2 Types of Noncrystalline Polymers

1. Glassy polymer
2. Rubbery polymers

$\}$ highly interpenetrated/entangled random Gaussian coils

Glass Transition Temperature

$$\varepsilon_{ij}$$

Two viewpoints:

*   Increasing T: When kT > magnitude of ε_{ij}, the thermal fluctuations can overcome local intermolecular bonds and the frozen ("glassy") structure becomes "fluid-like".

*   Decreasing T: As the temperature is lowered and T approaches T_g, the viscosity increases to ∞ and the material becomes "solid"

Free Volume Theory of T_g

Free volume, V_F – extra space beyond what is present in an ordered crystalline packing (beyond the interstitial volume).

$$V_F(T) \equiv V(T) - V_0(T)$$

- V_0 is occupied specific volume of atoms or molecules in the xline state *and* the spaces between them: $\sim V_{XL}$.

- V_F increases as T increases due to the difference in the thermal expansion coefficients (α_g vs α_l).

- $V_0(T) \approx V_{XL}(T)$ $\quad \leftrightarrow \quad$ can take $\alpha_g \approx \alpha_{XL}$

- $V_F(T) = V_F(T_g) + (T-T_g)\dfrac{dV_F}{dT}$ $\quad T > T_g$

- define <u>fractional free volume, f_F</u>: V_f/V
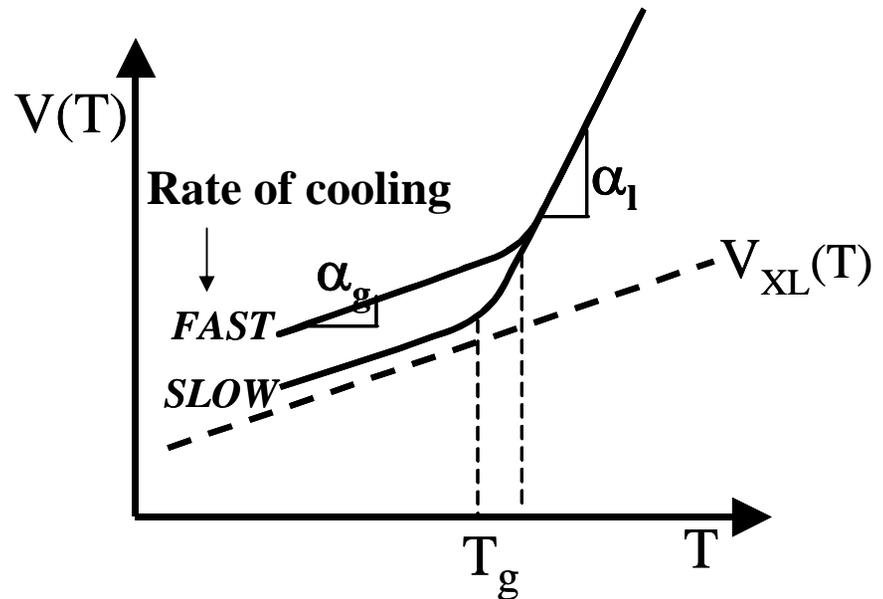
$$f_F(T) = f_F(T_g) + (T-T_g)\alpha_f \qquad \alpha_f = \alpha_l - \alpha_g$$

Viewpoint: T_g occurs when available free volume drops below critical threshold for structural rearrangement [VITRIFICATION POINT], *structure "jams up".*

T$_g$ Values of Amorphous Materials

Table of representative amorphous solids, their bonding types, and their glass transition temperatures removed due to copyright restrictions.

See Table 2.2 in Allen, S. M., and E.L. Thomas. *The Structure of Materials*. New York, NY: J. Wiley & Sons, 1999.

T$_g$ for Selected Polymers

Glass Transition Temperature for Selected Polymers

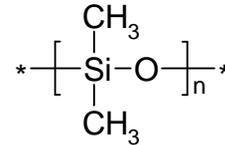| Organic Polymer	T$_\sigma$ (°C)	Organic Polymer	T$_\sigma$ (°C)
Polyacenaphthalene	264	Polyhexamethylene sebacamide	
Polyvinyl pyrrolidone	175	(nylon 6,10)	40
Poly-*o*-vinyl benzyl alcohol	160	Polyvinyl acetate	29
Poly-*p*-vinyl benzyl alcohol	140	Polyperfluoropropylene	11
Polymethacrylonitrile	120	Polymethyl acrylate	9
Polyacrylic acid	106	Polyvinylidene chloride	-17
Polymethyl methacrylate	105	Polyvinyl fluoride	-20
Polyvinyl formal	105	Poly-1-butene	-25
Polystyrene	100	Polyvinylidene fluoride	-39
Polyacrylonitrile	96	Poly-1-hexene	-50
Polyvinyl chloride	87	Polychloroprene	-50
Polyvinyl alcohol	85	Polyvinyl-*n*-butyl ether	-52
Polyvinyl acetal	82	Polytetramethylene sebacate	-57
Polyvinyl proprional	72	Polybutylene oxide	-60
Polythylene terephthalate	69	Polypropylene oxide	-60
Polyvinyl isobutyral	56	Poly-1-octene	-65
Polycaprolactam (nylon 6)	50	Polyethylene adipate	-70
Polyhexamethylene adipamide		Polyisobutylene	-70
(nylon 6,6)	50	Natural rubber	-72
Polyvinyl butyral	49	Polyisoprene	-73
Polychlorotrifluorethylene	45	Polydimethyl siloxane	-85
Ethyl cellulose	43	Polydimethyl siloxane	-123

