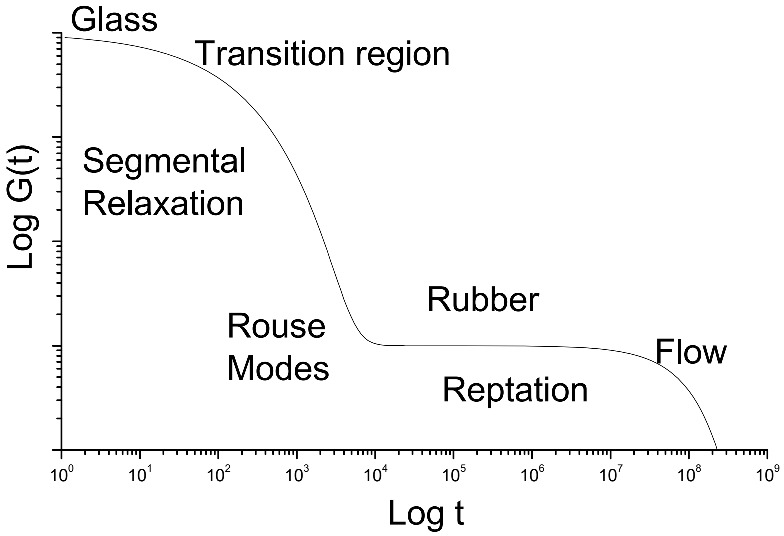
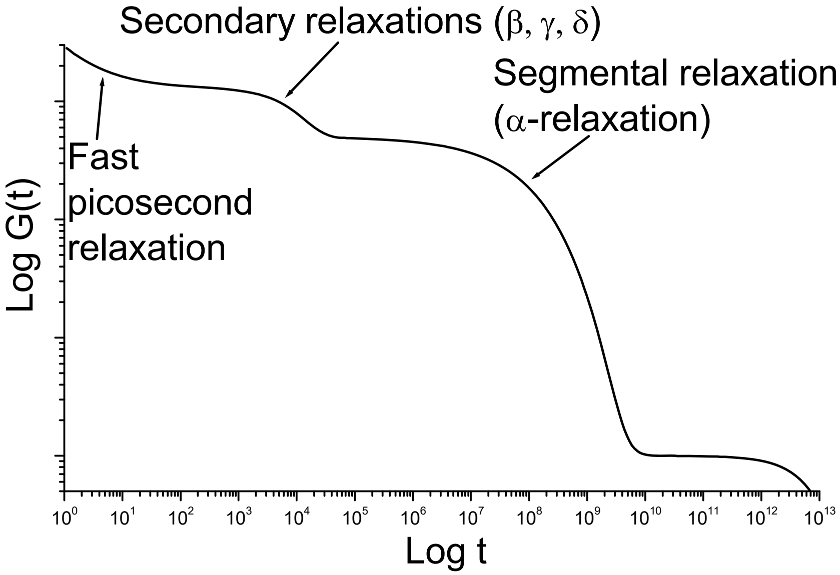
VII. Relaxations in Polymers and the Glass Transition.



Traditional presentation of relaxation map in polymers includes 4 regions:

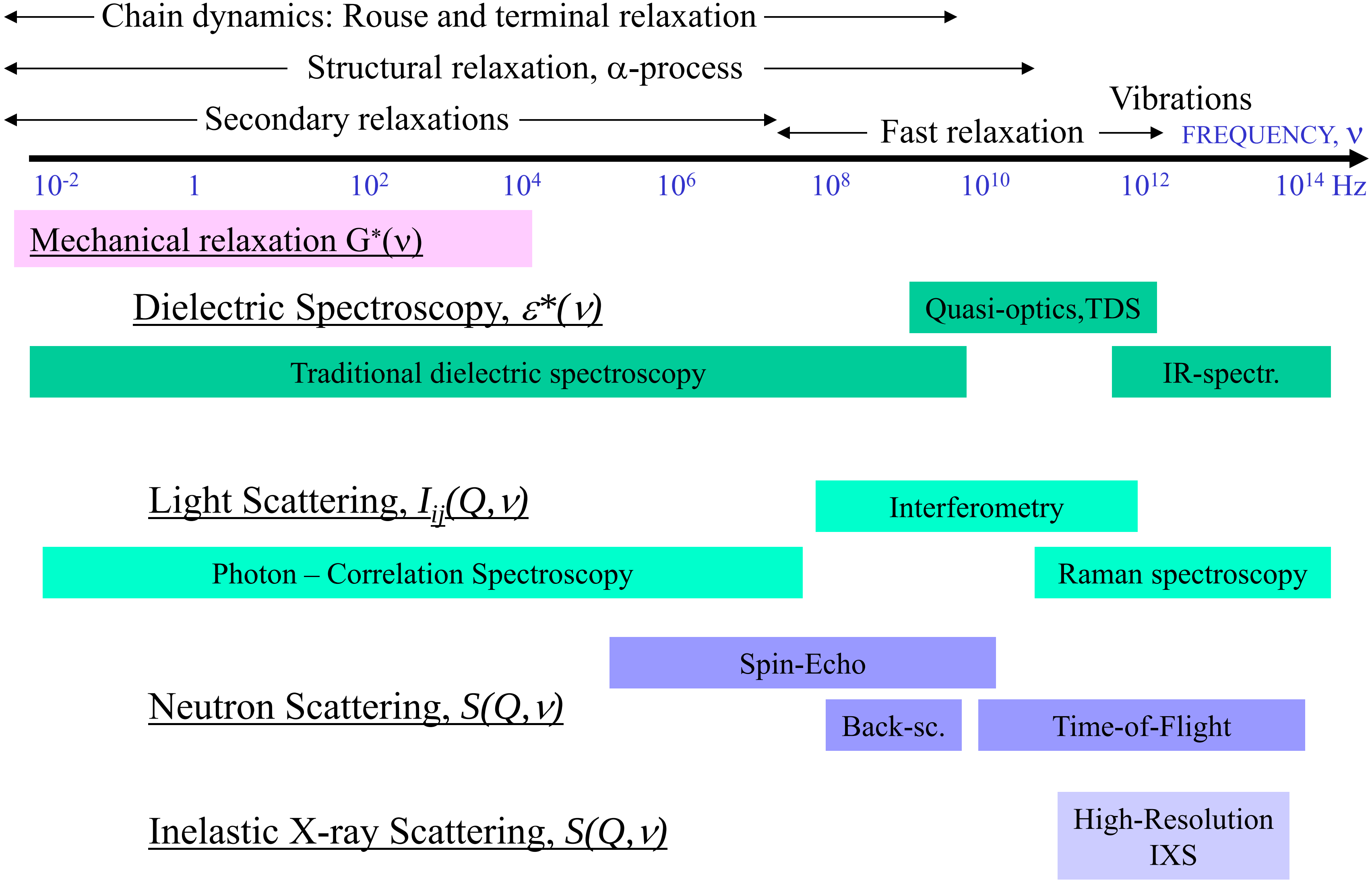
- -Glass-like behavior;
- -Transition region;
- -Rubbery plateau;
- -Terminal relaxation (flow).



However, there are a few relaxation processes even in a glassy state (or at time scales shorter than segmental relaxation).

In particular, secondary relaxations influence mechanical properties of polymers.

Frequency map of polymer dynamics



Chain dynamics: Rouse and terminal relaxation

Structural relaxation, α-process

Secondary relaxations

Fast relaxation

Vibrations

FREQUENCY, ν

10^{-2} 1 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12} 10^{14} Hz

Mechanical relaxation $G^*(\nu)$

Dielectric Spectroscopy, $\varepsilon^*(\nu)$

Quasi-optics,TDS

Traditional dielectric spectroscopy

IR-spectr.

Light Scattering, $I_{ij}(Q,\nu)$

Interferometry

Photon – Correlation Spectroscopy

Raman spectroscopy

Spin-Echo

Neutron Scattering, $S(Q,\nu)$

Back-sc.

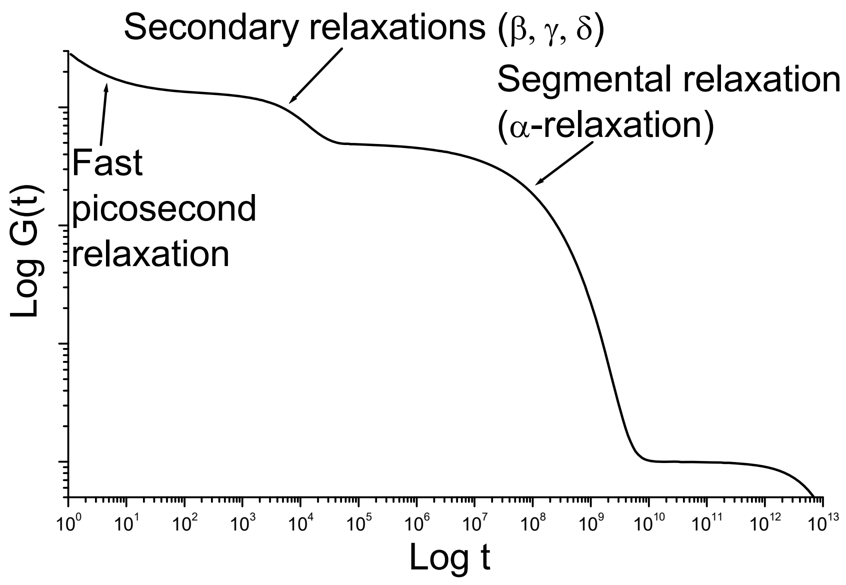
Time-of-Flight

Inelastic X-ray Scattering, $S(Q,\nu)$

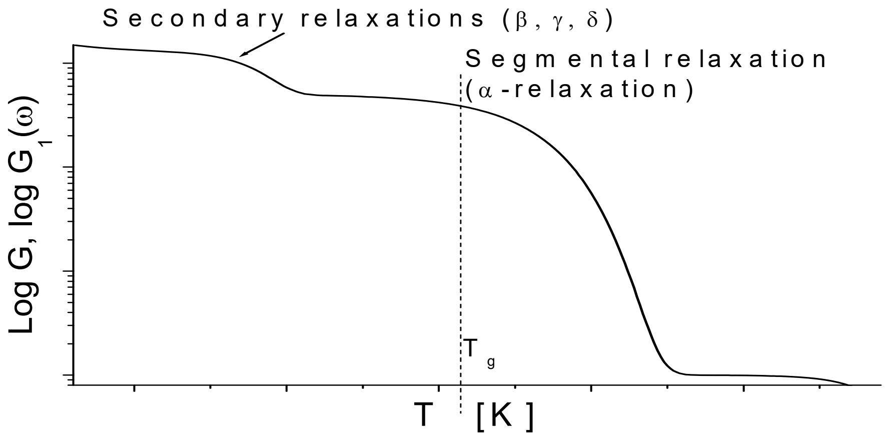
High-Resolution
IXS

Scattering techniques have an advantage due to additional variable – wave-vector Q

Time-Temperature Equivalence (Superposition)

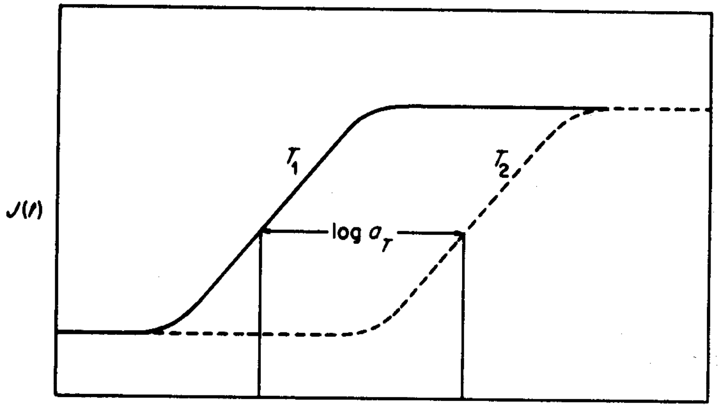


There are many relaxation processes in polymeric systems. They appear with different characteristic relaxation times, τ, or frequencies. The names of the processes (α-, β-, γ-) reflects the order in which the processes appear (excluding chain relaxation). There is no physical meaning behind these names. However, the α-process is usually assigned to the segmental relaxation.



Different experimental techniques should be used for measurements of the relaxation spectrum in so broad time or frequency range. Another way can be to change temperature and measure at fixed frequency. In particular, crossing the segmental relaxation usually marks the glass transition temperature Tg (depends on frequency).

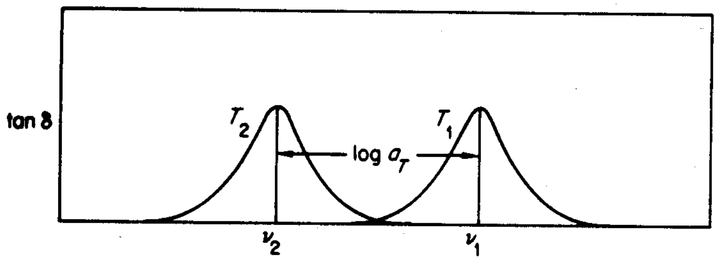
Comparison of two plots demonstrates that variations in time and in temperature can be equivalent.



(a)

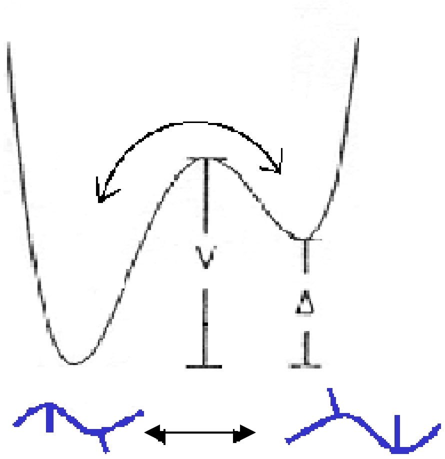
Time-temperature equivalence assumes that the viscoelastic behavior at one temperature can be related to that at another temperature by a change in the time scale only.

The compliances at T_1 and T_2 can be superimposed exactly by a horizontal shift Loga_T. Similarly, results of dynamic mechanical experiments measured at two different T can be shifted. a_T is the shift factor.



There are different corrections to the simple shift factor. In particular, superposition should incorporate a small vertical shift factor: $T_0\rho_0/T\rho$, ρ is the density.

Molecular rate process with a constant activation energy

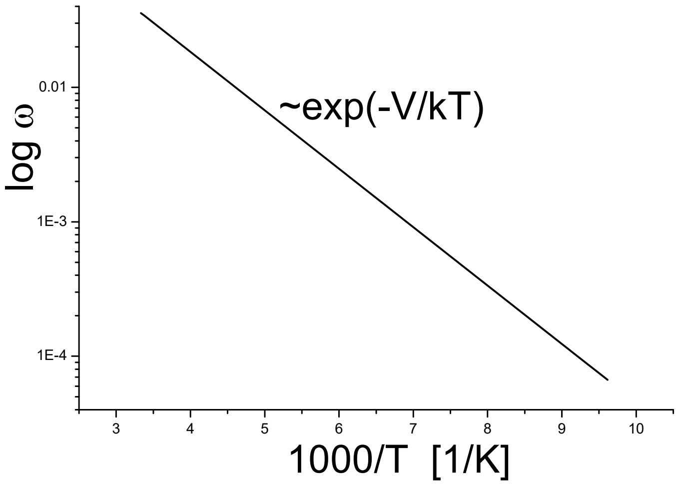


Let's assume that there are two different conformational states with energy difference Δ, separated by energy barrier V. In that case the relaxation time:

$$\tau = \tau_0 \exp\left(\frac{V}{kT}\right) \sec h\left(\frac{\Delta}{2kT}\right) \approx \tau_0 \exp\left(\frac{V}{kT}\right)$$

Here τ_0~10^{-12}-10^{-13} s. One can also introduce a relaxation rate:

$$\omega = \frac{1}{\tau} = \omega_0 \exp\left(-\frac{V}{kT}\right); \omega_0 = \frac{1}{\tau_0}$$



Arrhenius temperature dependence

This gives an activation or Arrhenius temperature dependence. It appears as a straight line for $ln\tau$ or $ln\omega$ vs 1/T.

