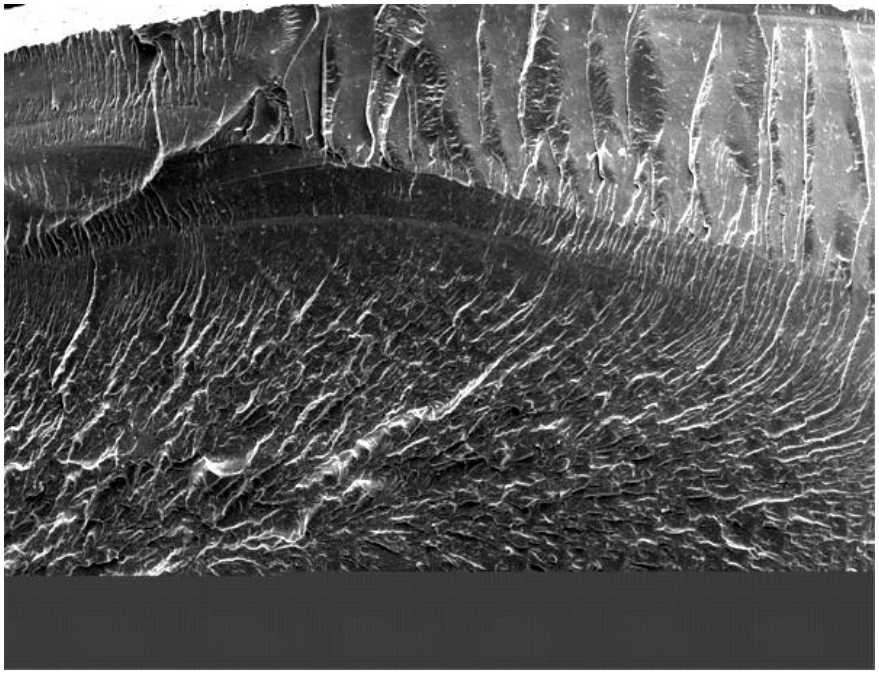


Slowly Deformed



Rapidly Deformed

The brittle fracture



The obvious brittle properties exhibited by the elastomer below the glass transition temperature were confirmed through an examination of the fracture surface via scanning electron microscopy (SEM). The fracture surface exhibited classic brittle crack features, including a generally smooth morphology with hackle marks. The fracture surface contained features normally observed on amorphous thermoplastic materials. Amorphous thermoplastics are used at temperatures below their glass transition temperature, and as such the similarity in fracture surface morphology between such materials and the subambient rubber represents the glassy, brittle state of the material, and not the composition of the material.

2.5.The Liquid Flow Region

- Polymer flows easily
- A composite modulus is observed for semi-crystalline polymers. The amorphous portions go through the glass transition, but the crystalline portion remains hard.

3.The Effect of Plasticizers

- Plasticizers are nonvolatile molecules dissolved in polymer(soften it).
- The glass-transition temp is lowered and rubbery plateau modulus is lowered.
- In semi-crystalline polymers lower the melting point or lower the crystallinity.

Adding a small amount of *plasticizer* to PVC can lower the T_g to – 40 degrees C. This addition renders the PVC a soft, flexible material at room temperature, ideal for applications such as garden hoses. A plasticized PVC hose can, however, become stiff and brittle in winter. In this case, as in any other, the relation of the T_g to the ambient temperature is what determines the choice of a given material in a particular application.

4.Methods Of Measuring Transitions

- **Definitions of the Terms “Transition,” “Relaxation,” and “Dispersion”.**
  - The term “transition” refers to a change of state induced by changing the temperature or pressure.
  - The term “relaxation” refers to the time required to respond to a change in temperature or pressure. It also implies some measure of the molecular motion, especially near a transition condition.
  - The term “dispersion” refers to the emission or absorption of energy—that is, a loss peak—at a transition. In practice, the literature sometimes uses these terms somewhat interchangeably.

4.Methods Of Measuring Transitions

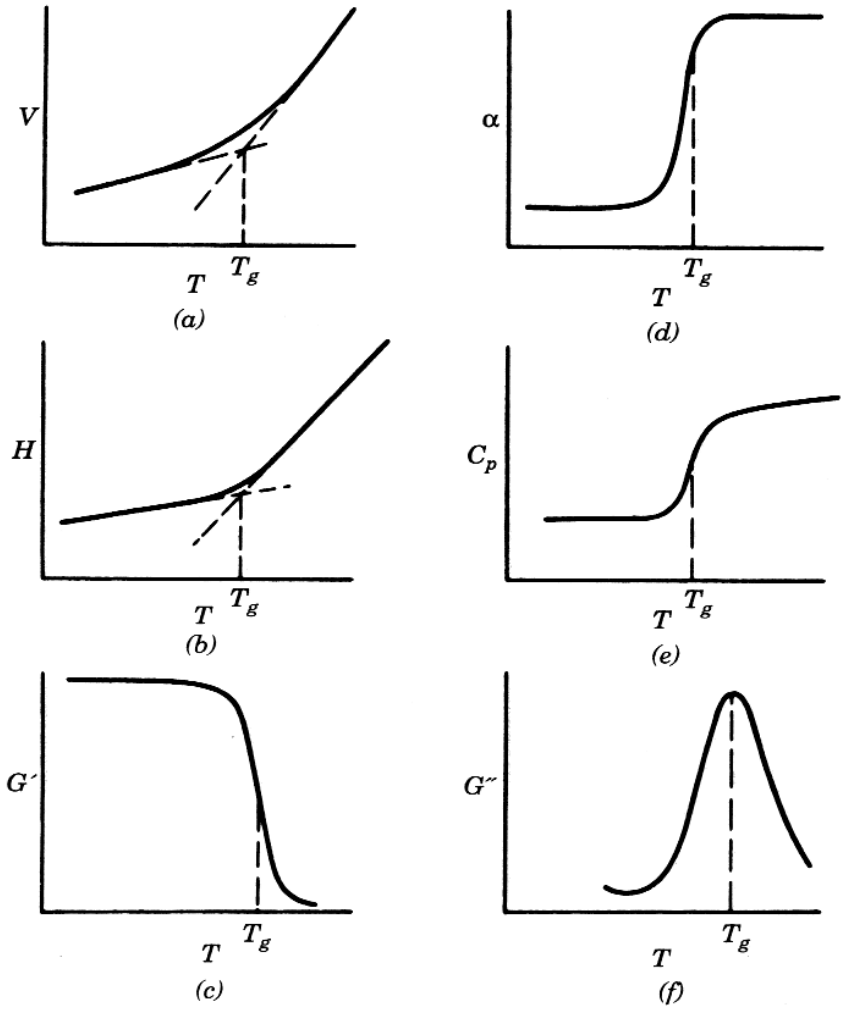


Figure 8.5 Idealized variations in volume, *V*, enthalpy, *H*, and storage shear modulus, *G′* as a function of temperature. Also shown are α, the volume coefficient of expansion, and C_p, the heat capacity, which are, respectively, the first derivatives of *V* and *H* with respect to temperature, and the loss shear modulus, *G″* (8).

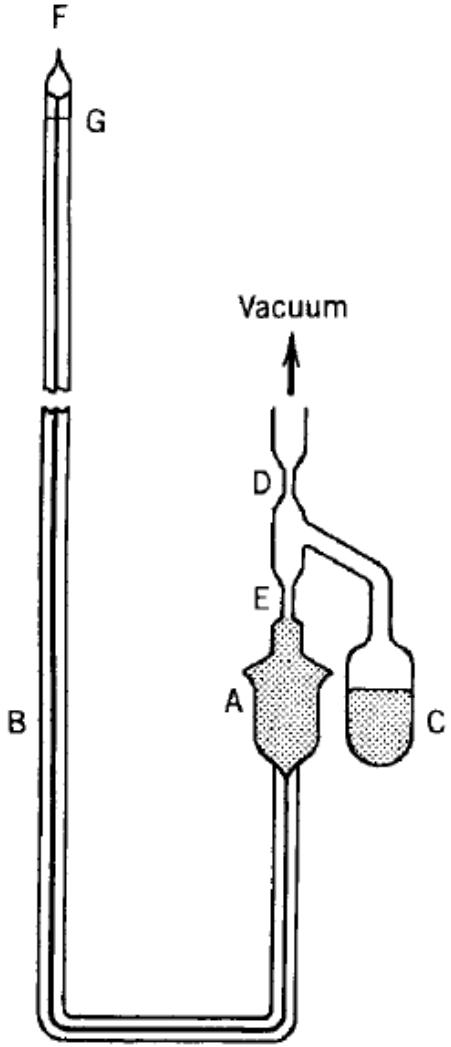
4.1. Experimental Methods

Table 8.5 Methods of measuring the glass transition and thermal properties

Method	Representative Instrumentation
Dilatometry	
Volume-temperature	Polymer confined by mercury (home made)
Linear expansivity	TMS + computer
Thermal	
DSC	Modulated DSC 2920 (TA Instruments)
DTA	DuPont 900
Calorimetric, C_p	Perkin-Elmer modulated DSC, Pyris 1
Mechanical	
Static	Gehman, Clash-Berg
Dynamic	Rheometrics RDA2 (Rheometrics Scientific)
Torsional Braid Analysis	TBA (Plastics Analysis Instruments)
Dielectric and magnetic	
Dielectric loss	DuPont Dielectric Analyzer, DEA 2920
Broad-line NMR	Joel JNH 3H60 Spectrometer
Melt viscosity	Weissenberg Rheogoniometer
TGA	HiRes TGA 2950 (TA Instruments)