Effects of Chemical Structure on T_g

- Onset of molecular mobility at T_g involves rotation of chain segments (comprised of ~ 10-30 repeat units) about the main chain. Such cooperative motion requires

  - #1 sufficient thermal energy (kT relative to $\Delta V(\phi)$) for ease of rotation about main chain bonds and to overcome local bonding

  - #2 sufficient V_F for the segments to move into.

- Requirements for a low T_g polymer:
  1. weak interaction between chains ε_{ij}
  2. easy rotation about main chain bonds $V(\phi)$
  3. abundant free volume V_F
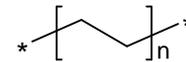
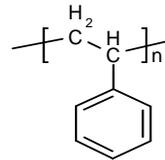# Chemical Structure vs. T_g

Low T_g Polymers		
Polydimethyl siloxane		-123 °C
Polyethylene (noncrystalline regions, T_m = 140C)		-133 °C
High T_g Polymers		
Polystyrene		105 °C
Polycarbonate		150 °C
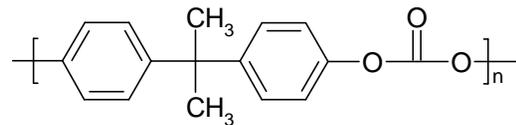
Influence of Backbone Flexibility on T_g

Repeat Unit	T_g, °C
$-CH_2-CH_2-$	-133
$-CH_2-CH_2-O-$	-67
	80
	84
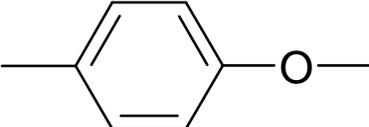
T_g: Influence of Steric Hinderance and ε_{ij}
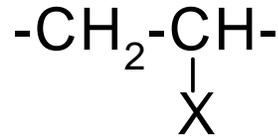
$$-CH_2-CH-$$
$$\overset{|}{X}$$

- steric hinderance

x = side group	T_g, ^oC
$-CH_3$	-23
$-CH_2-CH_3$	-24
$-CH_2-CH(CH_3)_2$	-16
$-CH_2-CH_2-CH_3$	50
⬡	100
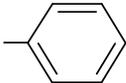
- polar chain-chain interactions

-Cl	81
-OH	85
-CN	97

Molecular Weight Dependence of T_g

Data show increase T_g with MW

Key Concept:

- ***Chain ends provide extra space and freedom for motion***

Image removed due to copyright restrictions.

Please see Fig. 3 in Fox, Thomas G., and Flory, Paul J. "Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight." *Journal of Applied Physics* 21 (June 1950): 581-591.

$$T_g(\overline{M}_n) = T_g^{\infty} - \frac{c}{\overline{M}_n}$$

T_g for Random Copolymers and Miscible Blends

• Random copolymers and miscible 2 component blend systems are homogeneous single phased materials and one can assume the rule of mixtures for fractional free volume of each component. This leads to simple relationships for T_g

$$T_{g,co} = T_{g,A} w_A + T_{g,B} w_B$$

where w_i is the weight fraction of component i

Controlling T_g with small molecule additives

Plasticizers

- low molar mass additives
- act to spread chains apart
- act as lubricant
    1) mediate chain-chain <u>polar</u> interactions
    2) add free volume

- Example: adding bis(2-ethylhexyl)phthalate (DOP) to neat PVC can significantly lower the Tg of the blend

$$(T_{g,\ PVC} = 70^oC, \qquad T_{g,\ DOP} = -80^oC)$$
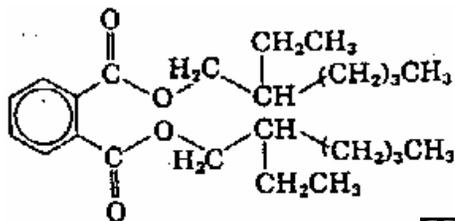
DOP