The slope gives an estimate of the barrier height V:

$$V = -k\frac{\partial(\ln\omega)}{\partial(\frac{1}{T})}$$

k is the Boltzman constant. Comparison of frequencies measured at two different temperatures (for example, frequency of $tan\delta$ maximum) gives the shift factor:

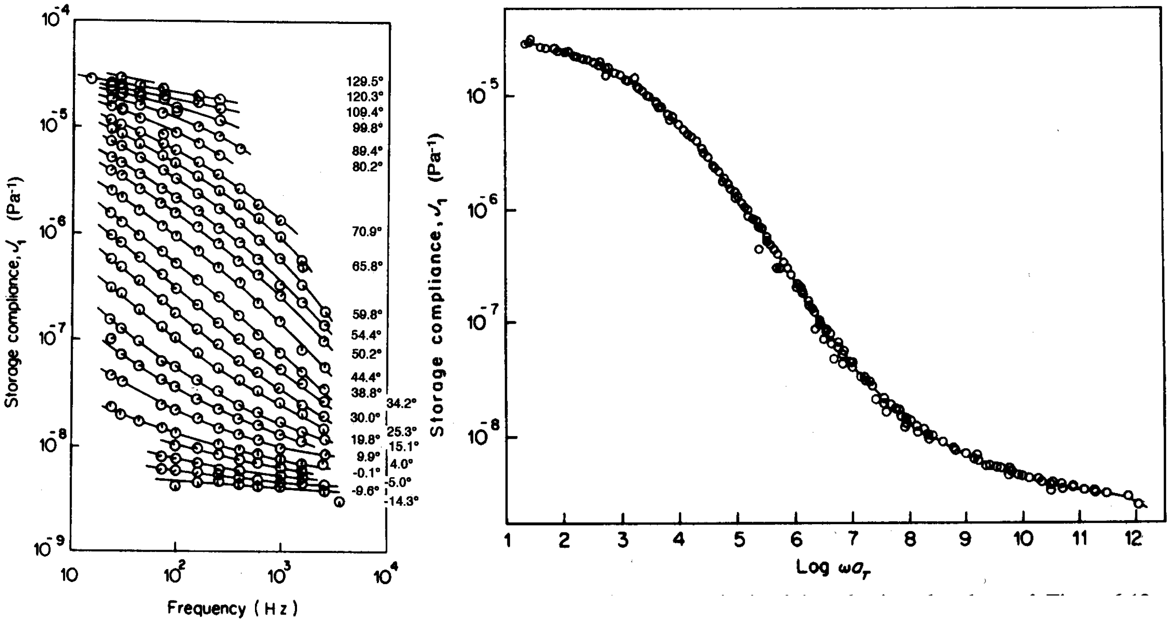
$$\log\left(\frac{\omega_1}{\omega_2}\right) = \log a_T = \frac{1}{\ln 10}\frac{V}{k}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = C\frac{T_1 - T_2}{T_1 T_2}$$

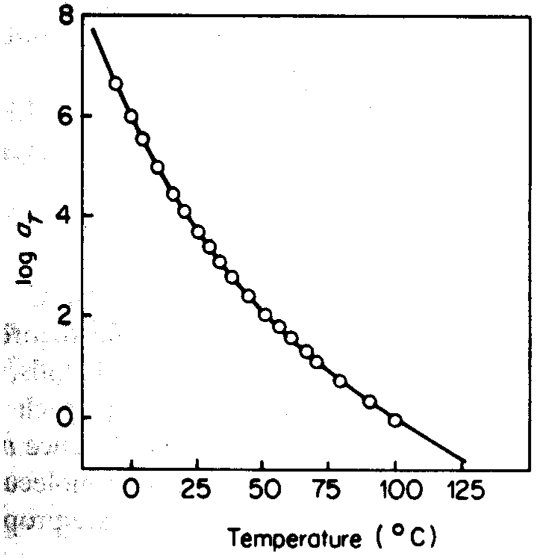
Secondary relaxations usually show Arrhenius temperature dependence with an activation energy V~20 kJ/mol. Segmental relaxation has strongly non-Arrhenius temperature dependence, i.e. its apparent activation energy is a function of temperature.

In reality there are many corrections to so simple picture. It was found that the shift factor for various polymeric systems is usually well described using Williams-Landel-Ferry (WLF) equation:

$$\log a_T = \frac{C_1(T - T_S)}{C_2 + (T - T_S)}$$

An example of storage compliance data for poly-n-octyl methacrylate. Composite curve obtained by plotting the data with suitable shift factors. Original data were extended over 2 decades only. The combined curve covers 11 orders in frequency.





Temperature dependence of the shift factor obtained for poly-n-octyl methacrylate in order to obtain the master curve shown on the previous slide. The temperature dependence is strongly non-Arrhenius and can be described by the WLF equation.

The time-temperature equivalence (or superposition) is used by many researchers for analysis of viscoelastic properties of polymers. You find it in all textbooks. It explicitly assumes that all viscoelastic processes have the same temperature variations. One should keep in mind, however, that in most cases the time-temperature superposition breaks down. It will be discussed later.

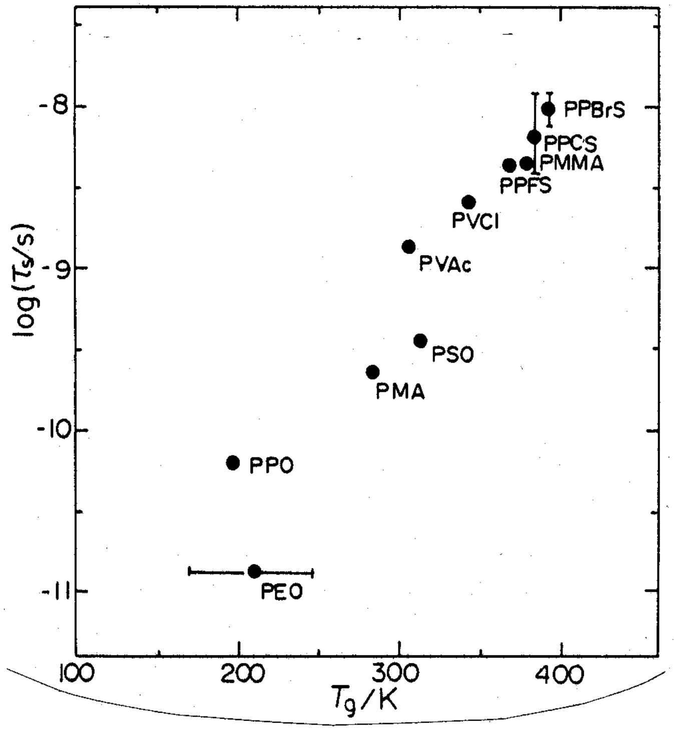
Segmental Relaxation (α-process)

The main structural relaxation in polymers is the segmental, so-called α-relaxation. It controls diffusion and viscosity, rotation of monomers. The α-process is the relaxation on time scale shorter than the rubbery plateau and the Rouse modes. It is responsible for the transition region and is associated with the glass transition.

It is usually ascribed to micro-Brownian motion of chain segments. Most authors agree that the α-process is related to conformational changes (like gauche trans transition). Because the glass transition is directly related to the α-relaxation, both, Tg and segmental relaxation (the α-process), show the same dependence on M_w and crosslinking.

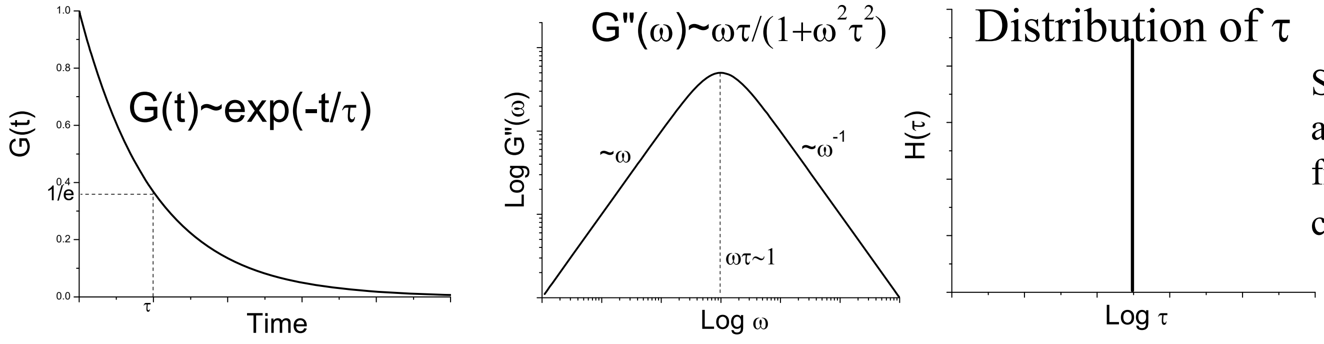
Many similarities between the glass transition in low-weight molecular systems and in polymers suggest that the chain connectivity is not required for this process.

A correlation between the dielectric relaxation time τ_s for the local segmental mode in dilute solution and Tg [Dielectric Spectroscopy of Polymeric Materials, Eds. J.Runt, J.Fitzgeraldp.279]. This observation supports direct relationship between segmental relaxation of a chain and Tg.



Spectral Shape of a Relaxation Peak

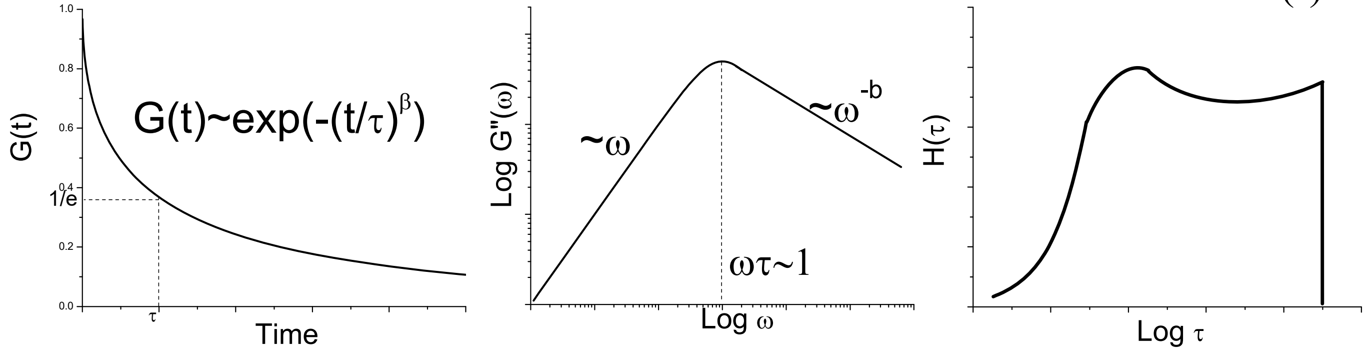
A simple relaxation process usually has a single exponential relaxation, $G(t) \propto \exp(-t/\tau)$.



Single exponential relaxation appears as a Lorentzian in the frequency domain and corresponds to a single τ

The α-process is not a single exponential decay, it is usually well described by a stretched exponential relaxation, the so-called Kolrausch-Williams-Watts (KWW) equation:

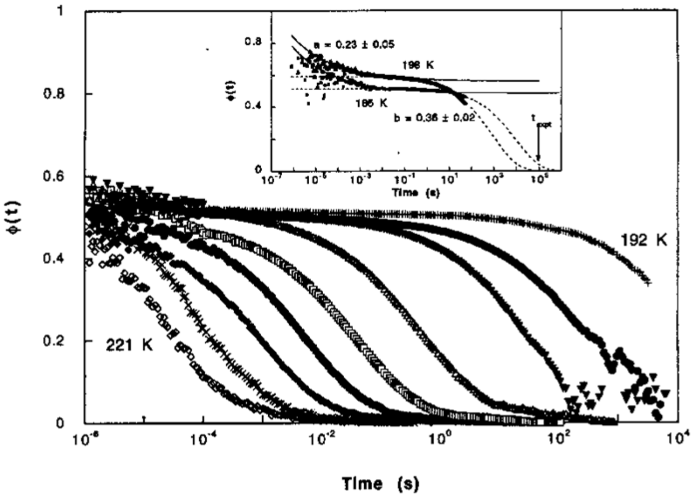
$$G(t) \propto \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right]$$



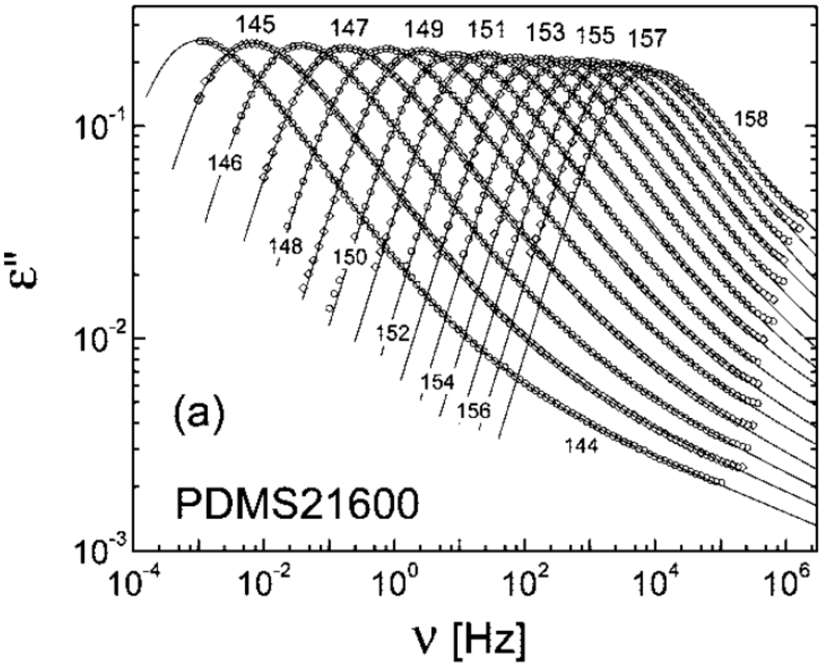
H(τ) is a distribution of τ, i.e. it characterizes how many relaxators have relaxation time τ.

Stretched exponential process is usually approximated by a Cole-Davidson distribution function. It is asymmetric and has extended high-frequency tail. Generally, $b \neq \beta_{KWW}$.

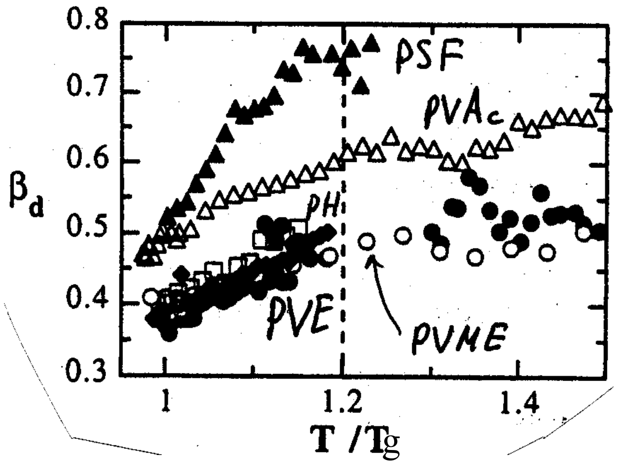
This stretched-exponential shape is not specific for the α-relaxation in polymers only. Many low-molecular weight liquids (especially in the supercooled state) demonstrate that. However, polymeric systems usually have higher stretching (e.g. lower values of β_{KWW}), β_{KWW}~0.35-0.7.



Intermediate scattering function ϕ(t) in PPG [Bergman, et al. **Phys.Rev.B 56**, 11619 (1997)] shows strong stretching of segmental relaxation.



Dielectric relaxation spectra in PDMS are also stretched [Hintermeyer, et al. **Macromolecules 41**, 9335(2008)].



Stretching parameter for different polymers [Colmenero, et al. **JPCM 11**, A363 (1999)].

The shape parameter depends on the system and varies with temperature. However, at higher T the temperature variations of β_{KWW} is weak.

There are two basic reasons for the stretched spectrum:

1. The process corresponds to a weighted sum of elementary processes each having a correlation function that may be exponential in time. E.g. it may be equivalent to a distribution of relaxation times
2. The process has a natural non-exponential dependence.

Temperature Dependence of Segmental Relaxation

The characteristic relaxation time of the segmental process, τ_α, demonstrates strongly non-Arrhenius temperature dependence in all polymers. It is usually described using Williams-Landel-Ferry (WLF) equation:

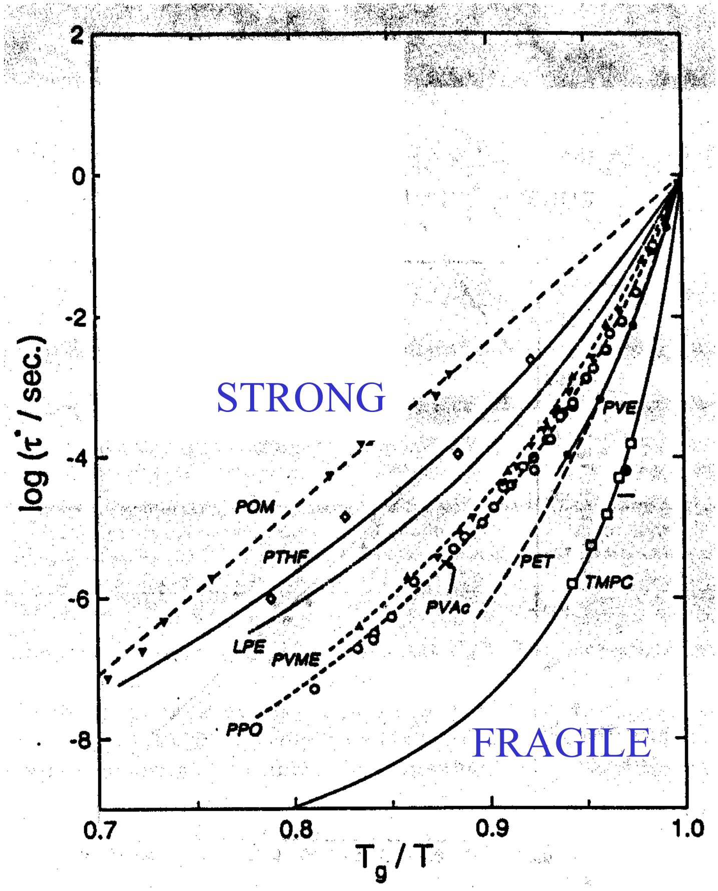
$$\log a_T = \log[\tau(T^*)/\tau(T)] = \frac{C_1(T-T^*)}{T-(T^*-C_2)}$$

Here T* is some reference temperature, often T*~Tg.