4.1.1. Dilatometry Studies

A mercury-based dilatometer. 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.*



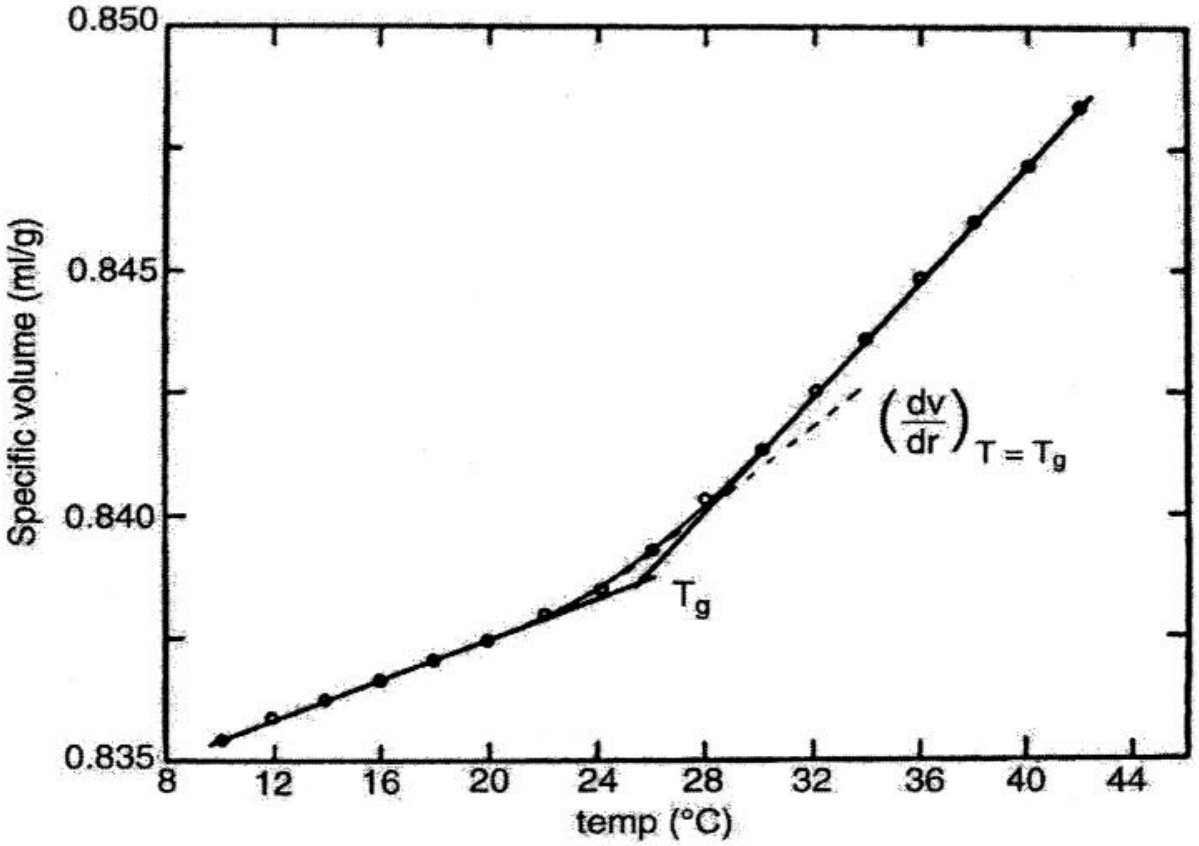
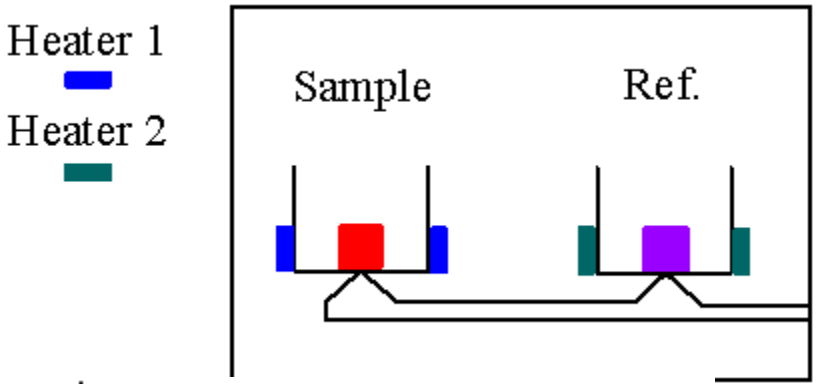
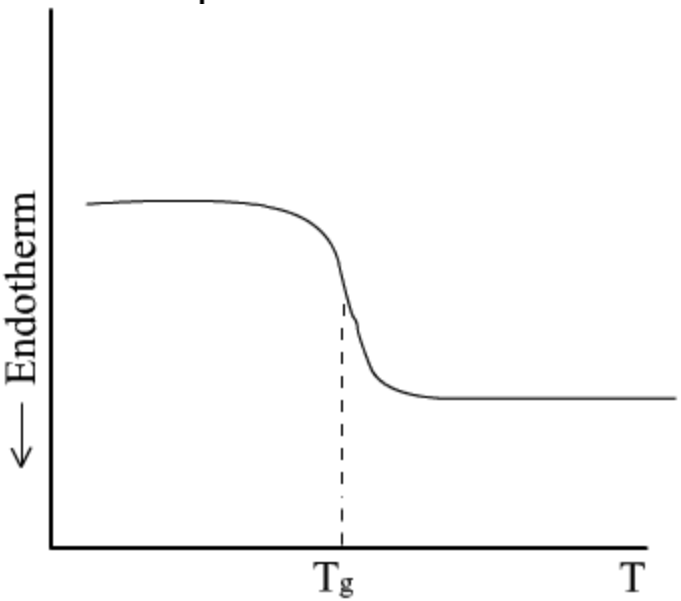


Figure 8.9 Dilatometric studies on branched poly(vinyl acetate) (23).

4.1.2. DSC Method





Some measurements that the DSC can make are:

Glass Transitions
Melting and Boiling Points
Crystallisation time and temperature
Percent Crystallinity
Heats of Fusion and Reactions
Specific Heat and Heat Capacity
Oxidative Stability
Rate and Degree of Cure
Reaction Kinetics
Percent Purity
Thermal Stability