$$T_{g,blend} = T_{g,DOP}\, W_{DOP} + T_{g,PVC}\, W_{PVC}$$

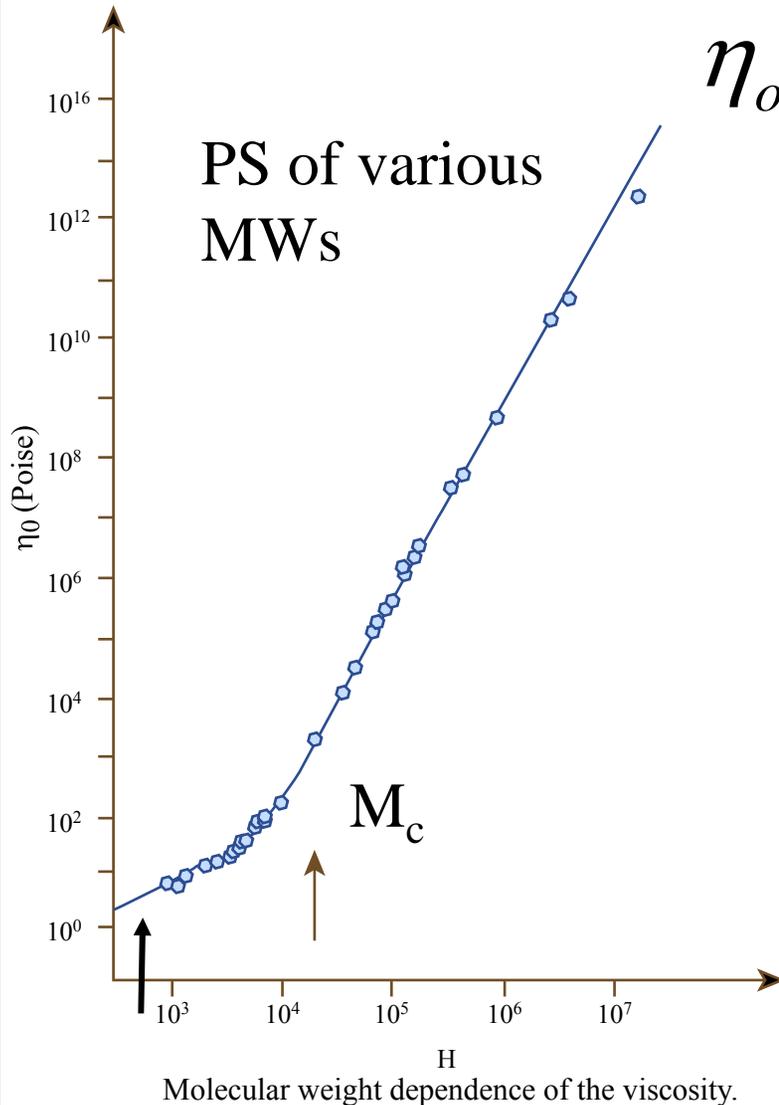# Controlling T_g cont'd

Antiplasticizers

- Small molecule additives which "fit" into regions between chains, lowering the overall V_F and *raising* the T_g of the 2 component system

$\eta_o(M)$ behavior for polymer melts

Molecular weight dependence of the viscosity.

PS of various MWs

M_c

η_o = zero shear rate melt viscosity

M_c
M_e

Viscosity units: Poise
= dynes • s/cm²
= g/cm • s

Characteristic molecular weights for selected Polymers.

Polymer species	M_e	M_c
Polystyrene	19 500	35 000
Poly(α-methyl styrene)	13 500	28 000
1,4-Polybutadiene	1 900	5 000
Polyvinyl acetate	12 000	24 500
Poly(dimethyl siloxane)	10 000	24 400
Polyethylene	1 300	3 800
1,4-Polyisoprene	6 300	10 000
Polyisobutylene	8 900	15 200