The same temperature dependence in non-polymeric systems is usually described by the Vogel-Fulcher-Tammann (VFT) equation:

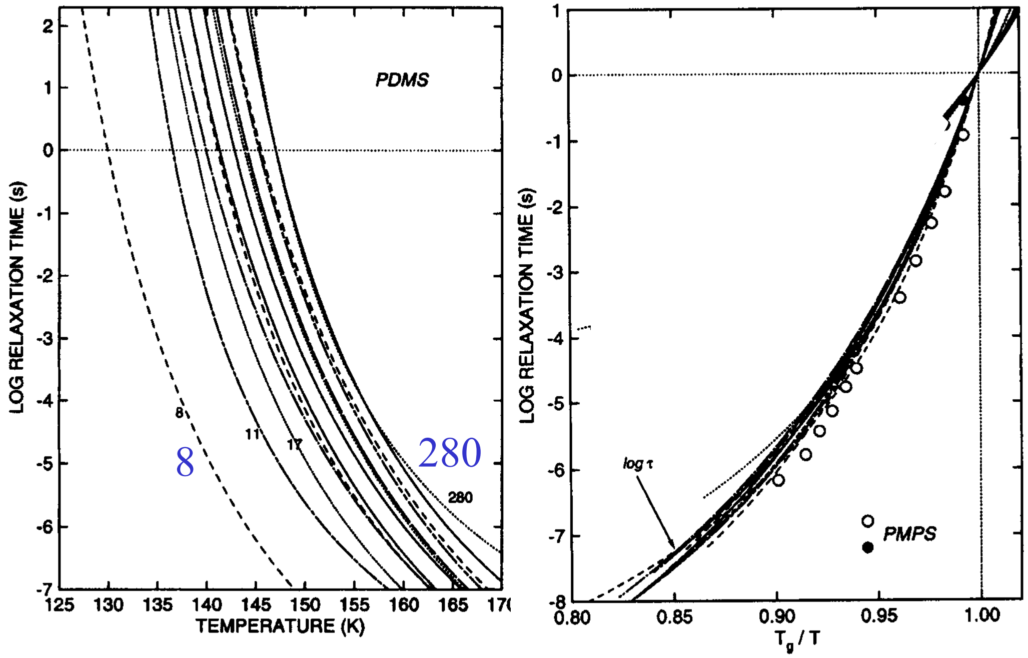
$$\tau = \tau_0 \exp\left[\frac{B}{T-T_0}\right]$$

The equations are equivalent: $C_2 = T^* - T_0$; $2.3 C_1 C_2 = B$, $C_1(T^*) = \log[\tau(T^*)/\tau_0]$.



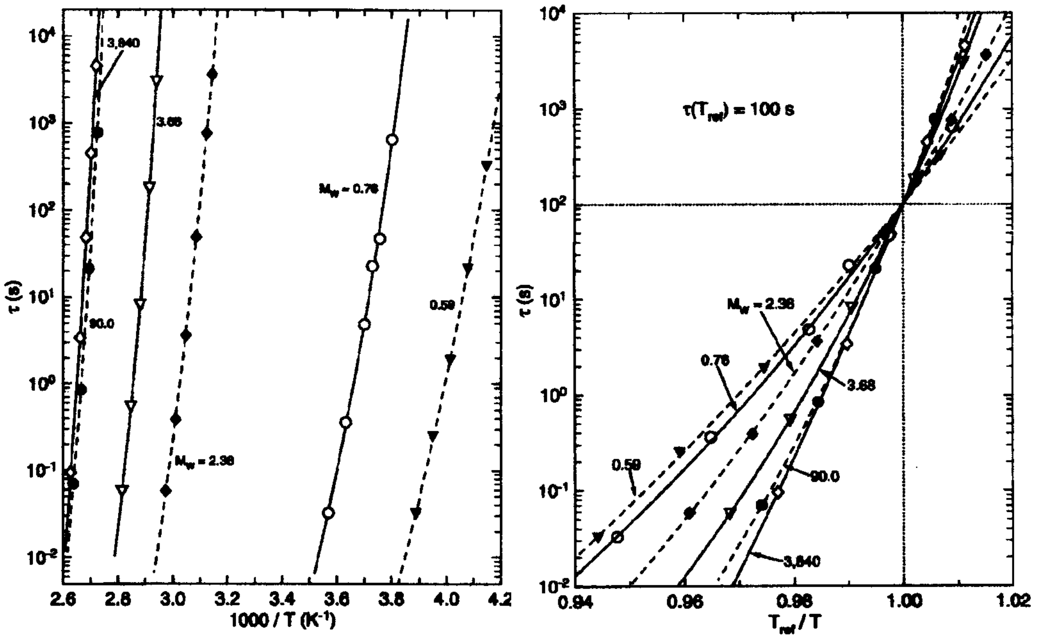
Different polymers show stronger or weaker deviations of τ_α from the Arrhenius behavior. The classification on strong and fragile systems has been suggested by Angell [in: Relaxation in Complex Systems, NRL, Washington, Eds.K.Ngai, G.Wright, 1984, p.3]. The systems that show Arrhenius-like temperature dependence of τ_α were called strong, strongly non-Arrhenius – fragile.

Degree of fragility can also be related to an apparent activation energy E_a around Tg (just a slope of $\ln(\tau_\alpha)$ vs 1/T around T~Tg). $E_a \sim B/(Tg-T_0)$ for some polymers can be large than the binding energy for C-C bond and has therefore no physical or chemical meaning. It reflects some cooperativity in motion.



τ_α of segmental relaxation depends on molecular weight of a chain: the lower is Mw the shorter is τ_α . This effect might depend on end groups of the chain. Traditional explanation is based on free volume ideas (will be discussed later).

Relaxation time in PDMS with different degree of polymerization (shown by numbers on the left) [Roland, Ngai, **Macromolecules 29**, 5747 (1996).]. In the case of PDMS, the temperature variations of τ_α for all molecular weights scale well with Tg (right) suggesting no change in fragility.

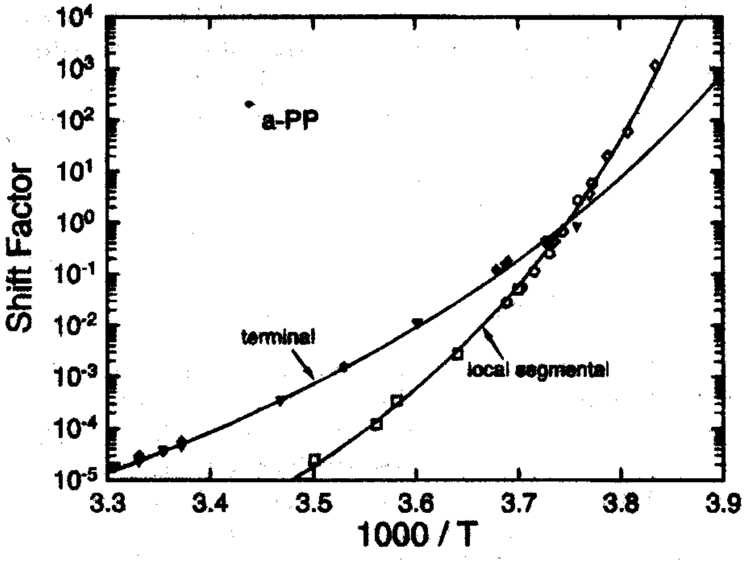


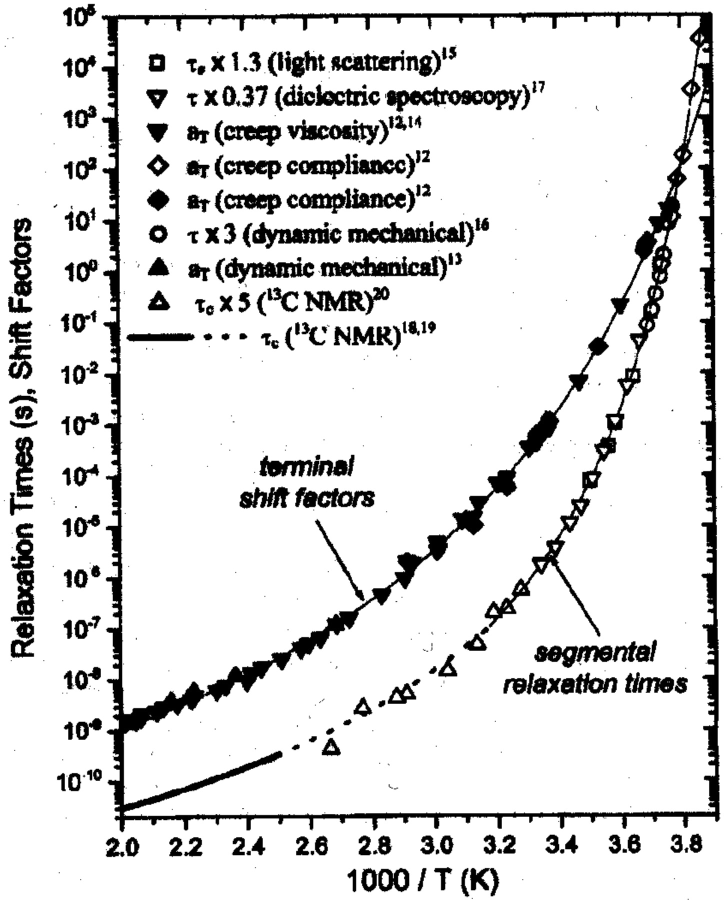
Similar results are presented for PS [Santangelo, Roland, **Macromolecules 31**, 4581 (1998)]. However, the fragility of PS chain appears to be dependent on Mw.

Recent ideas relate fragility to a rigidity of backbone and side groups. Rigid chains frustrate packing and increase fragility.

Thermorheological complexity (breakdown of time-temperature equivalence)

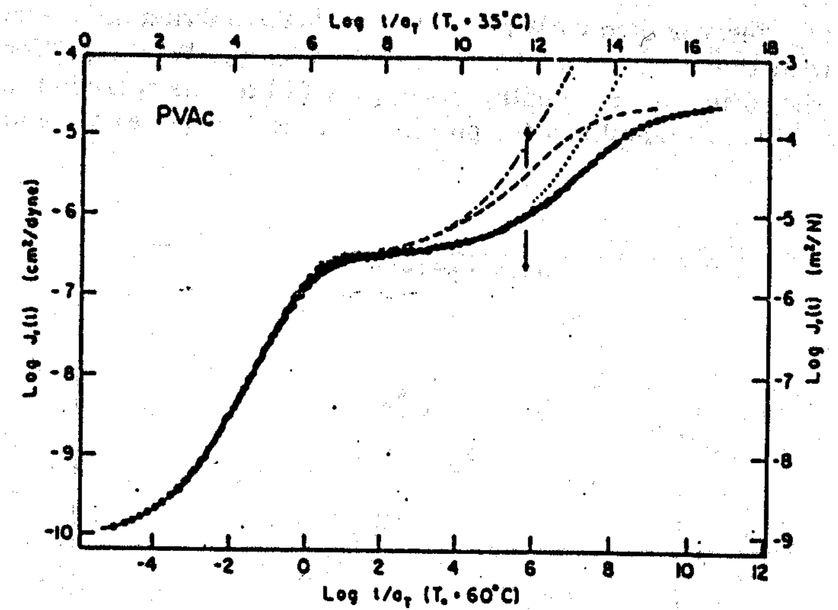
Developments of experimental techniques that are able to cover more than 5 orders in frequency provide more accurate tests of time-temperature equivalence. They clearly demonstrate breakdown of time-temperature equivalence principle for most of polymers: it appears that the shift factor is different for different relaxation modes.





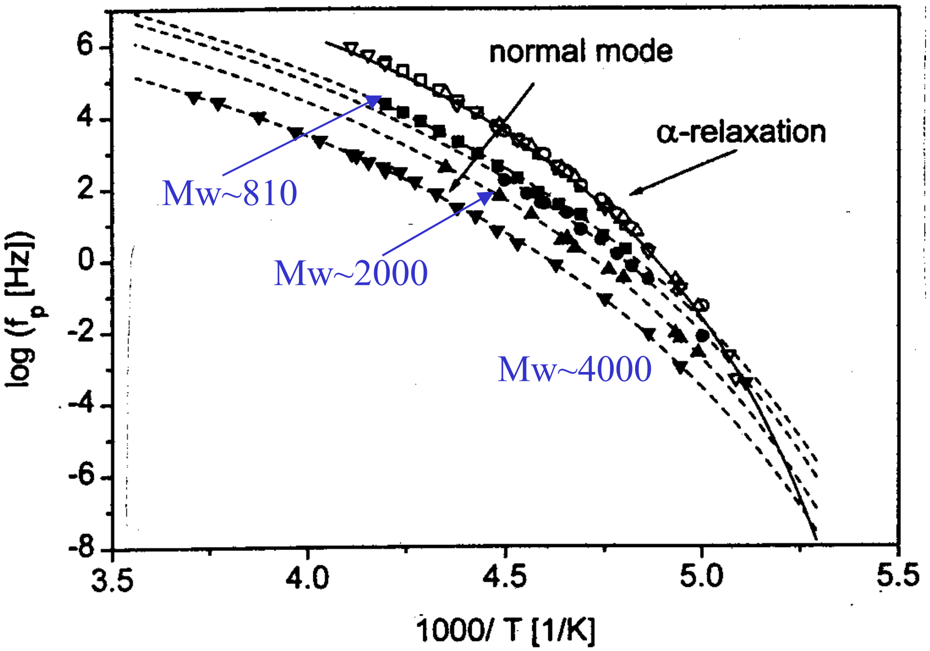
Atactic polypropylene, shift factors (right) and relaxation times (left) for terminal and segmental relaxations [**Macromolecules 29**, 3651 (1996) and **Macromolecules 34**, 6159 (2001)].

It seems that different processes have similar temperature dependence at high temperatures only [Roland, et al. **Macromolecules 34**, 6159 (2001)].

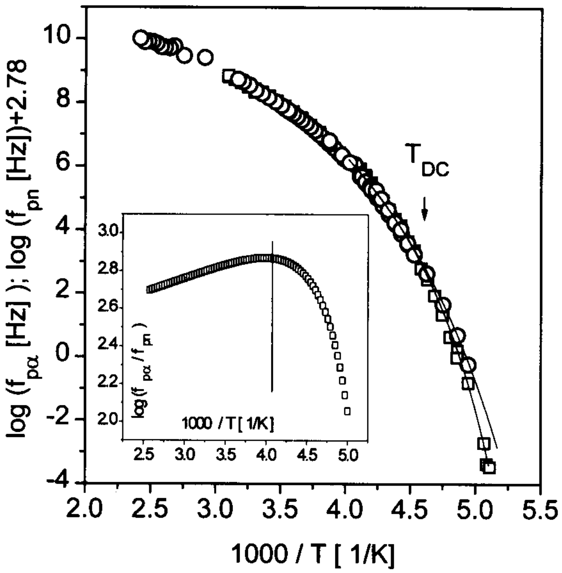


Breakdown of time-temperature equivalence appears also in the temperature dependence of the rubbery plateau in entangled polymers.

Compliance data for PVAc obtained at two reference temperatures (35 C and 60 C) show shortening of the plateau region by nearly two orders [Plazek, **Polym.J. 12**, 43 (1980)].



Dielectric relaxation spectroscopy allows measurements of normal and segmental modes at the same temperature, without use of time-temperature superposition. Normal modes show weaker temperature dependence than segmental relaxation. Data for PPG with different M_w [Dielectric spectroscopy of Polymeric Materials, ed. J.P.Runt and J.J.Fitzgerald].



Comparison of normal mode relaxation time to the segmental τ shows that they have similar temperature dependence at higher T. A difference increases drastically when the polymer approaches the glass transition temperature Tg [Dielectric spectroscopy of Polymeric Materials, ed. J.P.Runt and J.J.Fitzgerald].

Change of stretching parameter with temperature, different temperature dependence for α- and β- processes are additional evidences of the breakdown of time-temperature equivalence.

The reason for the breakdown of the time-temperature equivalence remains the subject of discussions. First of all, segmental relaxation is driven by energetic forces, while Rouse modes are entropic and reptation is controlled by a disenteglement time. Temperature dependence in the Rouse and reptation models is introduced through monomeric friction coefficient. Temperature variations of the friction coefficient may be different from temperature dependence of segmental relaxation.

Reptation model assumes that the same friction coefficient is involved in the Rouse modes at short times (inside the tube) and in the reptation modes at long times. The data on PVAc show that the friction coefficient might be different. Ferry and co-workers proposed [**J.Colloid Sci. 14**, 135(1959) and **17**, 10 (1962)] that a number of entanglements can be a function of temperature. It is not clear whether this is really the case.

Thus, one should be aware that time-temperature equivalence (superposition), although very often used and presented in all textbooks, is oversimplification that fails for many polymers.

Concluding Remarks:

1. Time-temperature superposition assumes that all relaxation processes have similar temperature dependence. It seems to be correct at high T, but it fails when temperature approaches Tg.

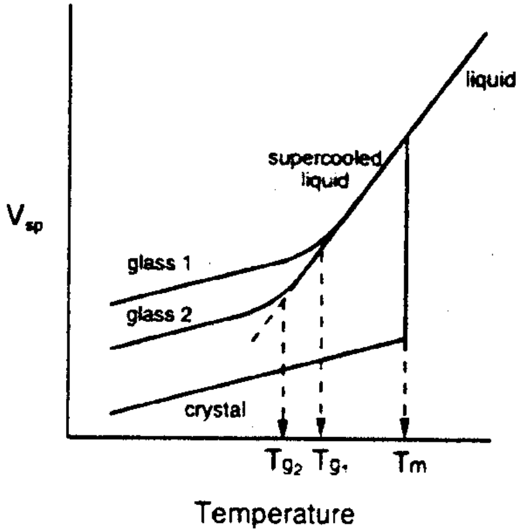
2. Spectral shape of segmental relaxation is always stretched (non-exponential). Stretching of the relaxation spectrum is a characteristic feature for relaxations in complex systems. The mechanism of the stretching (dynamic heterogeneity or intrinsically non-exponential process) remains unclear, although there are many indications of heterogeneous dynamics at time scale smaller than segmental relaxation time.

3. Segmental relaxation exhibits non-Arrhenius temperature dependence that is usually approximated by WLF or VFT equations. Steepness of temperature dependence of segmental dynamics (fragility) depends on chain rigidity.

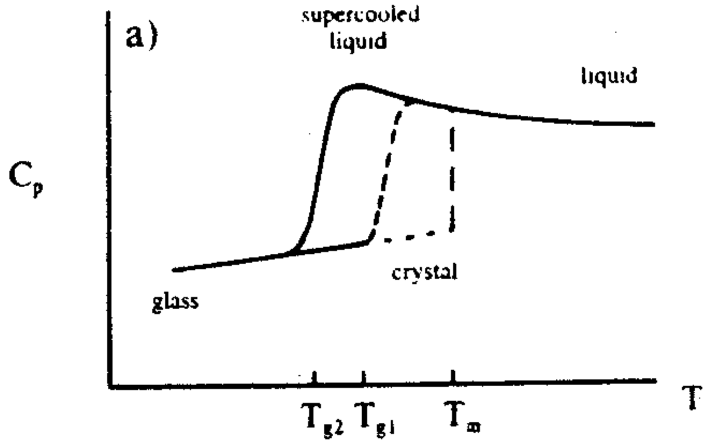
Glass Transition

Phenomenon of the Glass Transition

Glass transition is usually defined as a transition from a liquid state to a solid state. It appears as a sharp change of temperature dependence for many properties, including volume (density), entropy, elastic constants. The temperature where the change happens is called the glass transition temperature Tg.