4.1.2. DSC Method

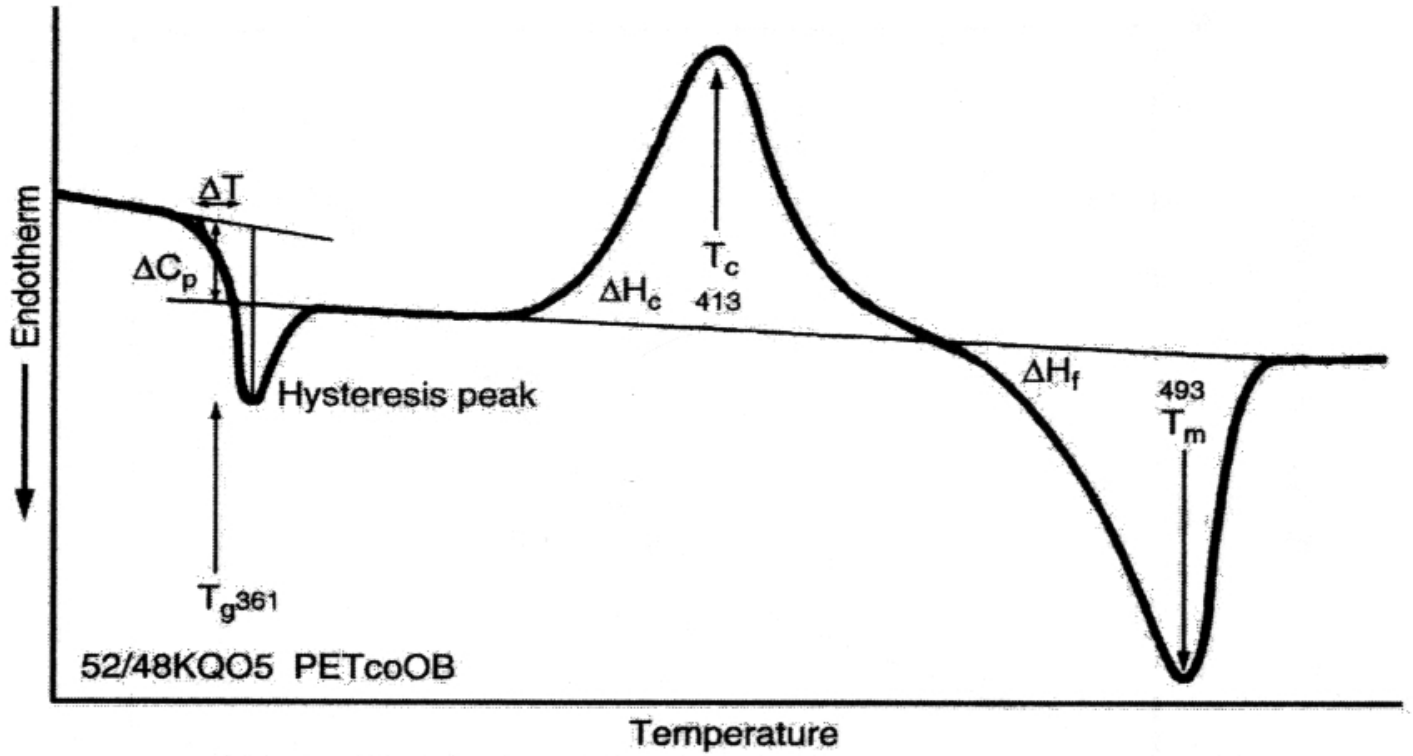
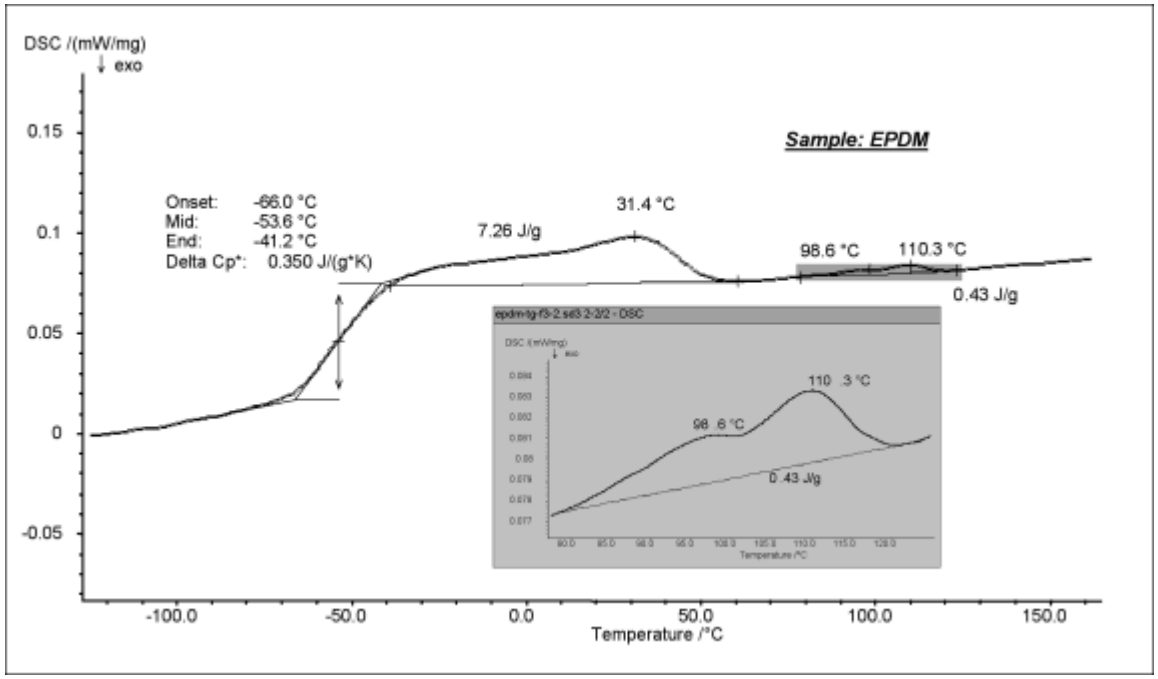
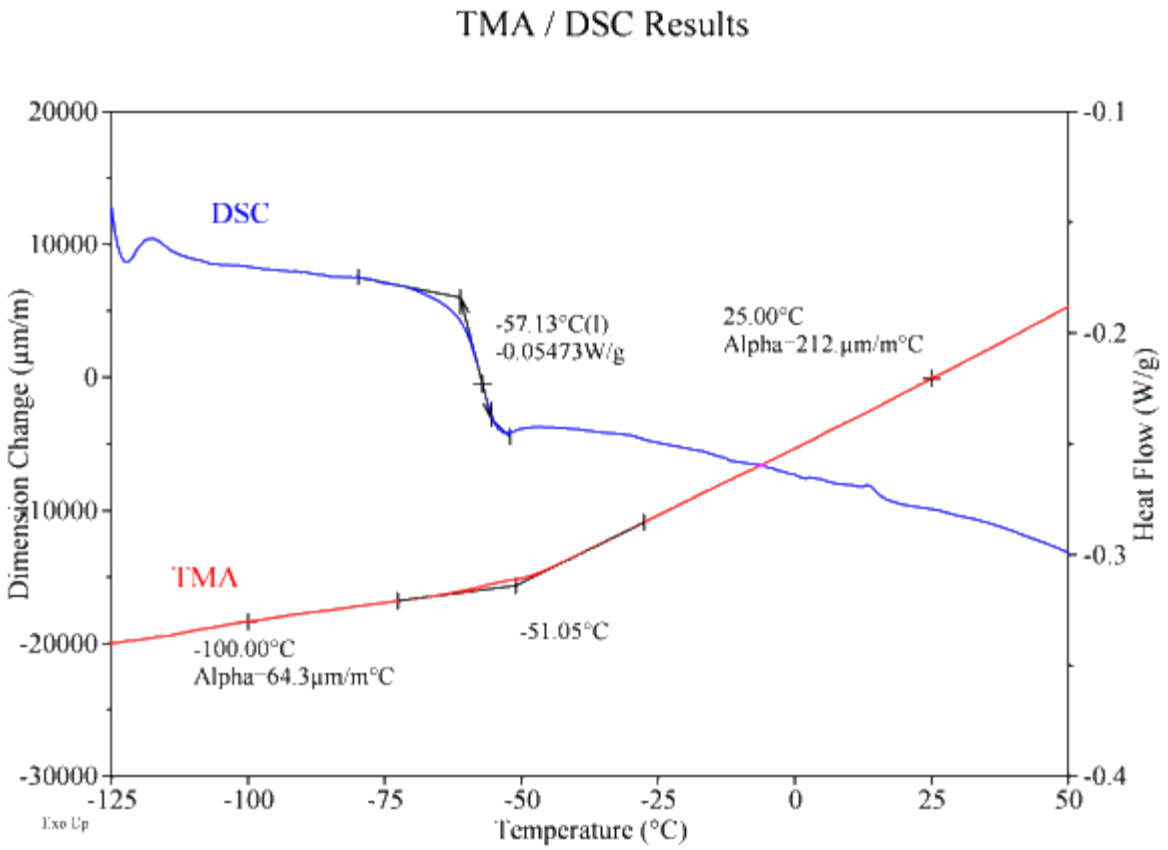


Figure 8.10 Example of a differential scanning calorimetry trace of poly(ethylene terephthalate-*stat*-*p*-oxbenzoate), quenched, reheated, and cooled at 0.5 K/min through the glass transition, and reheated for measurement at 10 K/min (28). T_g is taken at the temperature at which half the increase in heat capacity has occurred. The width of the glass transition is indicated by ΔT. Note that ΔH_c and ΔH_f are equal in magnitude but opposite in sign.

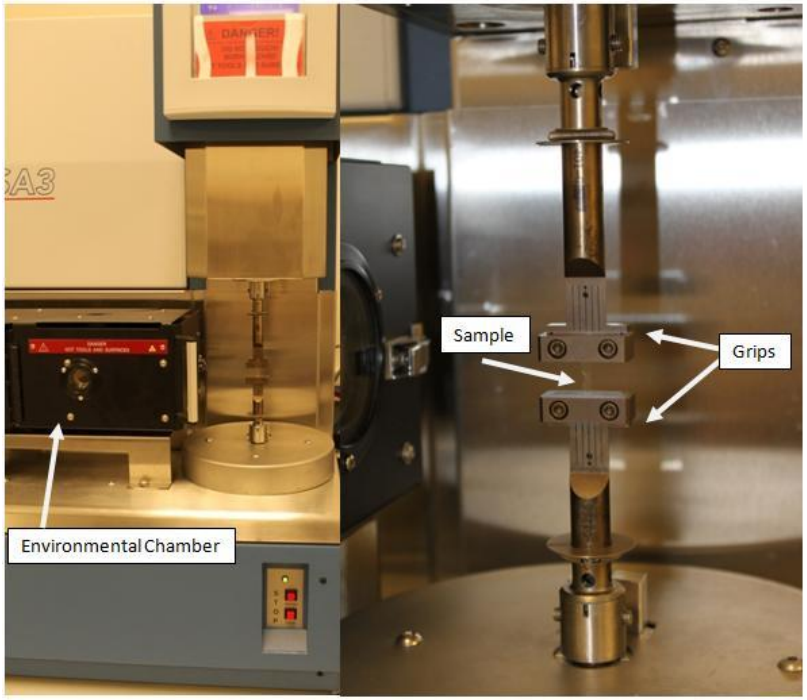


The thermal behavior of an EPDM rubber mixture was measured between –125 and 160°C at 10 K/min. The glass transition was detected at –52.5°C. The melting above the glass transition (peak temperature at 31.4°C) is typical for the behavior of a sequence-type EPDM. The further endothermal effects (at 98.6 and 110°C) are due to the evaporation of processing agents. The presentation in the separate window clearly shows the high sensitivity of the DSC 200 *F3 Maia*® even for small energetic effects (0.43 J/g).