Viscosity of Polymeric Melts

η_o is the zero shear rate limit of the melt viscosity

Log η_o

ScalingLaw :
inspect scaling of
log - log plots

3.4

1

M_c

Log MW
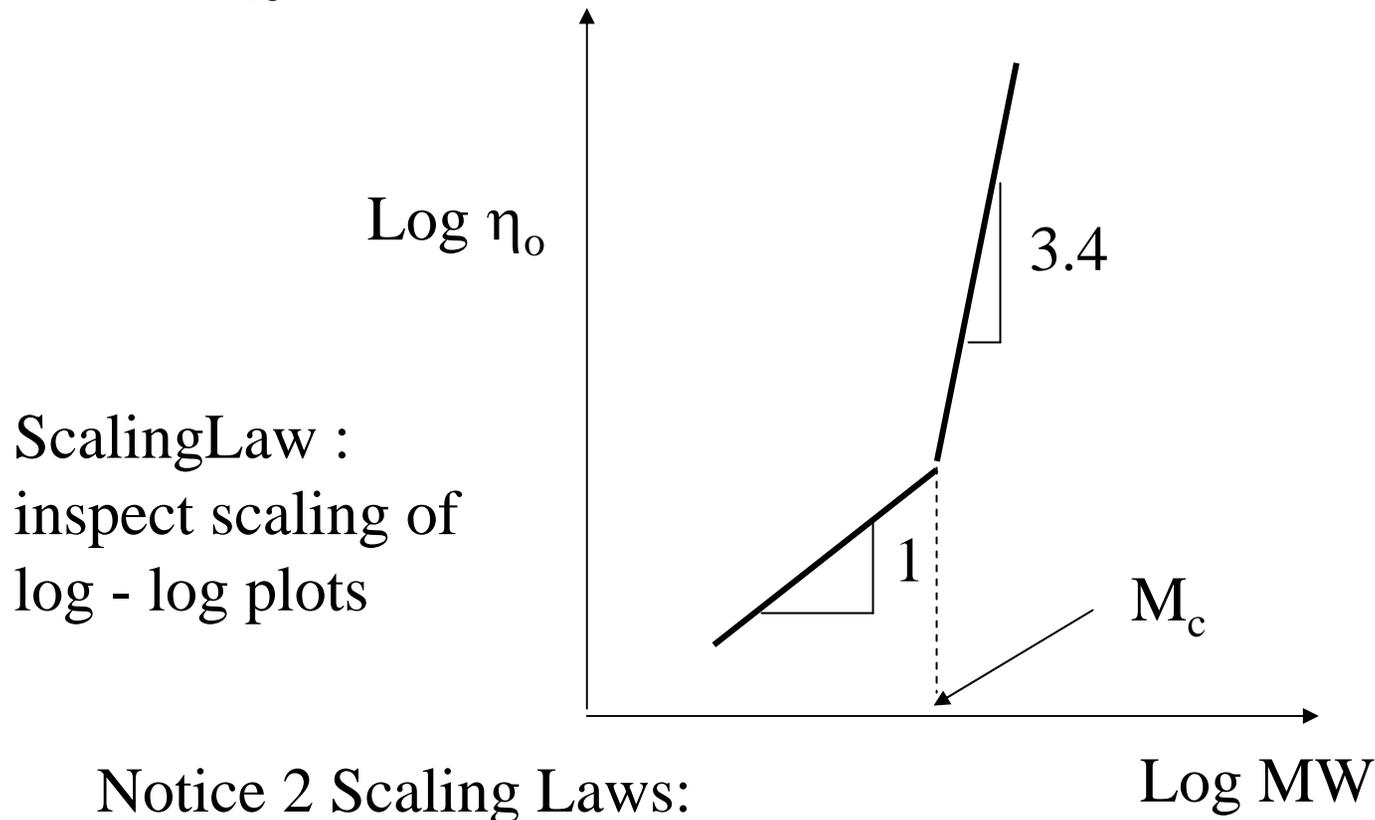
Notice 2 Scaling Laws:

- For low MW
- For high MW

$\eta_o \sim M$ called **Rouse** Regime

$\eta_o \sim M^{3.4}$ called **Reptation** Regime

Diffusivity (and Viscosity) of Polymer Melts

- Center of mass motion is important in determining the diffusivity (and viscosity) of a polymer melt.

- **Small Molecule Liquids** –move by random jumps into adjacent "holes" (free volume concept)

$$\text{typical } D(20\,C) \sim 10^{-5} \text{ cm}^2/\text{sec}$$

- **Polymeric Liquids**
  - $D(20\,C) \sim 10^{-14}$ to 10^{-18} cm^2/sec
  - 2 regimes of diffusivity vs molecular weight are observed.
    $D \sim M^{-1}$ and $D \sim M^{-2}$ (more scaling laws!)

More Scaling Laws – D(N) behavior

Example: PS melts
of various MWs

Image removed due to copyright restrictions.

Please see Fig. 2 in Watanabe, Hiroshi, and Kotaka, Tadao. "Viscoelastic and Diffusion Properties of Binary Blends of Monodisperse Polystyrenes." *Macromolecules* 20 (1987): 530-535.

Slope at lower MWs
is about 1.0

Slope increases
to ~ 2
for higher MWs

Rouse Chain Model

- Rouse chain = a flexible connected string of Brownian particles that interact with a featureless background viscous medium.

- The number of repeat units is less than the entanglement limit, the chain has small N, where $N < N_e$

- *Viscosity* depends on monomeric friction factor ξ_M and chain length x_2

$$\eta \sim \xi_M \cdot x_2 \; \text{ so } \; \eta \sim M^1$$

- *Diffusivity* depends on monomeric friction factor via Einstein

$$D = \frac{kT}{\xi} \qquad \text{Hence, } D \sim M^{-1}$$