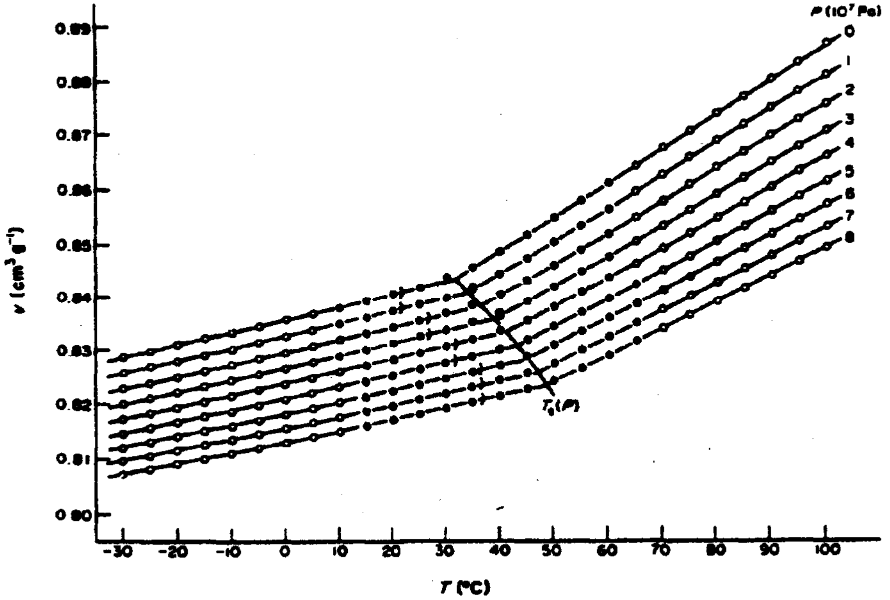
Temperature variations of volume. Tg depends on cooling rate.



Change in specific heat at temperatures around Tg.

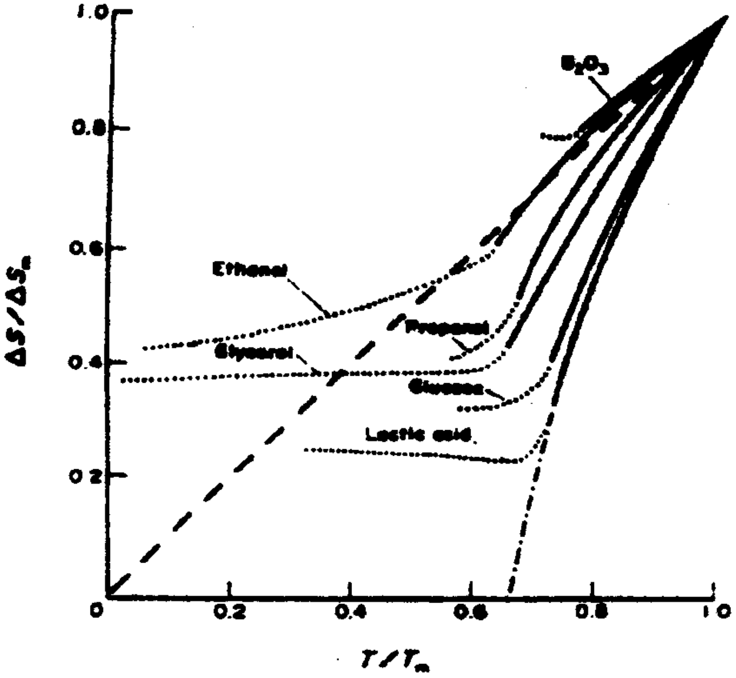
However, Tg is an ill-defined quantity. It depends on a cooling or heating rate. Due to that reason also another definition of Tg is accepted: Tg is a temperature where segmental relaxation time $\tau \sim 100$ sec. *There is no phase transition of any kind at Tg.*

The nature of the glass transition phenomenon remains a subject of discussions. However, the basic event of the observed transition from a liquid to a solid is a kinetic phenomenon. Glass transition is a freezing of segmental relaxation.



Glass transition depends on pressure: increase in P leads to increase in Tg of polymers. dTg/dP is different for different polymers.

This effect might be important for polymer processing where polymer melt is usually under some pressure.



The Kauzmann paradox

Considering changes of entropy, S, during cooling of a liquid state, Kauzmann paid attention [Kauzmann, **Chem.Rev. 43**, 219 (1948)] that extrapolated S of supercooled liquids may become lower than entropy of a crystal. That should happen at some temperature T_K.

That does not violate any thermodynamic law. However, it is difficult to expect that the entropy of a disordered state will be below the entropy of an ordered state.

T_K has been found close to T_0 VFT. That leads to speculation on existence of a real thermodynamic transition at $T \sim T_K \sim T_0$, that is avoided because the system falls out of equilibrium at Tg.

Several models were proposed to explain VFT or WLF equations for τ and to describe the glass transition:

-The free volume approach, assumes that the fractional free volume becomes 0 at $T \sim T_0$;

-Thermodynamic approach (Adam and Gibbs theory, Gibbs DiMarzio theory) treats the glass transition as a cooperative process, the degree of cooperativity increases when temperature decreases.

However, all the models are phenomenological, have some problems and the nature of this temperature dependence remains unclear.

Free Volume Approach

The basis is the Doolittle's viscosity equation:

$$\eta = a\exp(bv/v_f) \qquad (1)$$

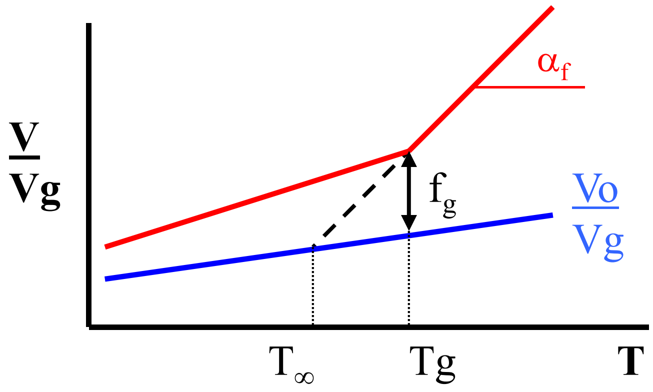
Here v_f is the free volume and v is the total volume. The same relation can be written for the relaxation time. The free volume is defined as $v_f = v - v_0$. Here v is the total macroscopic volume and v_0 is the actual molecular volume. The fractional free volume is usually assumed to vary with T:

$$f = v_f / v = f_g + \alpha_f (T - T_g) \qquad (2)$$

f_g is the fractional free volume frozen at Tg and a_f is the thermal expansion coefficient of the free volume. Substituting eq.2 in eq.1:

$$\log a_T = \log\frac{\eta}{\eta_g} = \frac{b}{2.3}\left(\frac{1}{f} - \frac{1}{f_g}\right) = -\frac{b}{2.3 f_g}\frac{T - T_g}{f_g/\alpha_f + T - T_g} \qquad (3)$$

Thus we have an equation similar to WLF equation, with T*=Tg, $C_1 = b/2.3f_g$; $C_2 = f_g/\alpha_f$. In that case one can relate the model parameters and WLF parameters: $f_g = b/2.3C_1$ and $\alpha_f = b/2.3C_1C_2$. However, because the constant b is an arbitrary parameter, no direct estimates of the free volume fraction can be obtained.



A simple picture behind the free volume approach is based on the assumption that an empty (free) volume is needed for molecular motion. This free volume decreases with decrease in T. That leads to slow down of the motion. Relaxation time at Tg crosses the experimental time scale and freezing of the structure (including free volume) occurs. It gives frozen free volume f_g. If one would cool the sample down with infinitely slow rate, $f_g=0$ will be reached at T_∞ that would be equivalent to T_0 of VFT equation.

When one considers b~1, the value for the free-volume fraction at Tg for many polymers falls in the range f_g~0.013-0.034. WLF proposed a “universal” value f_g~0.025. Later, another relation was also suggested: $f_g=10^{-4}*Tg+0.07$ [Boyer, Simha, **J.Polym.Sci.Polym.Lett. 11**, 33 (1973)]. It was further modified: f_g is not frozen at Tg; one should distinguish fractional empty free volume or dynamic free volume from total free volume.

Free volume approach has been extended to include pressure effects:

$$\log a_T = -\frac{b}{2.3 f_0}\frac{T - T_0 - \Theta(P)}{f_0/\alpha_f + T - T_g - \Theta(P)} \tag{4}$$

Here f_0 is f at $T=T_0$. Θ(P) is a function that depends on the pressure-dependent coefficient of thermal expansion of the free volume, $\alpha_f(P)$. It has been shown that the equation 4 describes reasonably well T- and P- dependencies for some polymers.

Nevertheless, the free-volume approach has been criticized for many problems. In some cases unreasonable parameters of the free volume should be assumed in order to describe data for some materials. It has been also demonstrated that holding free volume constant (by varying simultaneously P and T) leads to different viscosity, suggesting that not only density, but also temperature play role in the glass transition.

The influence of molecular weight on Tg, chain-end free volume approach

Tg for many polymers depends on molecular weight Mn. At not very low Mn, Fox-Flory empirical equation describes reasonably well the molecular weight dependence of Tg:

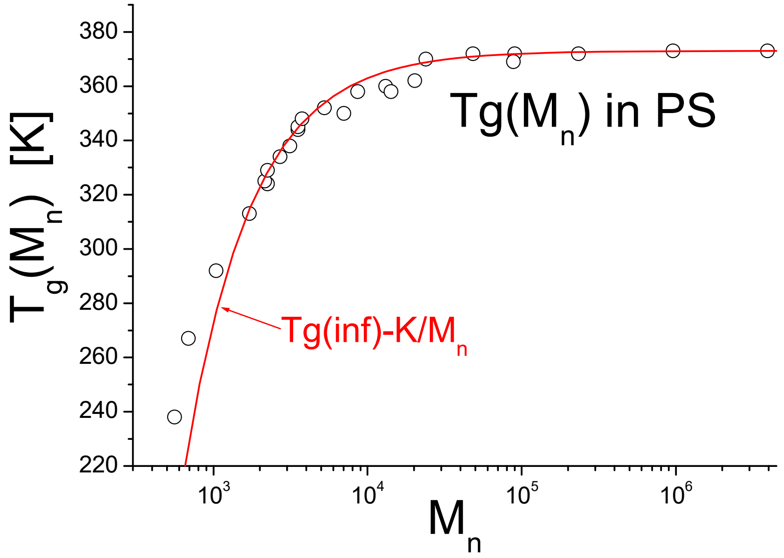
$$T_g(M_n) = T_g(\infty) - \frac{K}{M_n} \tag{5}$$

Free volume approach explains the Fox-Flory equation, assuming that chain ends contribute an excess free volume. In that case, decrease in Mn leads to increase of chain ends concentration and increase of free volume. Increase in free volume leads to decrease in Tg.

Let's assume that chain end has a free volume θ. Then the free volume per unit volume is $2\theta\rho N_A/Mn$, where ρ is density, N_A is Avogadro's constant. Assuming that f_g is independent of Mn, the excess free volume introduced by chain ends should be compensated by the thermal contraction:

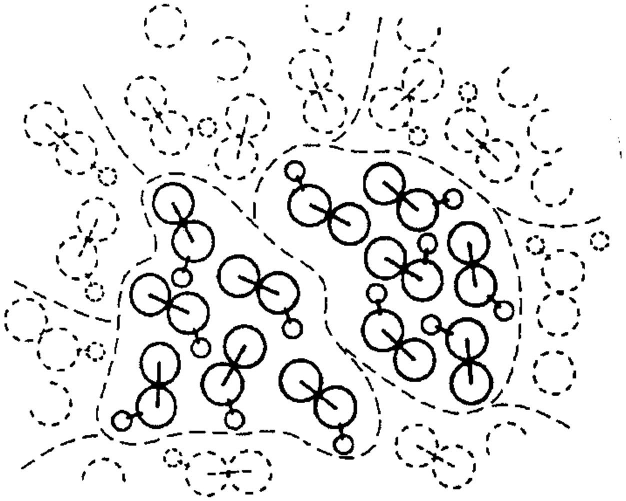
$$2\theta\rho N_A / M_n = \alpha_f [T_g(\infty) - T_g(M_n)] \quad \text{Then} \quad T_g(M_n) = T_g(\infty) - \frac{2\theta\rho N_A}{\alpha_f M_n} \tag{6}$$

The Fox-Flory equation is obtained with the constant $K=2\theta\rho N_A/\alpha_f$.



Thus, chain-end free volume idea describes well the molecular weight dependence of Tg. However, it is known that the free volume is not universal at Tg. Also, a simple free volume approach can not explain the behavior of Tg in ring polymers (will be discussed later.

Thermodynamic Approach



Any conformational changes require some cooperative motion of a few molecules (cooperative domain). Domain consists of z conformers, each has c_1 number of states. The conformational entropy for 1 mole of conformers in which there are N_z domains consisting of z conformers: $S_c = N_z k \ln c_1$

$$z = \frac{N_A}{N_z} = \frac{N_A k \ln c_1}{S_c} = \frac{s*}{S_c}$$

here s* is the conformational entropy of one mole of conformers where each conformer relaxes independently. At high T>T* when there is no cooperativity $s* = S_c$. At T<T* S_c drops faster than s*, assumption

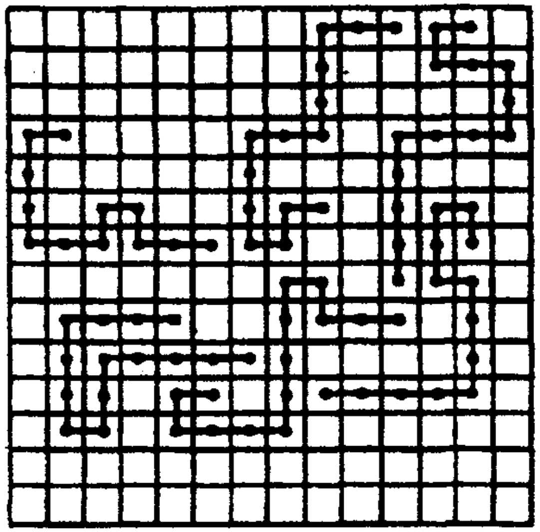
$$S_c = \frac{T*}{T*-T_0}\frac{T-T_0}{T}s*; \qquad \tau = \tau_0 \exp\left(\frac{C}{TS_c}\right)$$

An equation for relaxation time (Δμ is the energy barrier for one conformer to relax):

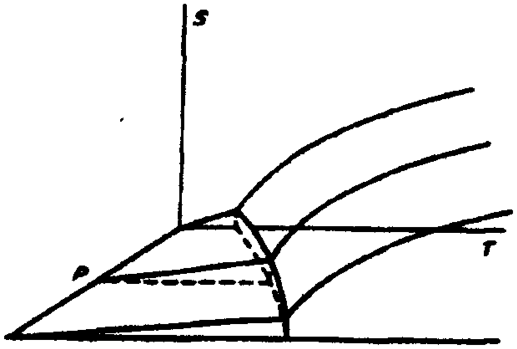
$$\ln(\tau/\tau*) = \frac{\Delta\mu}{k}\left[\frac{z}{T} - \frac{1}{T*}\right] = \frac{\Delta\mu}{k}\left[\frac{s*}{TS_c} - \frac{1}{T*}\right] = -\frac{\Delta\mu}{kT*}\frac{T-T*}{T-T_0} \qquad (7)$$

The eq.7 is equivalent to WLF or VFT equations.

Gibbs – DiMarzio theory



The theory is based on application of the lattice model of a polymer system to the glass transition problem. The polymer chains of degree of polymerization X have many configurations which fit onto the lattice of coordination number Z. Each chain has the lowest energy shape. Deviation of each bond from the lowest energy shape cost energy $\Delta\varepsilon$. The number of flexed out bonds is f. There are also n_0 vacant sites (holes) on the lattice. It results in additional hole energy per intermolecular bonds broken by introduction of the vacancies into the lattice (bond energy α).



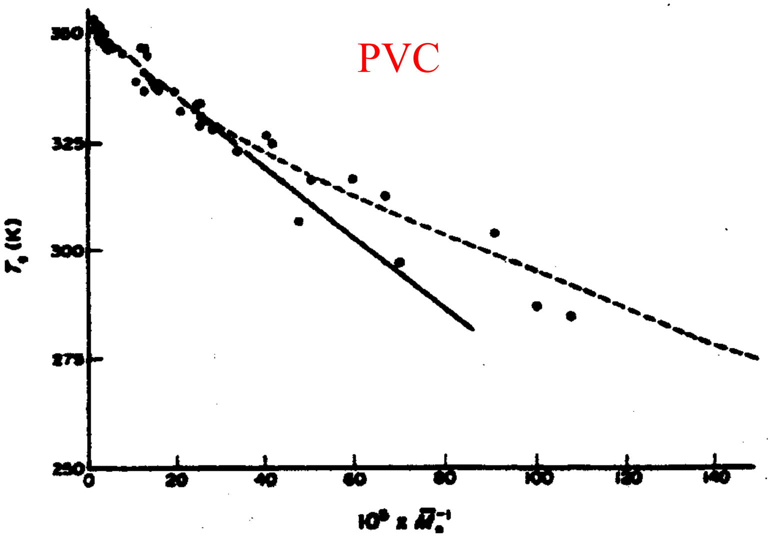
The lattice model predicts the existence of a true second-order transition at a temperature T_2. The number of allowed arrangements of the molecules decreases with decreasing T because: (i) the number of holes decreases; (ii) the configurational entropy of the molecules deceases because the chains favor low-energy states at lower T.The T(P) transition line defines the point $T_2(P)$ where the total configurational entropy first becomes 0. In that respect, the T(P) line represents the thermodynamic glass transition in experiments of long time-scale.