TMA / DSC Results
DSC
TMA
-57.13°C(I)
-0.05473W/g
25.00°C
Alpha=212.µm/m°C
-100.00°C
Alpha=64.3µm/m°C
-51.05°C
Dimension Change (µm/m)
Heat Flow (W/g)
Temperature (°C)
Exo Up
20000
10000
0
-10000
-20000
-30000
-0.1
-0.2
-0.3
-0.4
-125
-100
-75
-50
-25
0
25
50

4.1.3. Mechanical Methods

- Because of softening, mechanical methods are important
- Static or quasistatic methods (stress relaxation)
- Dynamic methods(dynamic mechanical spectroscopy, torsional braid analysis TBA)



4.1.4. A DMS (DMA) Study

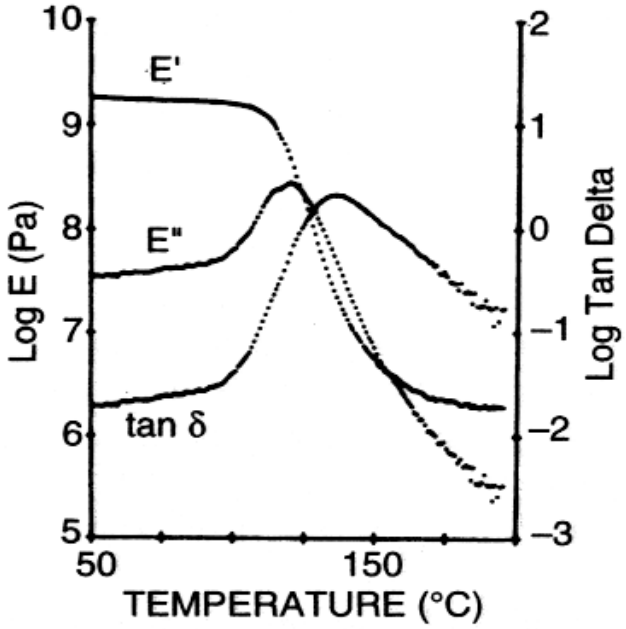
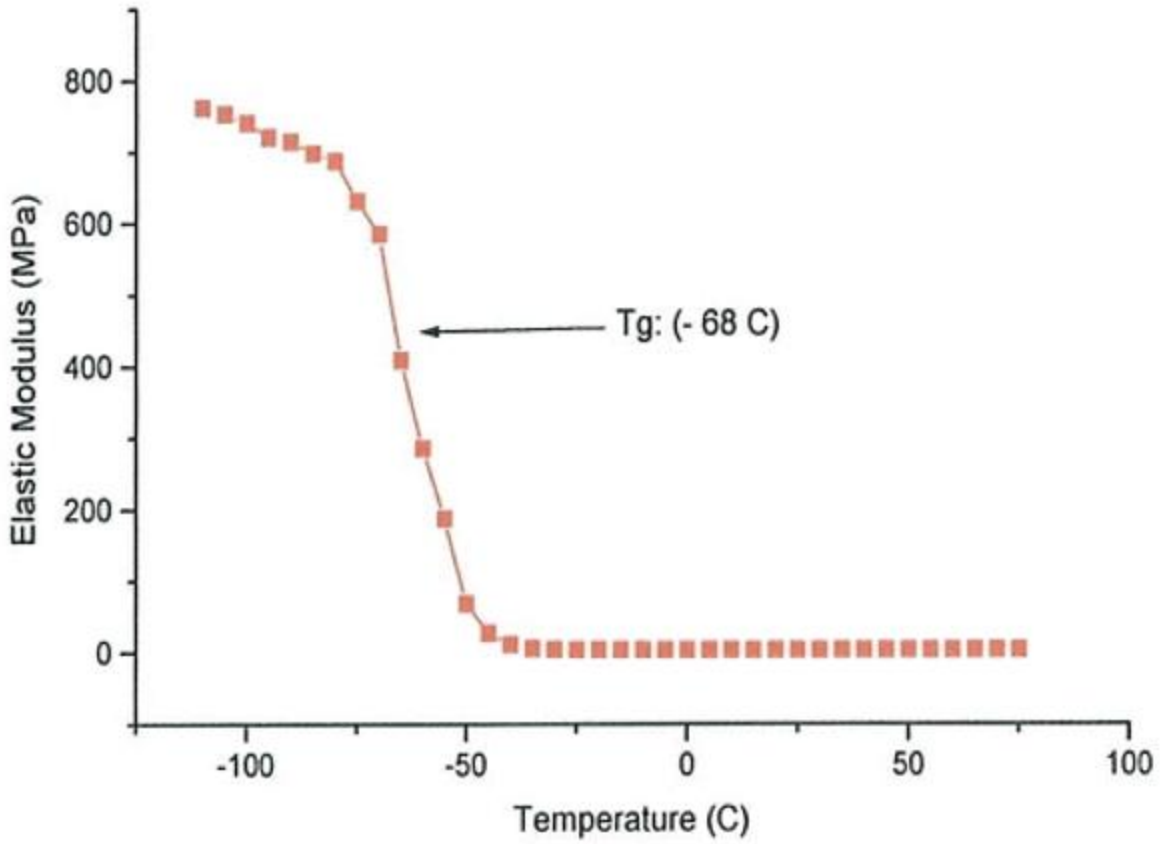


Figure 8.11 Dynamic mechanical spectroscopy on polystyrene cross-linked with 2% divinyl benzene. Data taken with a Rheovibron at 110 Hz. Note that the tan δ peak occurs at a slightly higher temperature than the *E″* peak (30). Experiment run by J. J. Fay, Lehigh University.

4.1.4. A DMS (DMA) Study

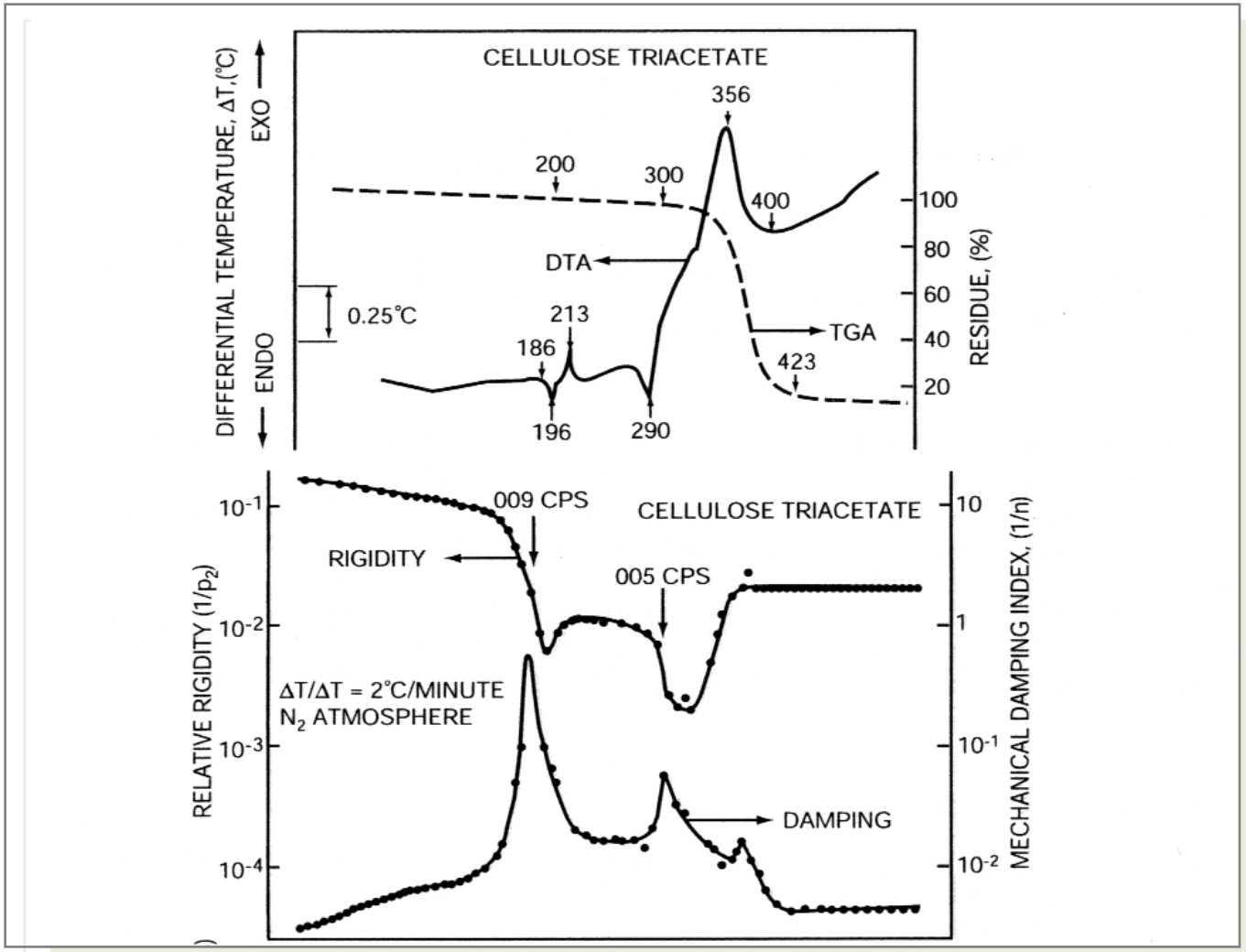


Polyisoprene

4.1.5. A TBA Study

Definition: A method of performing torsional tests on small amounts of materials in states in which they cannot support their own weight, e.g., liquid thermosetting resins. A glass braid is impregnated with a solution of the material to be tested. After evaporation of the solvent, the impregnated braid is used as a specimen in an apparatus which measures motion of the oscillating braid as it is being heated at programmed rate in a controlled atmosphere.