Gibbs DiMarzio theory gives rather complicated prediction for the molecular weight dependence of Tg [McKenna, **Compreh.Polym.Sci. 2**,311 (1989)]:

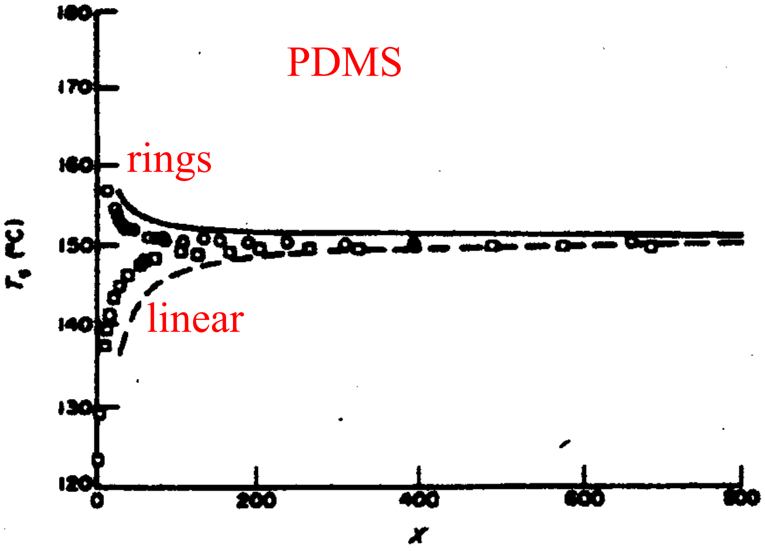
$$\frac{x}{x-3}\frac{\ln v_0}{1-v_0}+\frac{1+v_0}{1-v_0}\ln\left[\frac{(x+1)(1-v_0)}{2xv_0}+1\right]+\frac{\ln 3(x+1)}{x}=\frac{-2\frac{\Delta\varepsilon}{kT_g}\exp\left(-\frac{\Delta\varepsilon}{kT_g}\right)}{\left(1+2\exp\left(-\frac{\Delta\varepsilon}{kT_g}\right)\right)}-\ln\left[1+2\exp\left(-\frac{\Delta\varepsilon}{2kT_g}\right)\right] \qquad (8)$$

Here x is twice the degree of polymerization and v_0 is the volume fraction of holes, Tg is the glass transition temperature T_2. The eq.8 describes well Tg(Mn). It even describes the deviation from the Fox-Flory equation at smaller Mn.

The theory also makes an interesting prediction for ring polymers. It has been observed that Tg increases with decrease in Mn in ring PDMS. This behavior has been described qualitatively using the eq.8.



Tg vs 1/M in PVC. Solid line shows Fox-Flory relationship. The dashed lines shows Gibbs DiMarzio model predictions (eq.8) [from Pezzin, et al. **Eur.Polym.J. 6**, 1053(1970)].

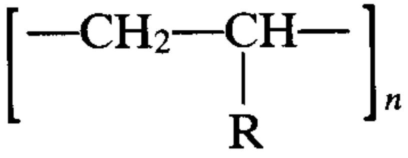


Tg in ring and linear PDMS compared to predictions of Gibbs-DiMarzio theory [from Guttman, DiMarzio, **Macromolecules**, 1988]

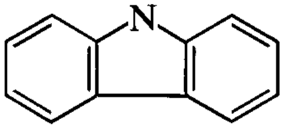
Influence of Molecular Structure and Architecture on Tg

Flexibility of the main-chain. Flexible group (for example, ether link) will enhance main-chain flexibility and reduce Tg. Inflexible group (for example, terephthalate) will increase Tg.
Si-O-Si is a very flexible link. As a result, PDMS has one of the lowest Tg known for polymers.

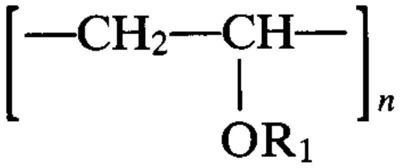
Influence of side groups. Bulky, inflexible side groups increase Tg .
Rigid and flexible side groups:



$$\left[-CH_2-\underset{R}{\underset{|}{CH}}- \right]_n$$

Polymer	R	Transition temperature in °C at ~1 Hz
Polypropylene	CH_3	0
Polystyrene	C_6H_5	116
Poly-N-vinylcarbazole		211

Increasing the length of flexible side groups reduces Tg, mostly due to increase in free volume.

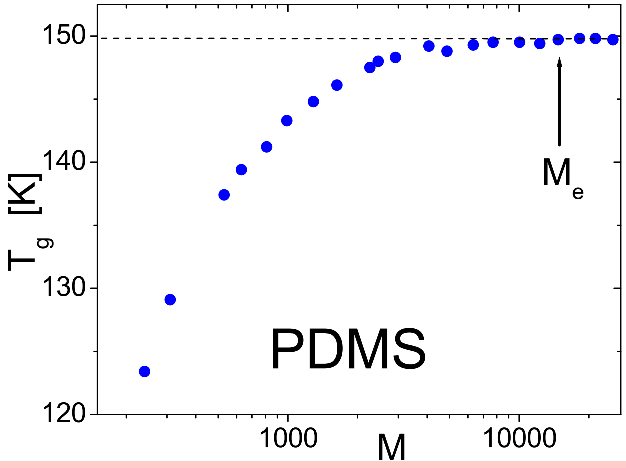


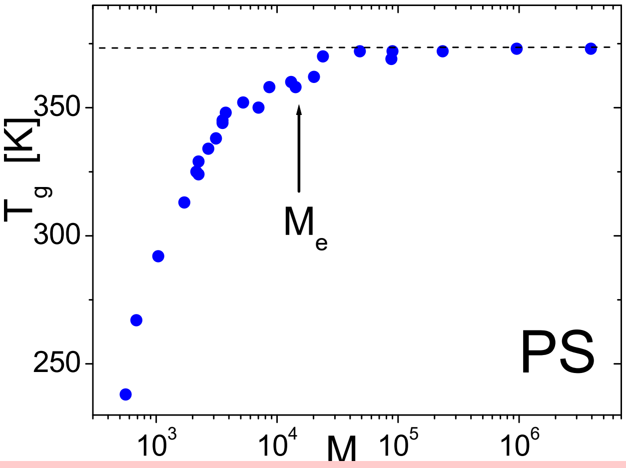
$$\left[-CH_2-\underset{OR_1}{\underset{|}{CH}}- \right]_n$$

Polymer	R_1	Transition temperature in °C at ~1 Hz
Polyvinyl n-butyl ether	$CH_2CH_2CH_2CH_3$	−32
Polyvinyl isobutyl ether	$CH_2CH(CH_3)_2$	−1
Polyvinyl t-butyl ether	$C(CH_3)_3$	+83

Configuration of the chain also plays important role:

➢Tacticity:	Example of syndiotatctic vs isotactic and atactic, e.g. PMMA
➢Microstructure:	Example of 1,2-PB and 1,4-PB
➢Positional isomerism:	Example hhPP, or ht-PP



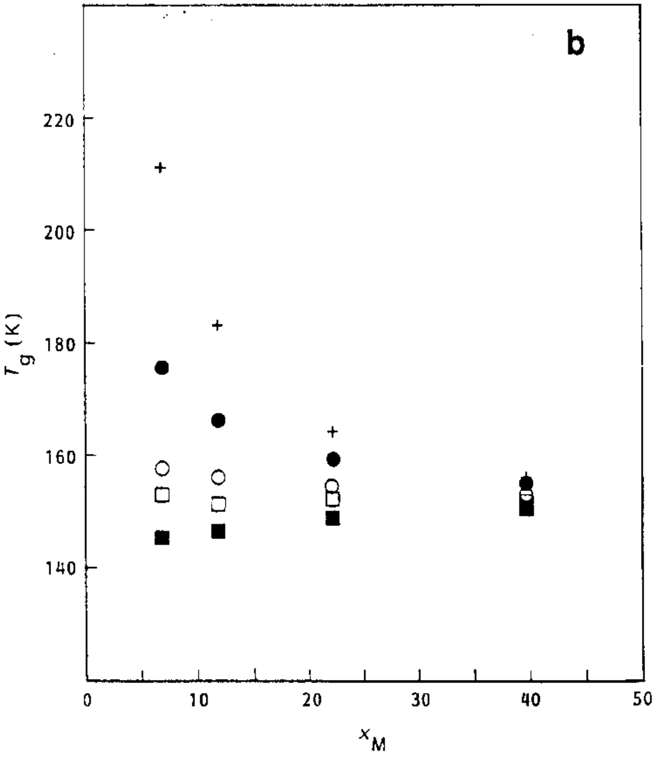


It is important to emphasize that the molecular weight dependence of Tg does not correlate with molecular weight between entanglements, M_e.

PDMS and PS have similar M_e but differ strongly in the molecular weight dependence of Tg.

Influence of end groups. We already discussed the idea of chain-end free volume approach that explains the molecular weight dependence of Tg. We also discussed that ring polymers (no ends) have different dependence of Tg on Mn.

It is possible to change direction of the molecular weight dependence of Tg by changing end groups. The stronger are interactions of the end groups the stronger will be increase of Tg with decrease in Mn.



Dependence of Tg on chain length (x_M – number of monomers) in PFB polymer with different end groups [Danusso, et al. **Polymer** **34**, 3687(1993)]: ■ - CH_2OCH_3 ; □ - $CH_2OSi(CH_3)_3$
o – CH_2OCOCF_3 ; ●- CH_2OH ; + - CH_2OK.

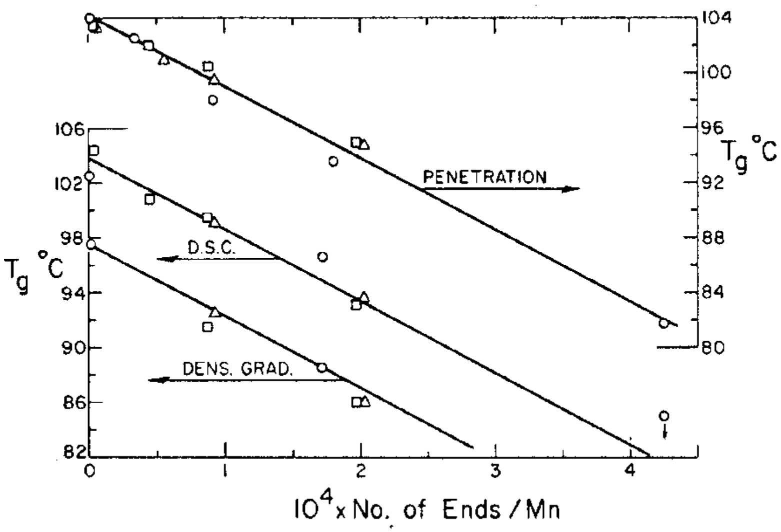
Influence of molecular architecture. Following chain-end free volume ideas (eqs.5,6), some authors [Roovers, Toporowski, **J.Appl.Pol.Sci.** **18**, 1685 (1974); K.L.Wooley, et al., **Macromolecules** **26**, 1514 (1993)] proposed modified Fox-Flory equation for star polymers:

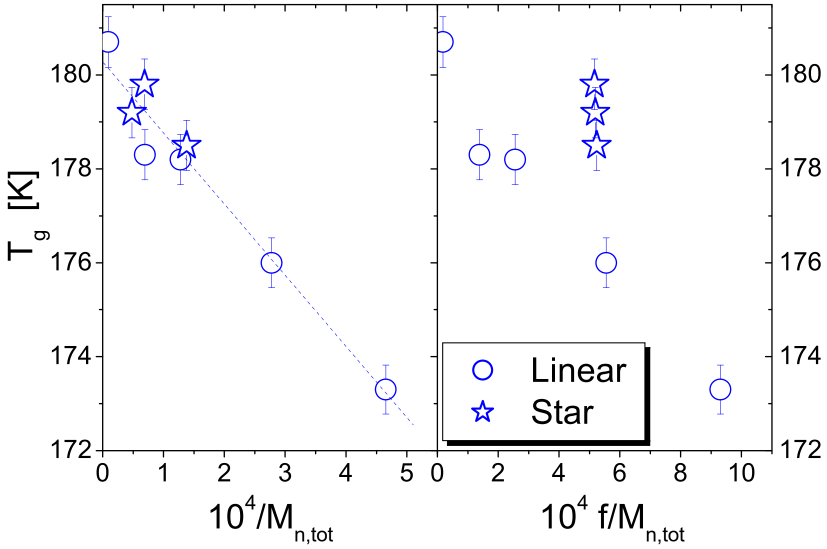
$$T_g = T_g(\infty) - \frac{f}{2}\frac{K}{M_n}$$

Here f is the number of arms and M_n is the total molecular weight. In that case, a linear chain is considered to be a two-arms star.

The proposed dependence has been observed for PS stars with 4 and 6 arms [Roovers, Toporowski, **J.Appl.Pol.Sci. 18**, 1685 (1974)].

This dependence, however, has not been observed in PI stars [C.Kow, et al., **Rub.Chem.Tech. 55**, 245(1982)].

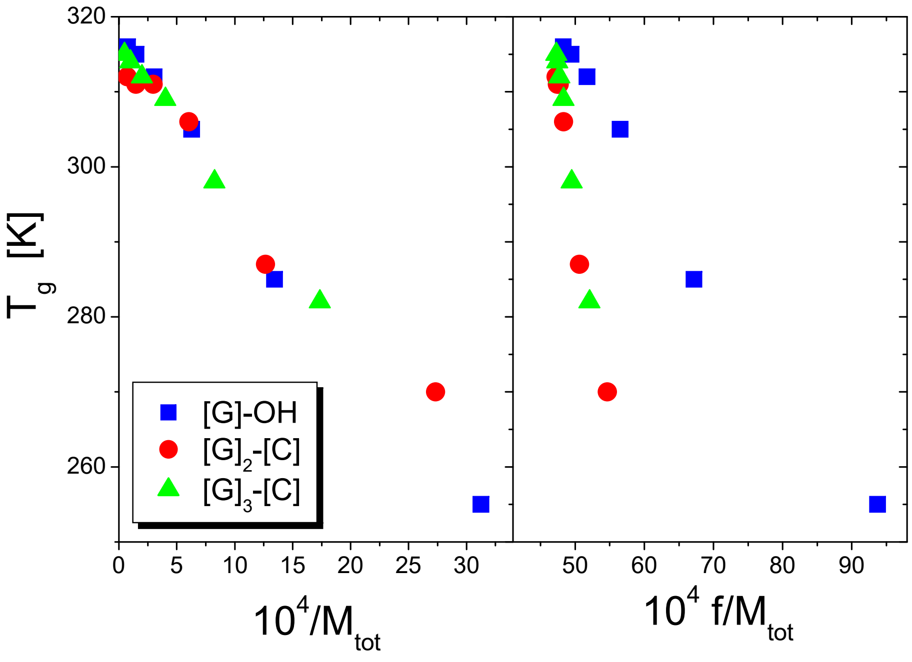


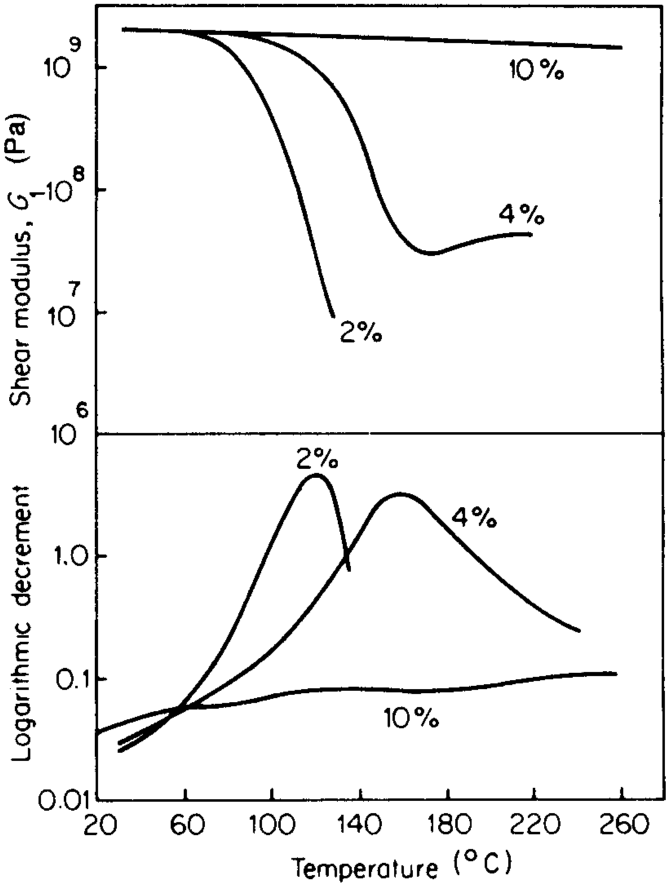


Analysis of PB stars demonstrate that Tg depends more on the total M_n than on architecture [A. Kisliuk, et al., **J.Polym.Sci.B 40**, 2431-2439 (2002)].

Thus influence of molecular architecture on Tg and segmental dynamics remains unclear and experimental data are controversial.