4.1.5. A TBA Study



4.1.6. Dielectric and Magnetic Methods

Dielectric methods are using sample as an electric capacitor.

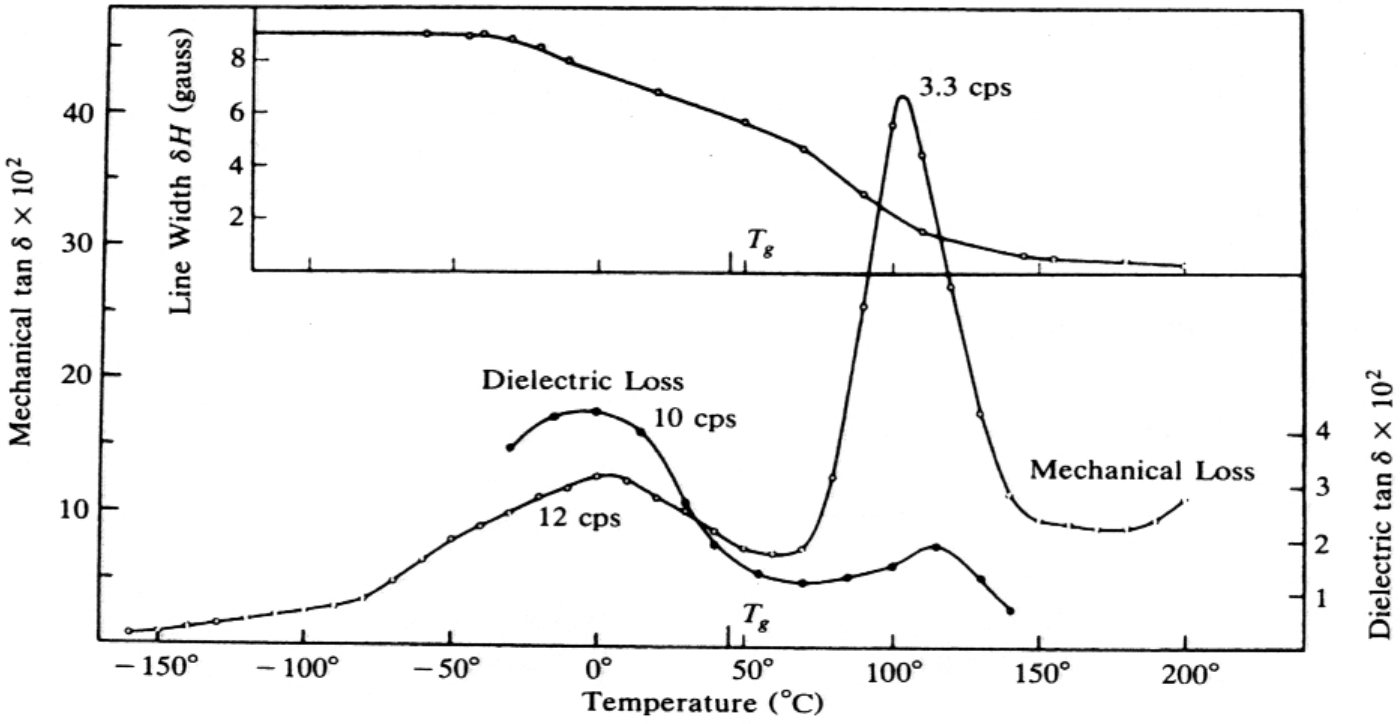


Figure 8.13 Mechanical and dielectric loss tangent tan δ and NMR absorption line width δH (maximum slope, in gauss) of polytrifluorochloroethylene (Kel-F) (40).

4.1.7. Magnetic Methods (Using NMR)

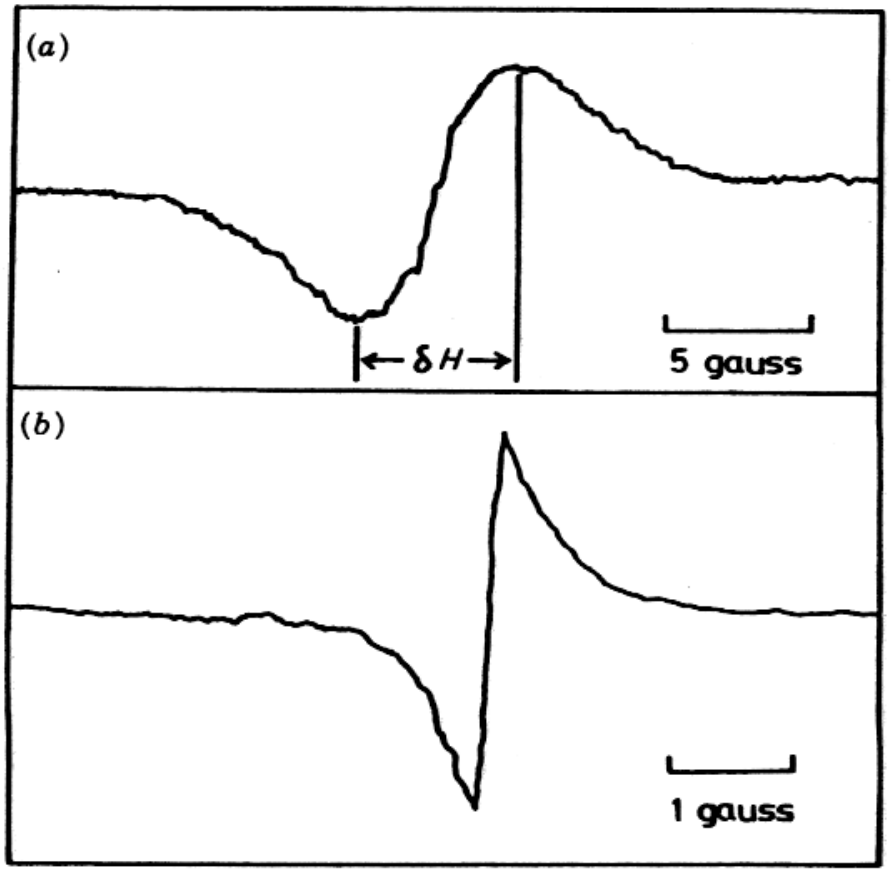


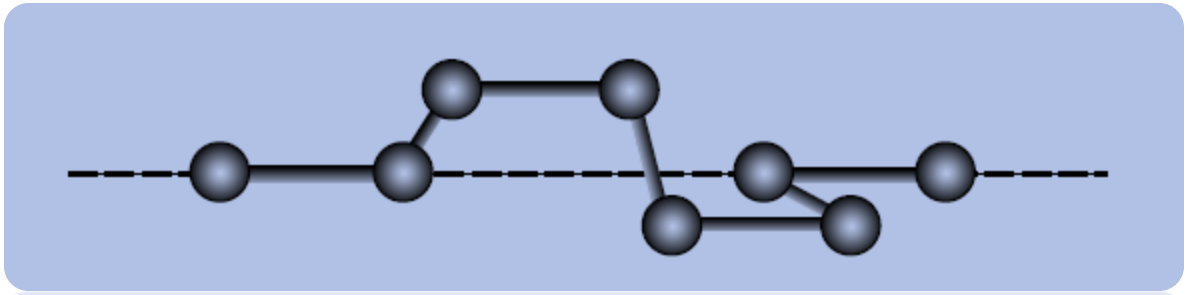
Figure 8.14 Broad-line NMR spectra of a cured epoxy resin. (*a*) Broad line at 291 K; (*b*) motionally narrowed line at 449 K (T_g + 39 K) (38).