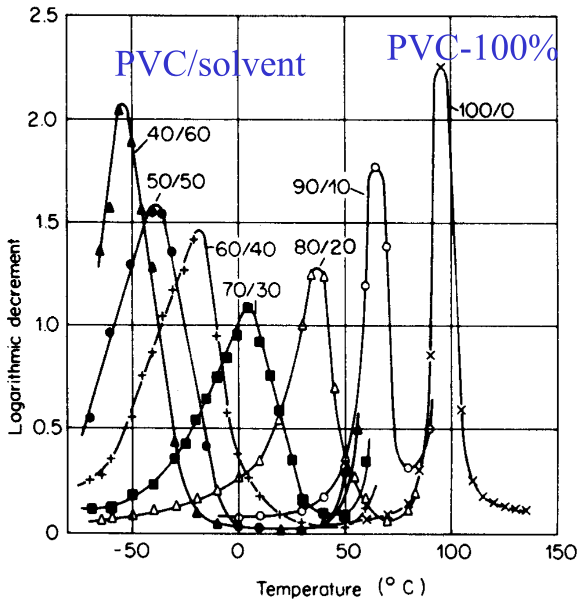
Validity of the chain-end free volume approach even for dendritic polymers was proposed in [Wooley, et al. **Macromolecules 26**, 1514 (1993)]. Tg in dendritic poly(benzyl ethers) with various microstructures scales with 1/M. However, it appears that it scales better with M_{tot} than with f/M_{tot}.

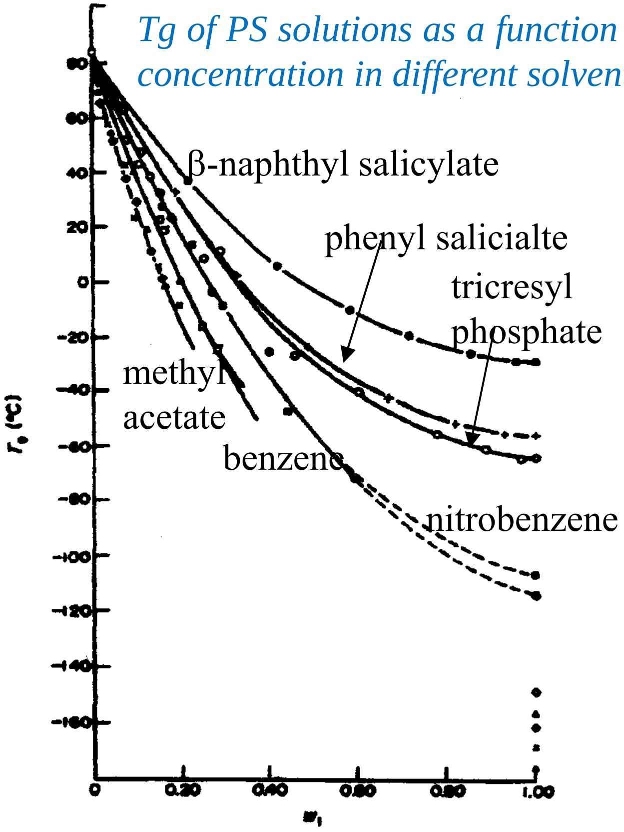




Influence of crosslinking. Chemical cross-links increase Tg. The main reason is an additional restriction on molecular motion, that reduces segmental mobility. At high concentration of cross-links, where motions of segments is significantly restricted, there is no glass transition.

Variation of Tg in polymer solutions, co-polymers and blends. Glass transition depends strongly on composition of polymer solutions, on a solvent used. Adding a solvent to a polymer usually leads to plasticization (decrease of Tg). The figure shows PVC plasticized with various amounts of di(ethylhexyl)phthalate.




Tg of PS solutions as a function of solvent concentration in different solvents.

Tg varies non-linear with concentration of solvents. One of the explanation is based on the free-volume approach. Fractional free volume of the solvent f_s is higher than that of the polymer f_p (solvent has lower Tg). Assuming that the fractional free volumes are not additive, the total fractional free volume:

$$f = v_s f_s + v_p f_p + k_v v_s v_p \qquad (11)$$

Here v_s and v_p are volume fractions, k is a negative constant ~10^{-2}. Eq.11 assumes that occupied volumes are additive and that agrees with measurements of density. Assuming iso-free-volume state at Tg the following dependence is predicted [McKenna]:

$$T_g(v_s) = \frac{v_s \alpha_s T_{gs} + v_p \alpha_p T_{gp} + k_v v_s v_p}{v_s \alpha_s + v_p \alpha_p} \qquad (12)$$

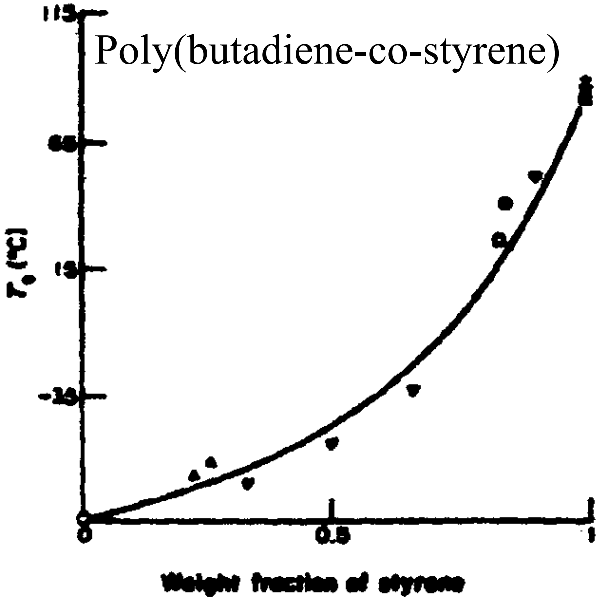
Here α is the thermal expansion coefficient of the fractional free volume. The eq.12 describes the data well with reasonable parameters.

Free volume ideas were also used for description of Tg in co-polymers [Gordon, Taylor, **J.Appl.Chem. 2**, 493 (1952)]:

The simplest approximation, although not the most accurate, is the Fox equation for Tg of random copolymers:

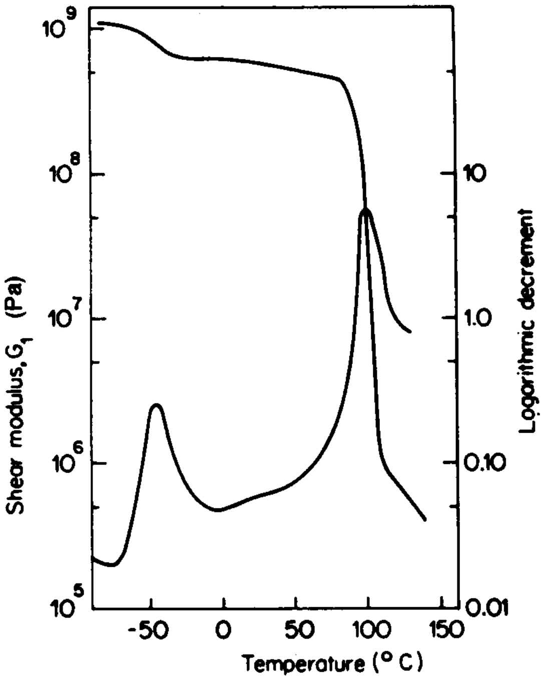
$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (13)$$

Here w_1 and w_2 are weight fraction of the copolymers 1 and 2, respectively.
It is based on considering entropy of the mixtures, and particular assumptions on changes at Tg of the copolymer.

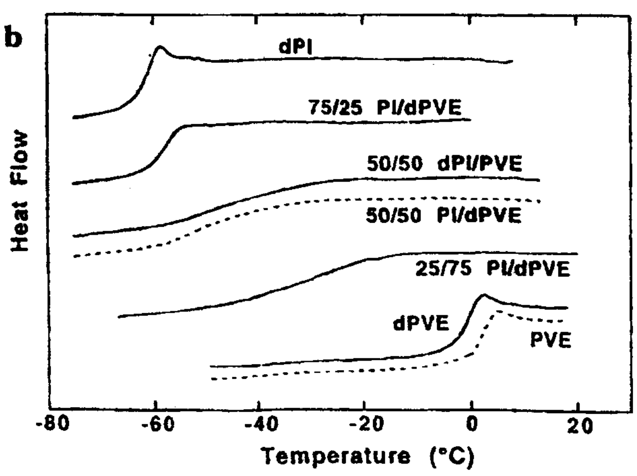


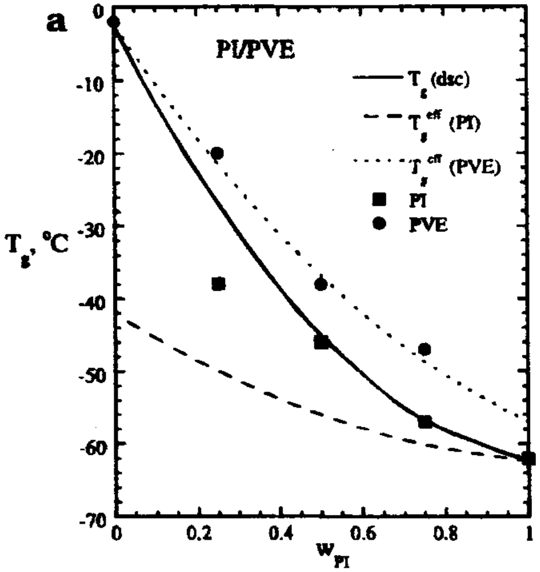
In the case of polymer blends there are two situations:

Immiscible blends show separate Tg for each of the components (2 Tg's for binary blends). Example of shear modulus and logarithmic decrement in blend of PS and styrene-butadiene co-polymer.
Separated Tg's will be observed also in block co-polymers of immiscible blocks.



A single Tg appears in DSC of miscible blends. It appears in between Tg's of the mixed components and the transition broadens. However, each component has its own relaxation time, and τ of the fast component slows down less than τ of the slow component speeds up. One can analyze it as Tg^{eff}.



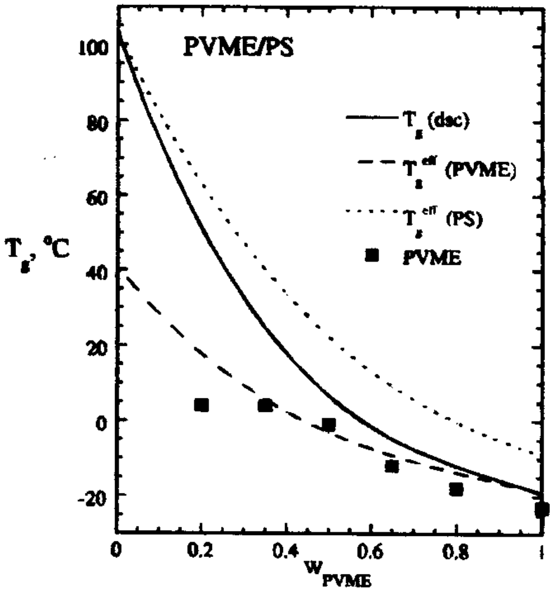


There are a few models proposed for the description of Tg in miscible polymer blends. One of the ideas was proposed by Lodge and McLeish [**Macromolecules** 33, 5278 (2000)], and takes into account effective concentration of monomers A and B around a typical monomer A: $\phi_{eff} = \phi_S + (1-\phi_S)\phi$

Where ϕ is the volume fraction of A component and ϕ_S is the "self-concentration" term:

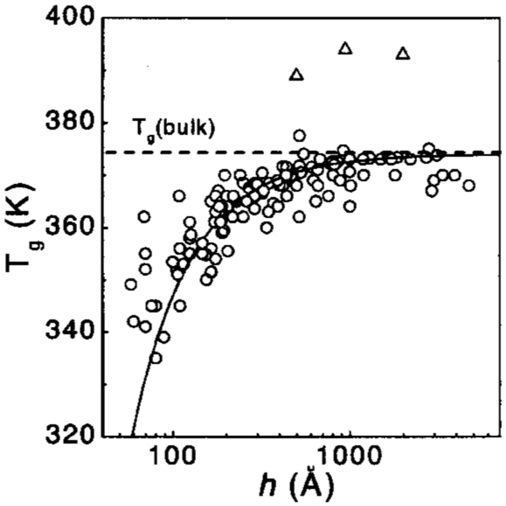
$$\phi_S = \frac{C_\infty m_0}{n_0 \rho N_A V} \qquad (14)$$

Here m_0 is mass of a monomer, n_0 is the number of backbone bonds per monomer, ρ is the density, V is a volume that influences the relaxation of a monomer. It is assumed to be $V \sim l_K^3$ (l_K is the Kuhn length).The main idea is that the monomer A experience higher concentration of A because of its connectivity. As a result, you have a distribution of ϕ_{eff}. The model explains many characteristic properties of relaxation and Tg in miscible blends, even gives good quantitative predictions for some systems. However, it fails for some other systems.

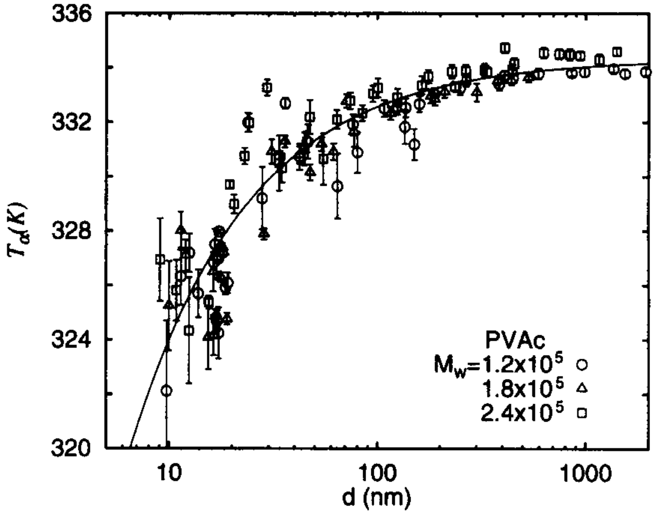


Glass transition in thin polymer films: Developments in nano science and nano technology leads to decrease of characteristic size of elements. Qualitative difference appears when we approach length scales ~5-50 nm.

One example of that is variation of Tg in thin polymer films [review by Forrest, Dalnoki-Veress, **Adv.Coll.Interf.Sci. 94**, 167 (2001)]. It has been observed that Tg of polymer films drops with decrease in film thickness h. The best polymer analyzed is PS. Various techniques show drop of Tg ~30-50K when h ~10 nm. Drop of Tg depends on substrate, suggesting importance of a polymer-substrate interactions. In particular, it has been shown that for polymer physically grafted to substrate Tg can increase with decrease in h.
Another example: PMMA on Au -> Tg decreases with decrease in h, while PMMA on SiO_2 -> Tg increases with decrease in h.



Tg in thin PS films as a function of thickness h.

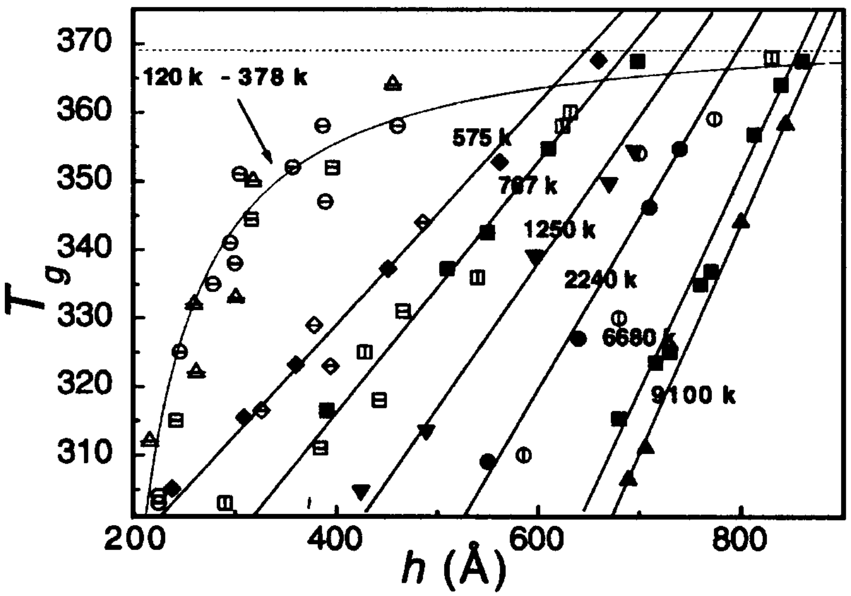


Tg in thin PVAc films [Fukao, et al., **J.Non.Cryst.Sol. 307-310,** 517 (2002)].

No significant dependence of the effect on Mw has been observed in thin supported films. Tg(h) is usually described by an equation:

$$T_g(h) = T_g^{bulk}\left[1-\left(\frac{a}{h}\right)^{\delta}\right]$$

Even stronger effect has been reported for thin free standing films (no substrate). In that case, strong dependence of the effect on molecular weight has been observed. There are two regimes: lower M_w (for PS~120,000 – 370,000), and higher M_w (>370,000).
Effect at lower M_w is similar to the effect in supported films but is ~2 time stronger.
Much stronger dependence appears at higher M_w, it starts to deviate from the bulk behavior at h~R_{EE} (end-to-end distance).



Current consensus is that these results are experimental artifact, and effect is much smaller.

Traditional picture for these variations is related to a surface layer that is assumed to have higher mobility than the bulk polymer. Of course, if it interacts strongly with a substrate, it might have lower mobility. The thickness of the layer might be different for different polymers and for PS is estimated to be ~3.5-4 nm. Decreasing the thickness of the film enhances the influence of the layer on the film properties.