Other Transitions

- As the temperature of a polymer is lowered continuously, the sample may exhibit several second-order transitions.
- By custom, the glass transition is designated the as α transition, and successively lower temperature transitions are called the β, γ, . . . transitions.
- One important second-order transition appears above *Tg, designated the* T_{ll} *(liquid–liquid) transition.*
- *If the polymer* is semicrystalline, it will also melt at a temperature above *Tg.*

The Schatzki Crankshaft Mechanism: a) *Main-Chain Motions*

- There appear to be two major mechanisms for transitions in the glassy state : Main chain and Side chain Motions



Schatzki's crankshaft motion requires at least four —CH2— groups in succession. As illustrated, for eight —CH2— groups, bonds 1 and 7 are collinear and intervening —CH2— units can rotate in the manner of a crankshaft.

The transition of polyethylene occurring near -120°C is thought to involve the Schatzki mechanism.

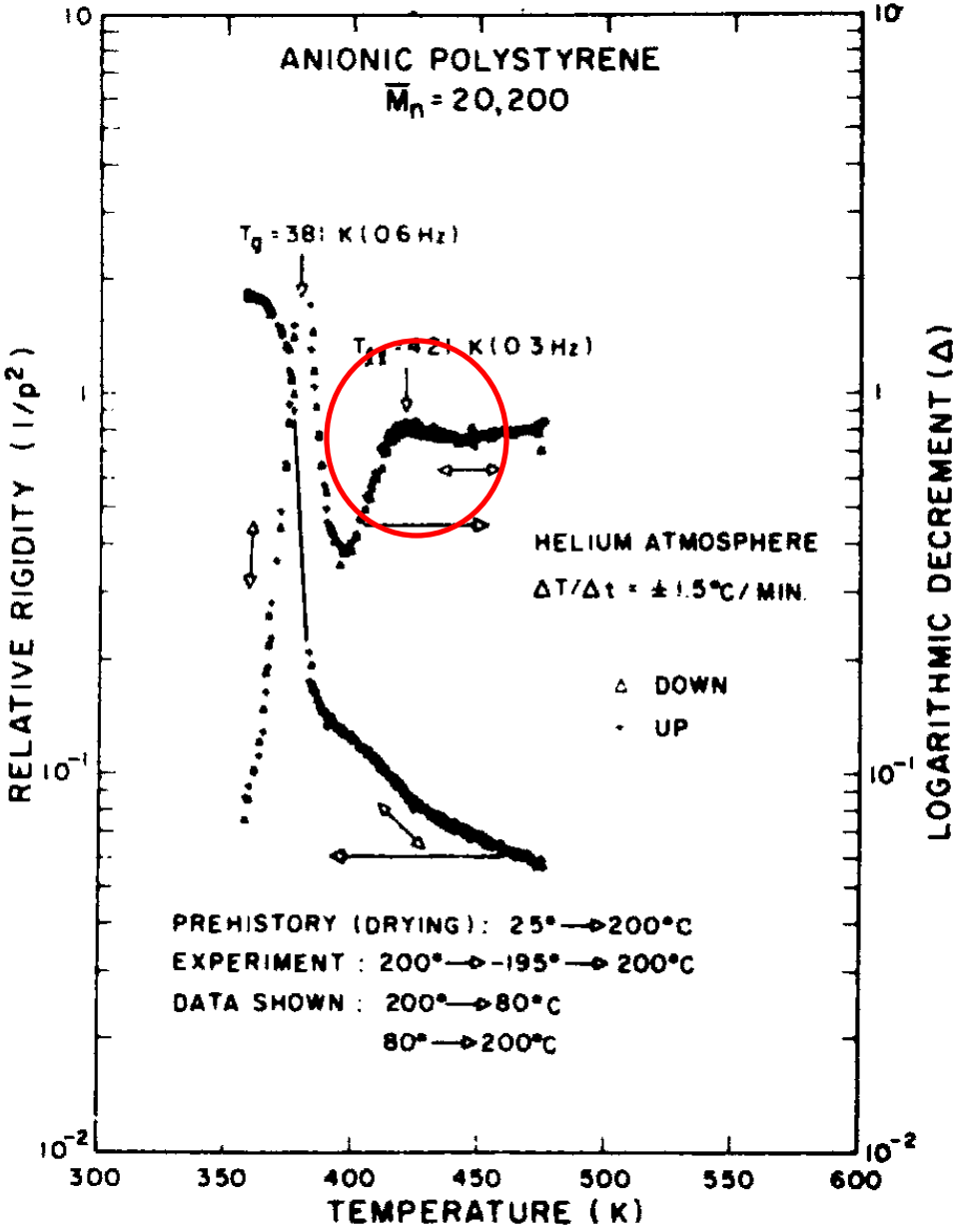
b) Side-Chain Motions

- Many polymers have considerable side-chain "foliage," and these groups can, of course, have their own motions.
- A major difference between main-chain and side-chain motions is the toughness imparted to the polymer.

- Low-temperature main-chain motions act to absorb energy much better than the equivalent side-chain motions, in the face of impact blows. When the main-chain motions absorb energy under these conditions, they tend to prevent main-chain rupture.

The T_{ll} *Transition*

- The T_{ll} *transition occurs above the glass transition* and is thought to represent the onset of the ability of the entire polymer molecule to move as a unit.
- Although there is much evidence supporting the existence of a *Tll ,* it is surrounded by much controversy.
- The observed (in TBA analysis) T_{ll} *transition* may be related to reptation.


ANIONIC POLYSTYRENE
$\overline{M}_n$ = 20,200
T_g = 381 K (0.6 Hz)
T_{γ} = 42 K (0.3 Hz)
HELIUM ATMOSPHERE
ΔT/Δt = ±1.5°C/MIN.
△ DOWN
• UP
PREHISTORY (DRYING): 25° → 200°C
EXPERIMENT : 200° → -195° → 200°C
DATA SHOWN : 200° → 80°C
80° → 200°C
RELATIVE RIGIDITY (1/p²)
LOGARITHMIC DECREMENT (Δ)
TEMPERATURE (K)
10
1
10⁻¹
10⁻²
300
350
400
450
500
550
600

Many polymers show evidence of several transitions besides *Tg.*

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

The onset of de Gennes reptation is probably associated with *Tg, the motions being experimentally identified at Tg + 20°C.*

5. Theories of Glass Transition

- The Free-Volume Theory
- The Kinetic Theory
- Thermodynamic Theory

5.1. The Free-Volume Theory

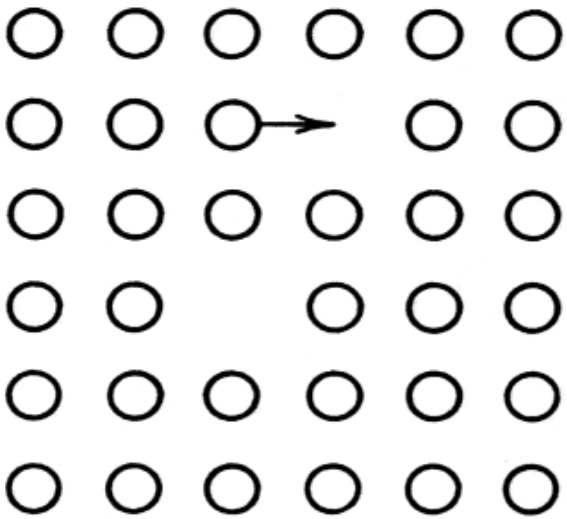


Figure 8.21 A quasi-crystalline lattice exhibiting vacancies, or holes. Circles represent molecules; arrow indicates molecular motion.

The important point is that molecular motion cannot take place without the
presence of holes. These holes, collectively, are called free volume.

5.1.1. Iso-Free Volume State

Fox and Flory Eq. In 1950 Fox and Flory (74) studied the glass transition and free volume of polystyrene as a function of molecular weight and relaxation time. For infinite molecular weight, they found that the specific free volume, *vf, could be expressed above Tg as*

$$\nu_f = K + (\alpha_R - \alpha_G)T$$

ν_f =specific free volume, ***K*** is related to free volume at 0°K, α_R and α_G cubic expansion in rubbery and glassy state.

They concluded that (a) below *Tg the local* conformational arrangement of the polymer segments was independent of both molecular weight and temperature and (b) the glass transition temperature was an iso–free-volume state.