Surface layer

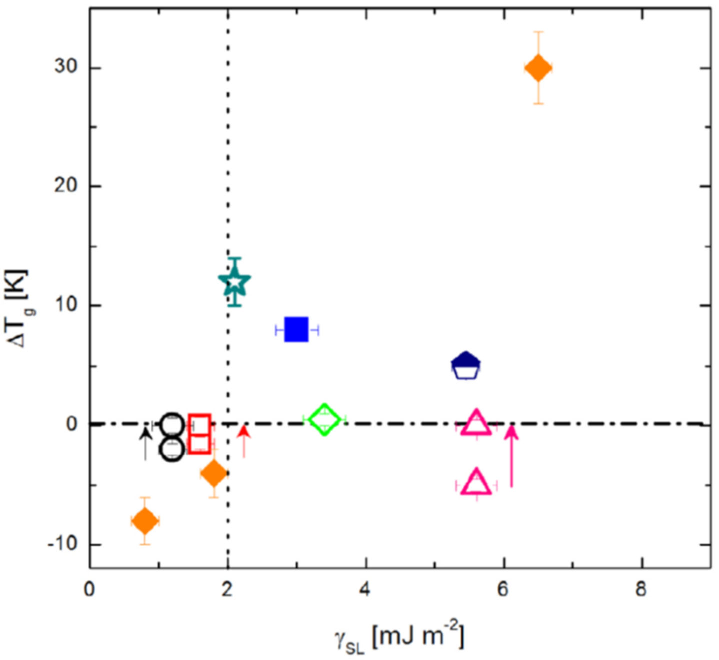
Bulk properties

Surface layer

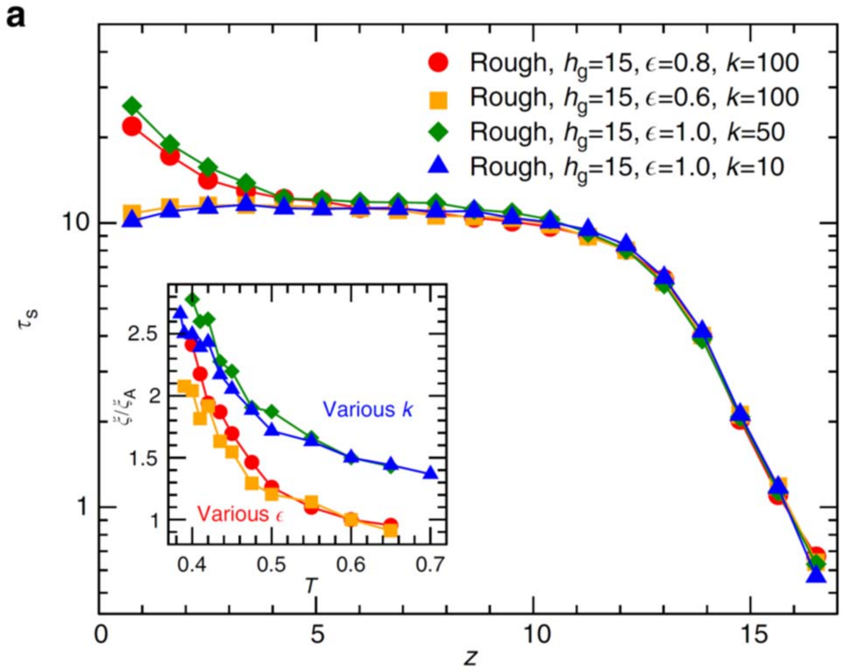
Film

This idea explains why the effect appears to be stronger in free-standing films. There are many microscopic models that try to explain details of the effect, in particular, for free-standing films with high Mw polymers. However, no one of them can describe all the data consistently.

It was demonstrated that changes of dynamics of thin polymer films depend strongly on annealing. Equilibration time is usually many decades longer than the longest chain relaxation time. This effect is attributed to a very long chain adsorption time.



Attempts to relate the shift in Tg of thin films to the polymer-substrate interactions did not reveal strong correlations, just a trend [**Rep. Progr. Phys. 80**, 036602 (2017)].



Computer simulations suggest that the thickness of the interfacial layer is just a few segments (i.e. a few nm) [**Nature Comm. 5,** 4163 (2014)].

Similar interfacial layer is also formed around nanoparticles in polymer nanocomposites, and in polymers confined to some porous structures.

Concluding remarks

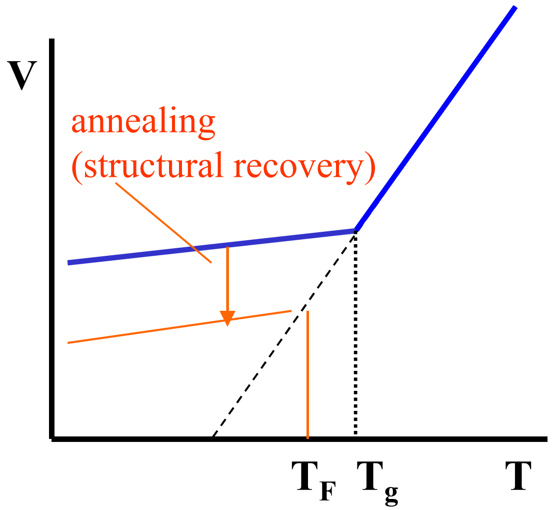
1. Glass transition in polymers is “freezing” of segmental relaxation. Tg is an ill-defined quantity. It corresponds to the temperature at which segmental relaxation time becomes comparable to the laboratory time scale (cooling rate).

2. There are two main approaches for description of the glass transition: free volume and thermodynamic (Gibbs-DiMarzio). Both describe the phenomena qualitatively and both have various problems.

3. Chemical structure, chain length and architecture of macromolecules affect their glass transition temperature.

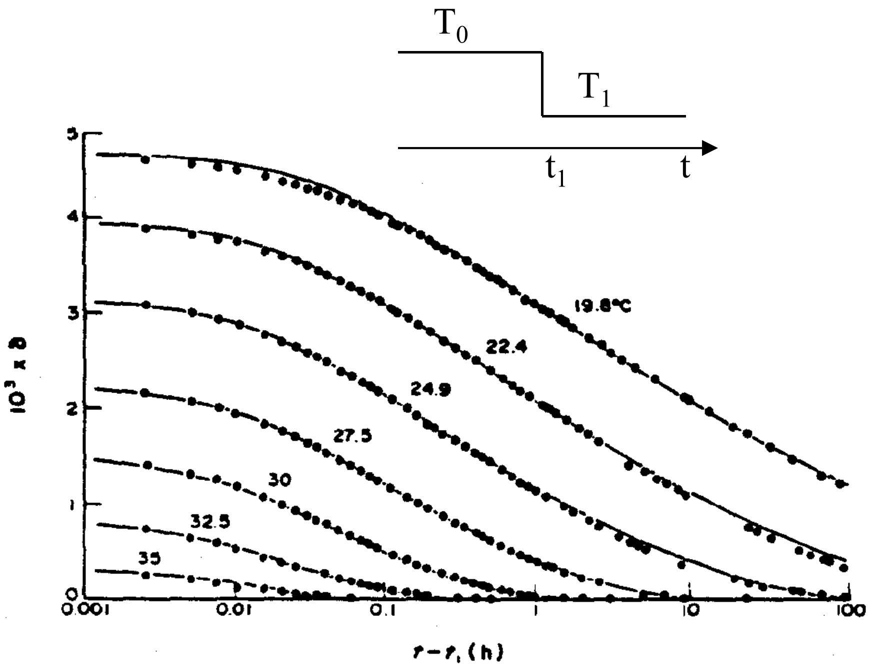
4. Confinement effect leads to variation of Tg in thin polymer films and in nanocomposites. Detailed microscopic mechanism of these variations remains a topic of active discussion.

Structural Recovery and Aging



Polymer system falls out of equilibrium (deviates from equilibrium liquid behavior) when cooled below its Tg. Properties of non-equilibrium system depends on cooling rate and annealing (aging).

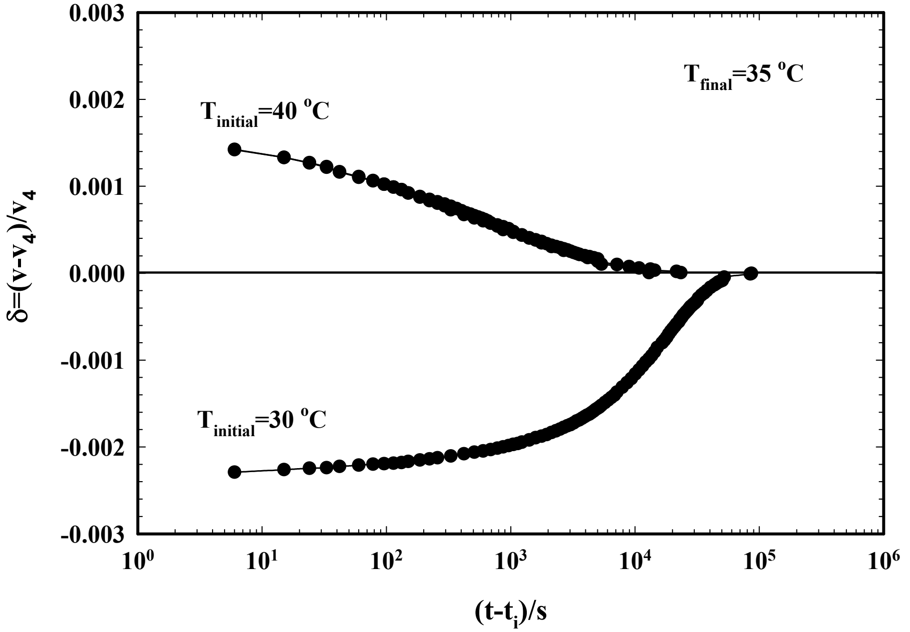
To characterize non-equilibrium state, the ideas of fictive temperature T_F has been suggested. T_F is a temperature at which an equilibrium property will be equal to the property in the glassy (non-equilibrium) state. T_F depends on quenching rate and annealing parameters.
However, it appears that T_F can be different for different properties.



Studies of structural recovery and aging is extremely important for application of solid polymers.

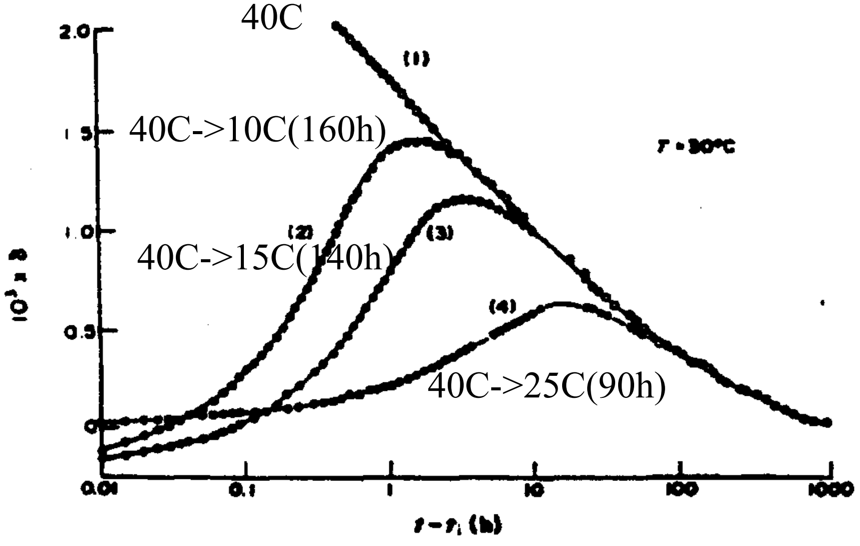
Usually various types of temperature jumps experiments are used [McKenna].

An example of *intrinsic isotherms* experiment on glucose (volume contraction) after quenching from Tg~40^{o}C. Departure from equilibrium varies non-liner with T, time required to reach equilibrium increases strongly with decrease in T and time-decay is stretched-exponential.



Another general property is *asymmetry of recovery*.
Temperature jump ΔT might be from above or from below. Recovery of equilibrium property is faster when jump is from above because initial structure is more mobile.

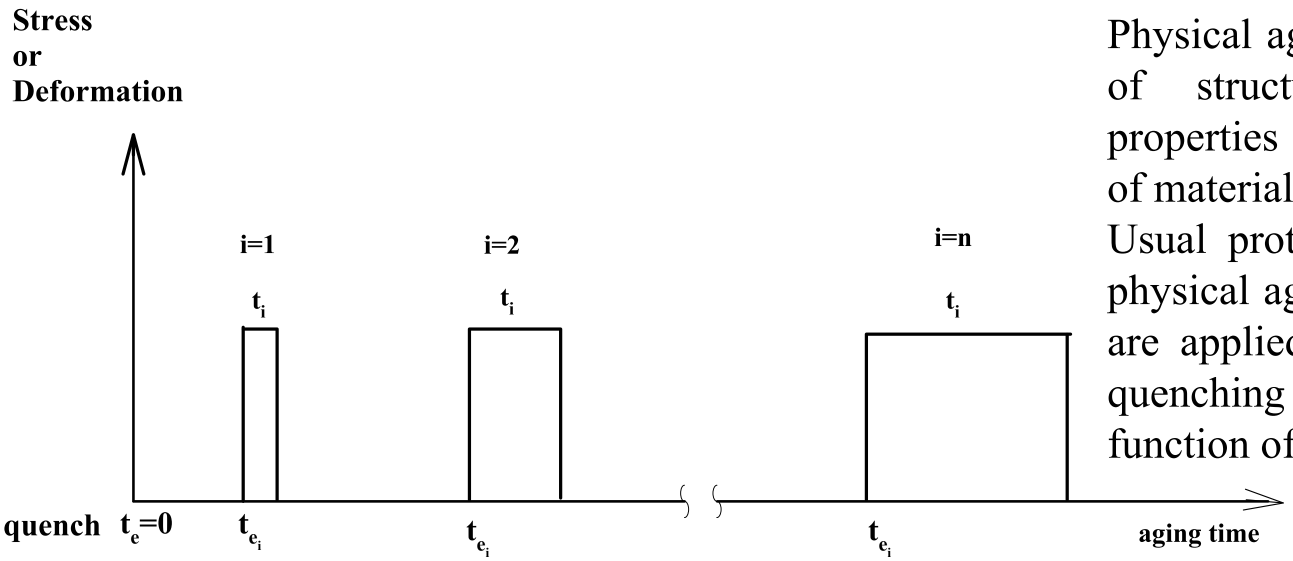
An example of volume recovery for PVA at T=35°C.



One of more complicated kinetics arises when material does not recover at initial T and then is heated to a higher T. *Memory effect* of a thermal history appears in this experiments.

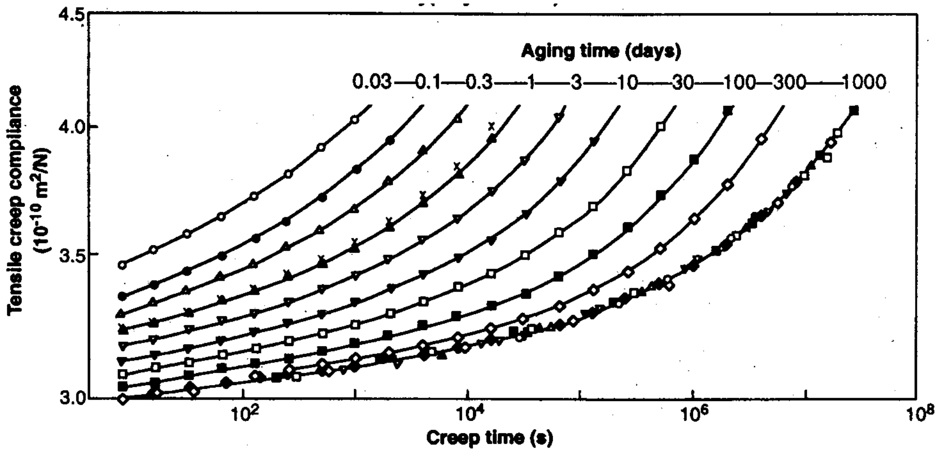
Isothermal evolution at T=30°C for PVA with various initial (before jump) temperatures.

Physical Aging



Physical aging is related to influence of structural recovery on various properties (mechanical, viscoelastic) of materials.

Usual protocol used for analysis of physical aging. Stress or deformation are applied after some time t_e after quenching and τ is measured as a function of t_e.



Here is an example of creep experiment in PVC as a function of aging time t_e. The sample was quenched from 90°C (Tg~80°C) down to 20°C.

The retardation spectrum is a function of two times, τ and t_e, i.e. τ depends on instantaneous structure.

An aging time shift factor a_{te} is introduced:

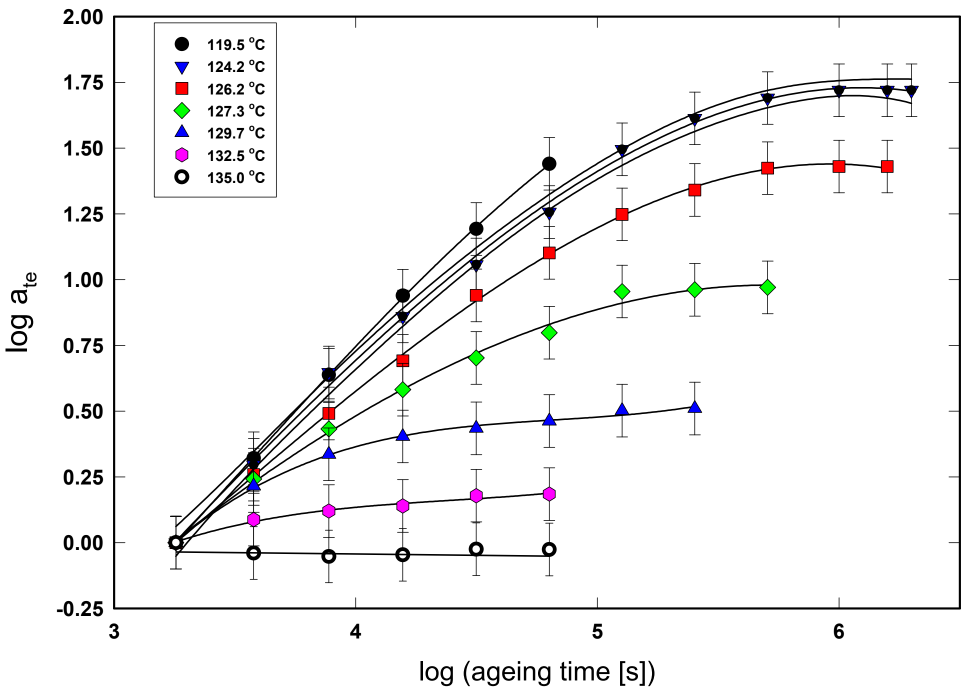
$$a_{te} = \tau(t_e)/\tau(t_{e,r})$$

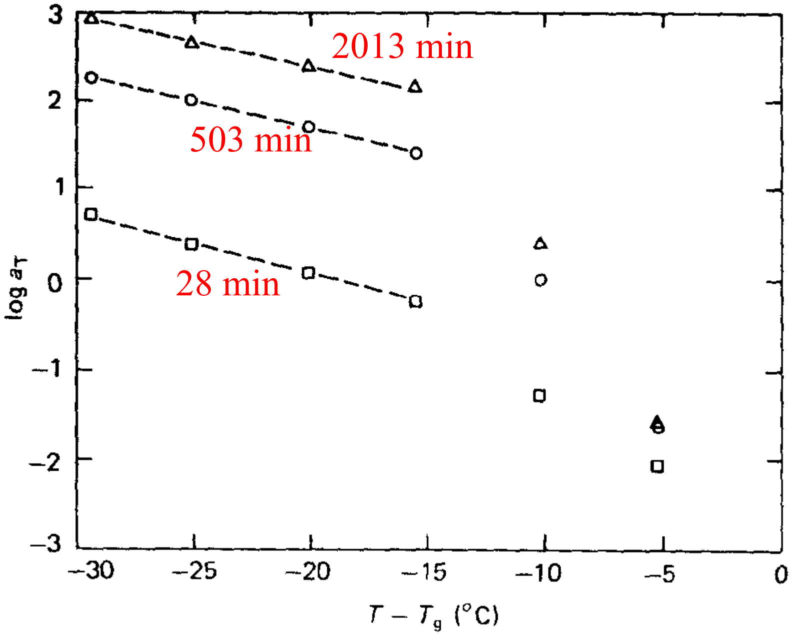
Usually also time-aging time superposition is assumed.