5.1.1. Iso-Free Volume State

Simha and Boyer then postulated that
the free volume at $T = Tg$ *should be defined as*

$$v - (v_{0,R} + \alpha_G T) = v_f$$

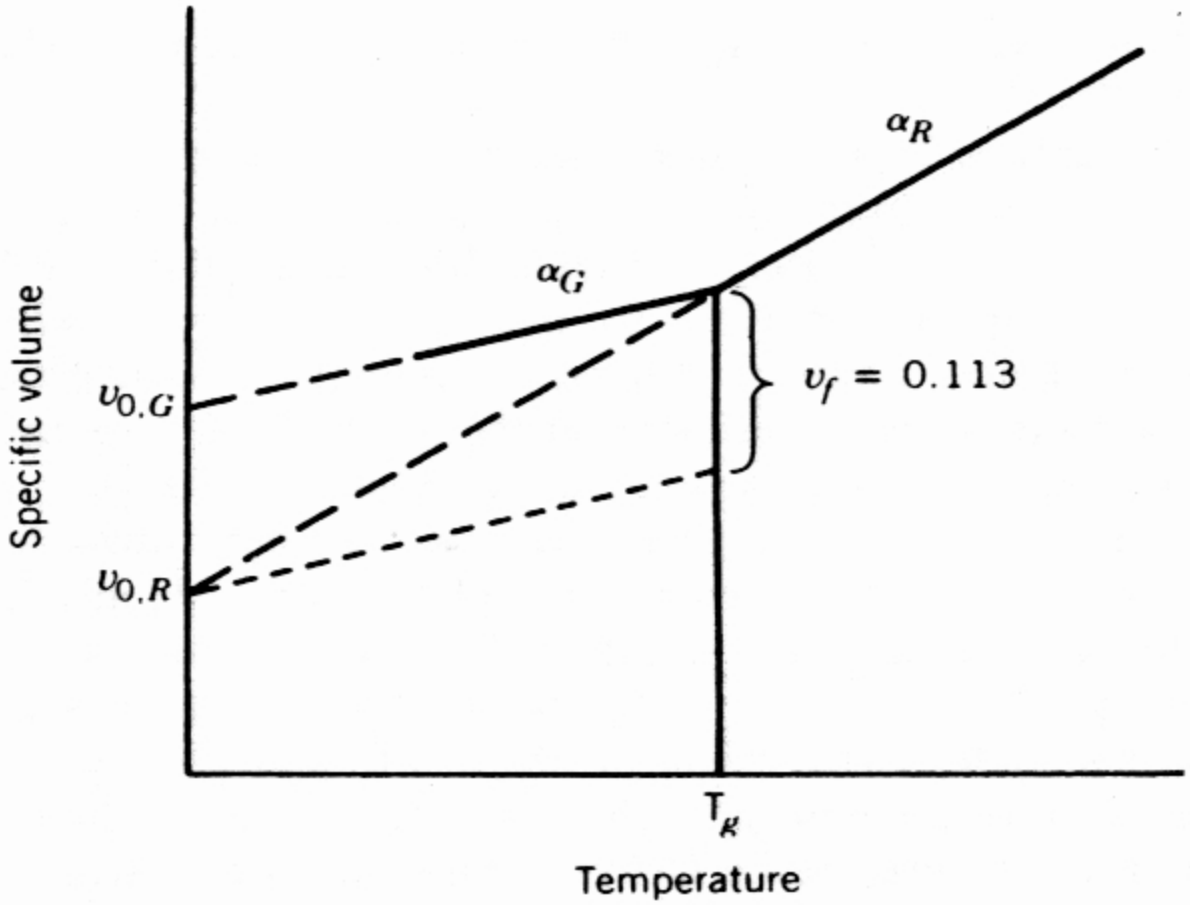


Figure 8.22 A schematic diagram illustrating free volume as calculated by Simha and Boyer.

$$v - (v_{0,R} + \alpha_G T) = v_f \qquad v = v_{0,R} + \alpha_R T$$

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

$$K_1 = (\alpha_R - \alpha_G) T_g = 0.113$$

Table 8.7 Glass transition temperature as an iso–free-volume state (71)

Polymer	T_g, K	$\alpha_G \times 10^4$ K^{-1}	$\alpha_R \times 10^4$ K^{-1}	$\alpha_R T_g$	$(\alpha_R - \alpha_G)$	$(\alpha_R - \alpha_G)T_g$
Polyethylene	143	7.1	13.5	0.192	7.4	0.105
Poly(dimethyl siloxane)	150	—	12	0.180	9.3	0.140
Polytetrafluoro-ethylene	160	3.0	8.3	0.133	7.0	0.112
Polybutadiene	188	—	7.8	0.147	5.8	0.109
Polyisobutylene	199.4	—	6.18	0.123	4.70	0.094
Hevea rubber	201	—	6.16	0.124	4.1	0.082
Polyurethane	213	—	8.02	0.171	6.04	0.129
Poly(vinylidene chloride)	256	—	5.7	0.146	4.5	0.115
Poly(methyl acrylate)	282	—	5.6	0.158	2.9	0.082
Poly(vinyl acetate)	302	2.1	5.98	0.18	3.9	0.118
Poly(4-methyl pentene-1)	302	3.4	7.61	0.23	3.78	0.114
Poly(vinyl chloride)	355	2.2	5.2	0.185	3.1	0.110
Polystyrene	373	2.0	5.5	0.205	3.0	0.112
Poly(methyl methacrylate)	378	2.6	5.1	0.182	2.80	0.113

Source: See also J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.

Note: The quantity α represents the volume coefficient of expansion. The linear coefficients of expansion are approximately 1/3 of the volume coefficients of expansion. The quantities α_G (determined at 20°C) and α_R represent the glassy and rubbery states, respectively, the former being a typical value for the polymer (semicrystalline for polyethylene and polytetrafluoroethylene) while the latter is calculated for the 100% amorphous polymer. However, the quantities $\alpha_R - \alpha_G$ and $(\alpha_R - \alpha_G)T_g$ are calculated on the basis of 100% amorphous polymer.

5.1.2. The WLF Equation (Williams-Landel-Ferry)

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

$$\frac{B}{2.303 f_0} = 17.44$$

$$\frac{f_0}{\alpha_f} = 51.6$$

B , a constant, f_0 fractional free volume at T_g, α_f expansion coefficient of free volume

An example for using WLF Eq.

Suppose a polymer has a glass transition temperature of 0°C. At 40°C, it has a melt viscosity of 2.5×10^5 poises (P) (2.5×10^4 Pa · s). What will its viscosity be at 50°C?

First calculate η_g:

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

$$\log \eta_g = \log 2.5 \times 10^5 + \frac{17.44(313 - 273)}{51.6 + (313 - 273)}$$

$$\log \eta_g = 13.013$$

Polymers often have melt viscosities near 10^{13} P at their glass transition temperature, 1.03×10^{13} P in this case.

Now calculate the new viscosity:

$$\log \eta = 13.013 - \frac{17.44(323 - 273)}{51.6 + (323 - 273)}$$

$$\eta = 2.69 \times 10^4 \text{ P} \quad \text{or} \quad 2.69 \times 10^3 \text{ Pa} \cdot \text{s}$$

Thus a 10°C increase in temperature has decreased the melt viscosity by approximately a factor of 10 in this range. The WLF equation can be used to calculate shift factors (Section 8.6.1.2), failure envelopes (Section 11.2.5.2), and much more.

5.2. The Kinetic Theory

T_g values obtained for a polymeric systems depends on experiment time scale, showing that free-volume thory is also Kinetic nature.Slower experiment results in lower *Tg*

$$\log A_T = \log\left(\frac{t}{t_g}\right) = -\frac{17.44(T - T_g)}{51.6 + T - T_g}$$

if the time frame of an experiment is decreased by a factor of 10 near *Tg*,

$$\lim_{T \to T_g} \left(\frac{\log A_T}{T - T_g} \right) = -0.338$$

$$\ln\left(\frac{\eta}{\eta_0}\right) = \ln A_T = \ln\left(\frac{t}{t_0}\right)$$

$$T - T_g = \frac{-1.0}{-0.338} = 3.0$$

5.3. Thermodynamic Theory

What about infinite time alotted to establish a quiet equilibrium?

The Gibbs and DiMarizo Theory:In infinitely slow experiments a glassy phase will eventually emerge whose entropy is negligibly higher than that of crystal.

Summary of the Theories

- Free-Volume theory provides relationships between coefficients of expansion below and above Tg and yields equations relating viscoelastic motion to the variables of time and temp.
- The kinetic theory defines Tg as the temp. 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 experiment.

Summary (contd.)

- The thermodynamic theory introduce the notion of equilibrium and the requirements for a true second-order transition.

Glass transition theory box scores

Theory	Advantages	Disadvantages
Free-volume theory	1. Time and temperature of viscoelastic 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

6. Effect of Molecular Weight on T_g

a) Linear Polymers

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

PS as an example:

$$T_g = 106 - \frac{2.1\times10^5}{M_n}, \text{ at low heating rates}$$

$$T_g = 100 - \frac{1.8\times10^5}{M_n}, \text{ at normal heating rates}$$

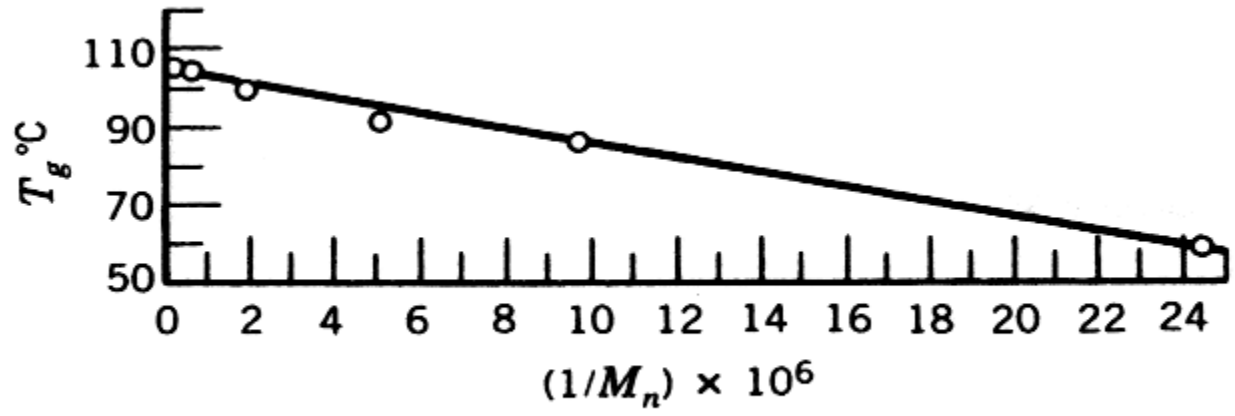


Figure 8.26 The glass transition temperature of polystyrene as a function of $1/M_n$ (102).

8. Effect of Copolymerization on T_g

(one phase system)

$$\ln T_g = \frac{M_1 \Delta C_{p1} \ln T_{g1} + M_2 \Delta C_{p2} \ln T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}}$$

$$T_g \approx \frac{M_1 \Delta C_{p1} T_{g1} + M_2 \Delta C_{p2} T_{g2}}{M_1 \Delta C_{p1} + M_2 \Delta C_{p2}}$$

Fox Eq.

$$\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}}$$

Pochan Eq.

If $\Delta C_{p1} \approx \Delta C_{p2}$

$$\ln T_g = M_1 \ln T_{g1} + M_2 \ln T_{g2}$$

or

$$T_g = M_1 T_{g1} + M_2 T_{g2}$$

Two-phase system

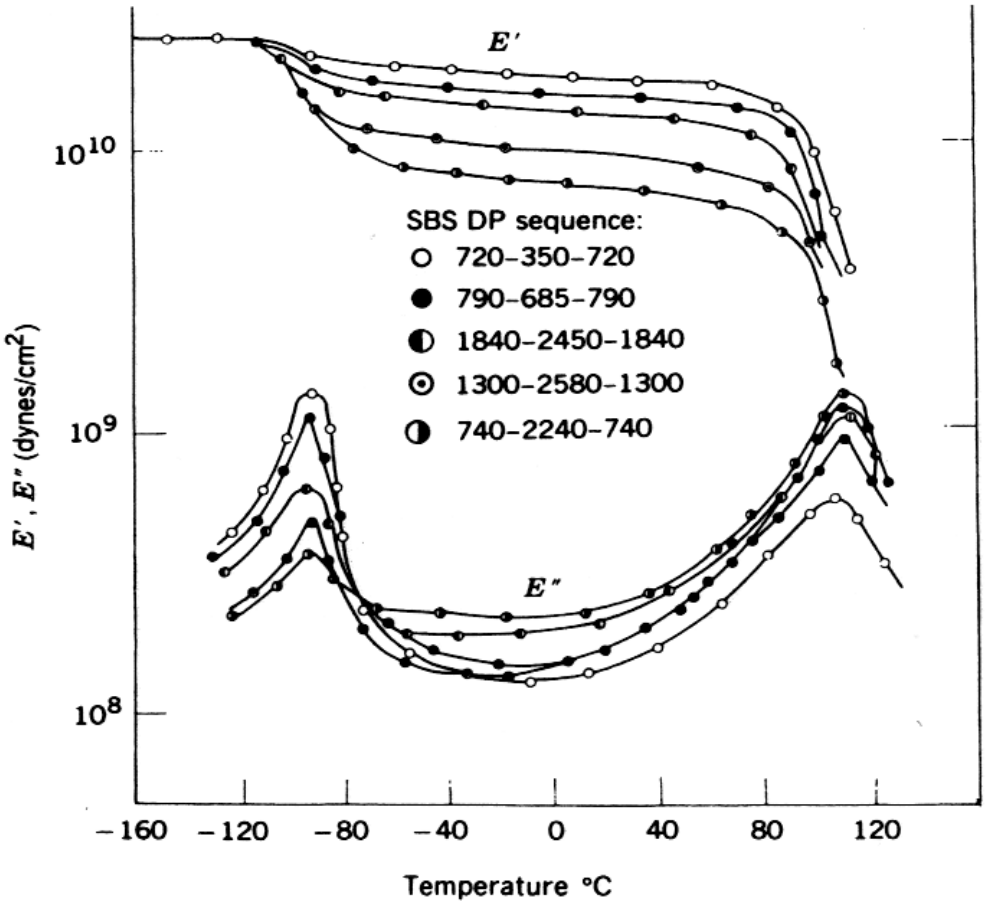


Figure 8.29 Dynamic mechanical behavior of polystyrene–*block*–polybutadiene–*block*–polystyrene, a function of the styrene–butadiene mole ratio (112,113).

9. Dependence of T_g on Chemical Structure

- Factors that increase the energy required for onset of molecular motions Increase Tg
- Those that decrease energy requirements decrease Tg

Table 8.11 Factors affecting T_g (131)

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

10. Effect of Side Chains

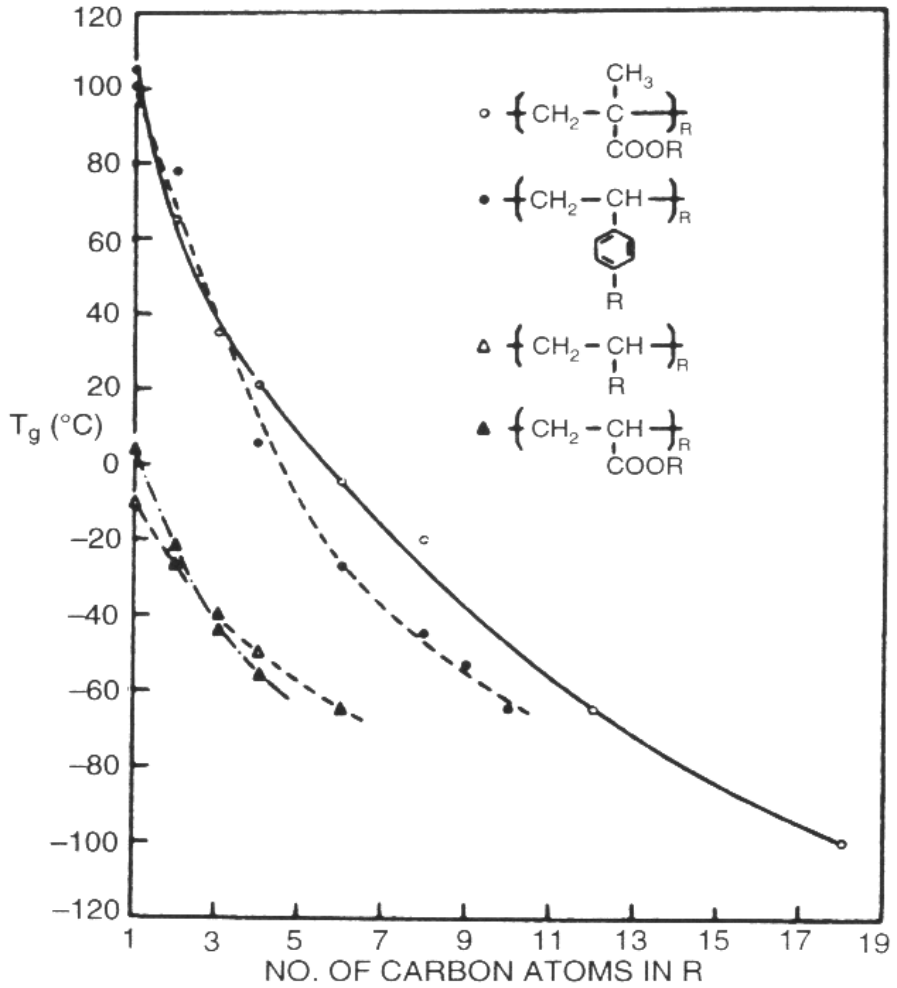


Figure 8.32 Effect of side-chain lengths on the glass transition temperatures of poly-methacrylates [○ (S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985, 1957)]; poly-*p*-alkyl styrenes [● (W. G. Barb, *J. Polym. Sci.*, **37**, 515, 1959)]; poly-α-olefins [△ (M. L. Dannis, *J. Appl. Polym. 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 [▲ (J. A. Shetter, *Polym. Lett.*, **1**, 209, 1963)] (135).

11. Effect of Tacticity

Table 8.12 Effect of tacticity on the glass transition temperatures of polyacrylates and polymethacrylates (137)

	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

12. Definition of Elastomers, Plastics, Adhesives and Fibers

- **An Elastomer is a cross-linked, amorphous polymer above its Tg. (A rubber Band)**
- **Adhesive is a linear or branched amorphous above its Tg. It must be able to flow on a molecular scale to grip surfaces.**
- **A plastic is usually below its Tg if its amorphous. Crystalline plastics may be either above or below their Tg's.**
- **Fibers are always composed of crystalline polymers, their Tg is usually near to ambient temperature**

End of Chapter 3