Aging time shift factor in PC at different temperatures. Strong temperature dependence is observed. The initial shift rate

$$\mu = d\log(a_{te})/d\log(t_e) \sim 1$$

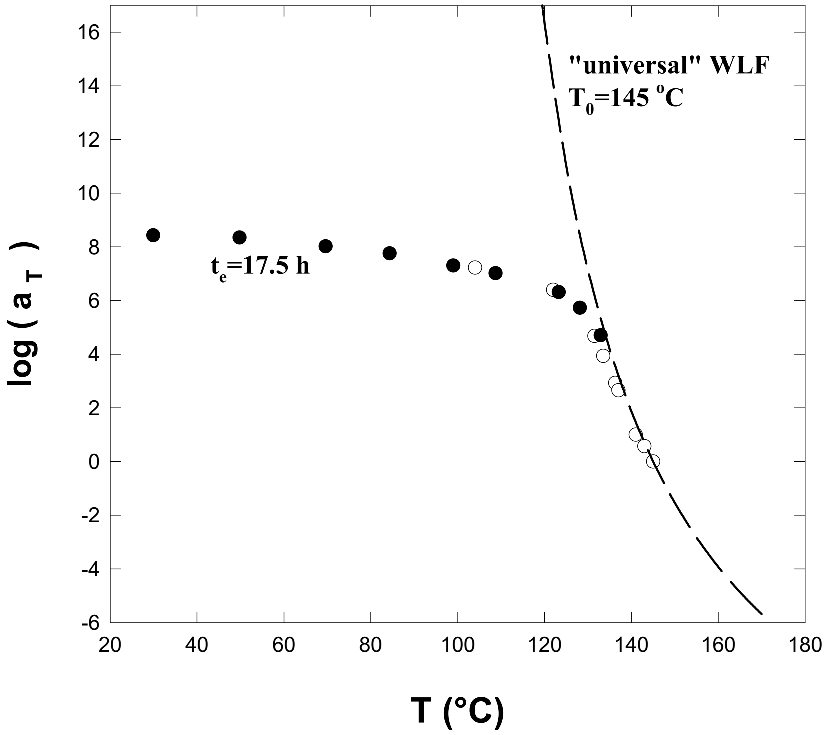
is similar for different T.





Temperature shift factor as a function of T-Tg for DGEBA at various aging time. A transition from one regime (weaker T dependence) to WLF behavior at higher T is observed.

Polycarbonate



Analysis of shift factor clearly shows changes at T~Tg. It changes from WLF behavior in equilibrium (T>Tg) to nearly Arrhenius behavior at lower T. However, the shift factor below Tg depends strongly on aging time t_e.

It seems that at long enough t_e the shift factor will reach WLF behavior. This question, however, remains unclear due to very long time of aging required at T much below Tg.

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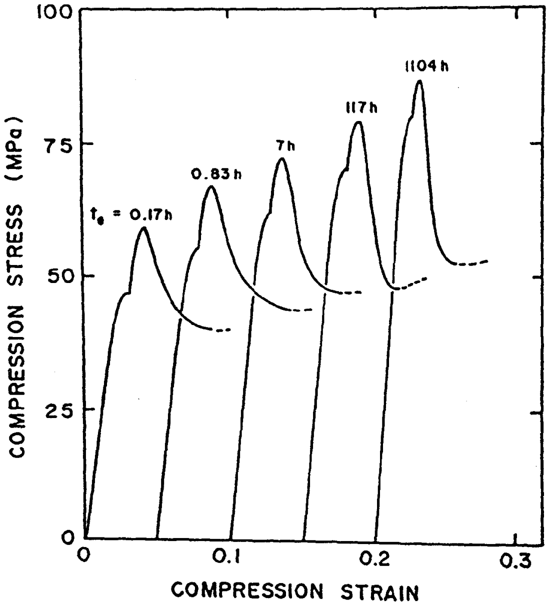
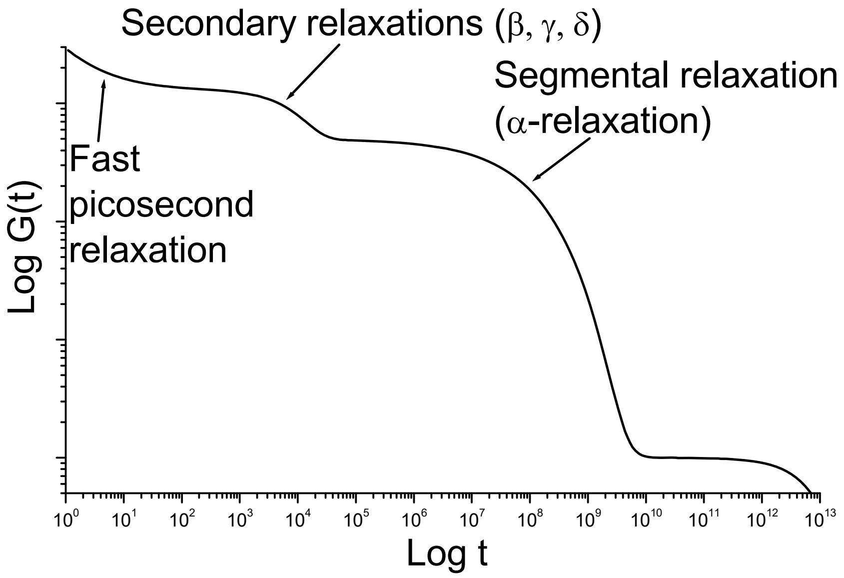


FIG. 14—*Typical compression stress-strain curves for an epoxy glass aged for different amounts of time, as indicated. Test and aging temperatures were* T_g − *10 K. (After Ref* 51.) *"Double-yield" is due to increasing strain rate at top of first yield.*

Effect of Aging on Engineering Properties

Aging cause yield strength to increase by ~40%.
Creep rupture lifetime increases upon aging.
Many other engineering properties of polymers experience significant changes with aging. These effects should be taken into account in design of materials for various applications.

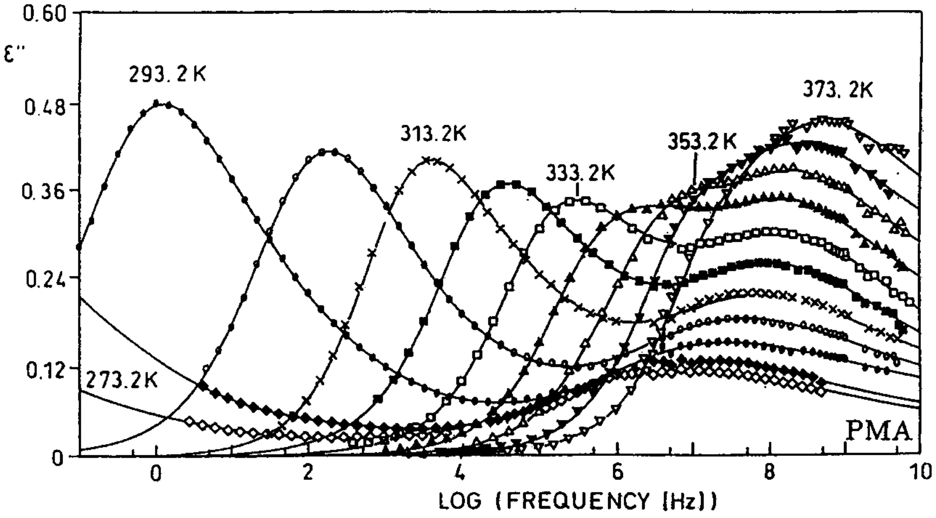
Secondary Relaxation



The main structural relaxation process (segmental relaxation) is frozen below Tg and secondary relaxations become the most important processes.

Secondary relaxation is a local process, mostly intra-molecular. It has Arrhenius temperature dependence.

Secondary relaxation defines mechanical and many other properties of solid polymers.



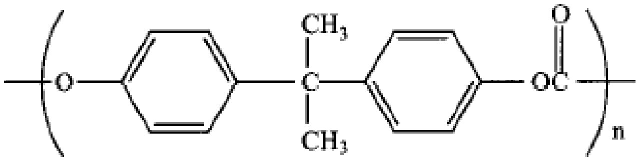
Dielectric loss spectra of poly(methyl acrylate) at different T [Dielectric spectroscopy of Polymeric Materials, Eds. Rund, Fitzgerald, p.85]. Segmental relaxation disappears from the accessible frequency window and only β-relaxation is left.
It shows much weaker temperature dependence, its spectrum is very broad and symmetric.

In many papers, secondary relaxation is ascribed to motion of side groups. But this is not correct in general.

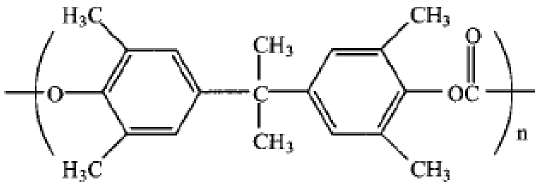
γ-relaxation in polycarbonates [A.Yee and co-workers, **Macromolecules 24**, 1905(1991), and **31**, 7865 (1998)]

It is difficult to identify unambiguously the molecular origin of secondary relaxation. In the case of PC, the motion of carbonate group alone is too small, the π-flip motion of rings cannot induce mechanical relaxation since it is a jump between two symmetrical positions.

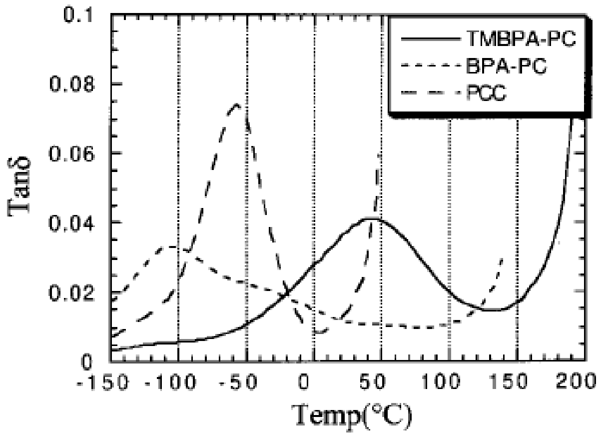
In order to identify structural units responsible for the γ-relaxation, different PC were compared.



BPA-PC (Bisphenol A polycarbonate)



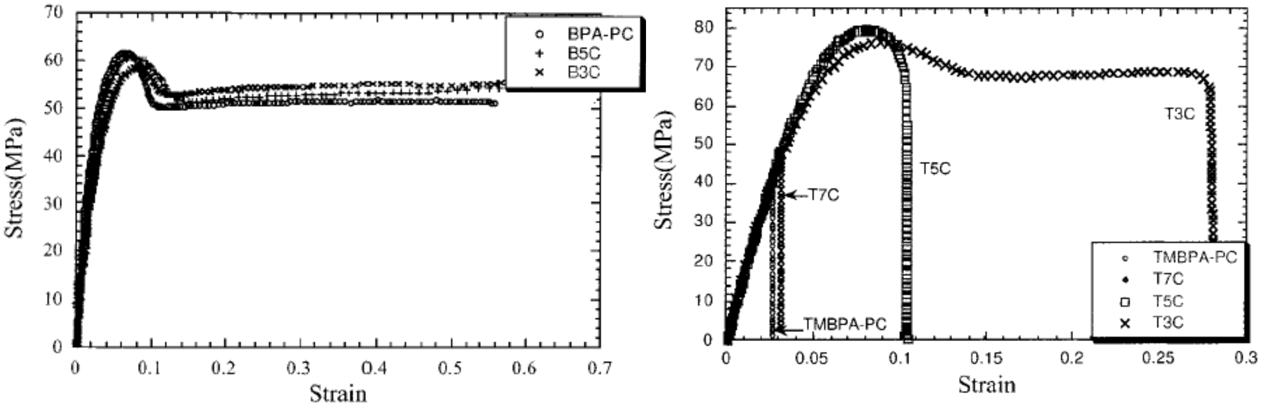
TMBPA-PC (Tetramethylbisphenol A polycarbonate)

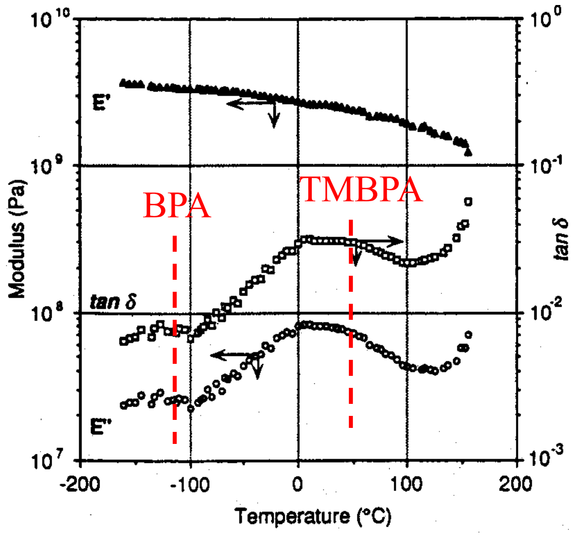


Dynamic mechanical relaxation at 1 Hz in BPA-PC, TMBPA-PC and a polymer with flexible cyclohexylene ring. Strong shift of the γ-peak to higher T is observed. The shift is ascribed to restriction of phenyl ring flips because of methyl groups.

BPA-PC shows ductile behavior while TMBPA-PC shows brittle behavior. Thus, activation of γ-relaxation is important for ductile behavior. Putting flexible links every 3-5 monomers, one can make TMBPA-PC ductile

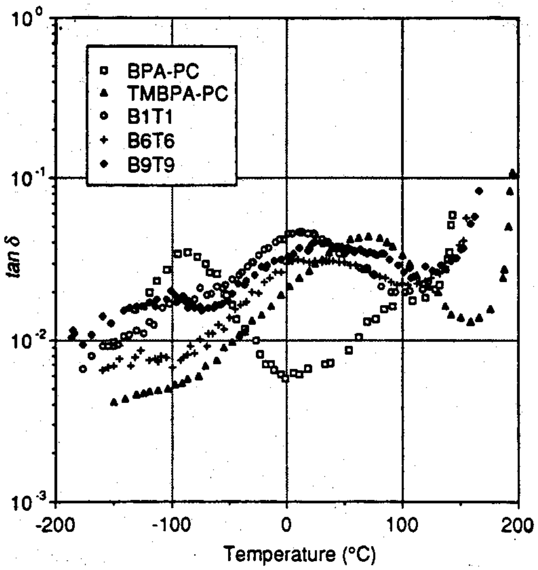
Stress-strain curves at room T with strain rate ~$3*10^{-3}$ 1/s

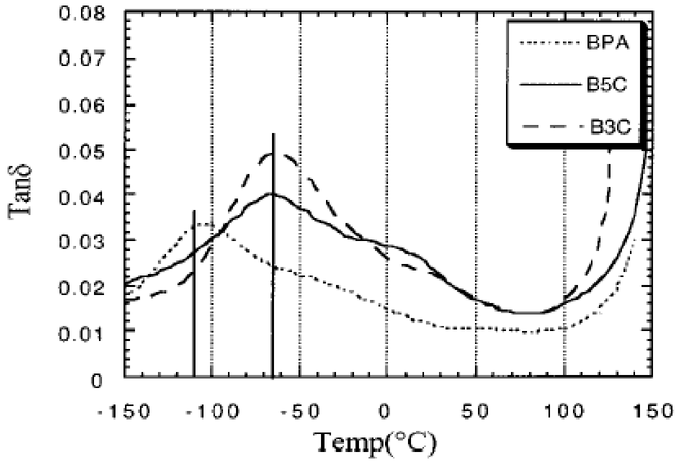




Random copolymer of BPA- and TMBPA-carbonate shows a single relaxation peak. This result shows that the cooperativity in the motion extends over more than one repeating unit. A cooperative motion of chain segments including both monomer units must be involved.

Mechanical relaxation at 11 Hz in different block-copolymers. Two separated peaks appear only in the systems with block length ~9 monomers. It shows that extend of cooperativity is >6-7 monomers. N_e in BPA-PC is ~9.

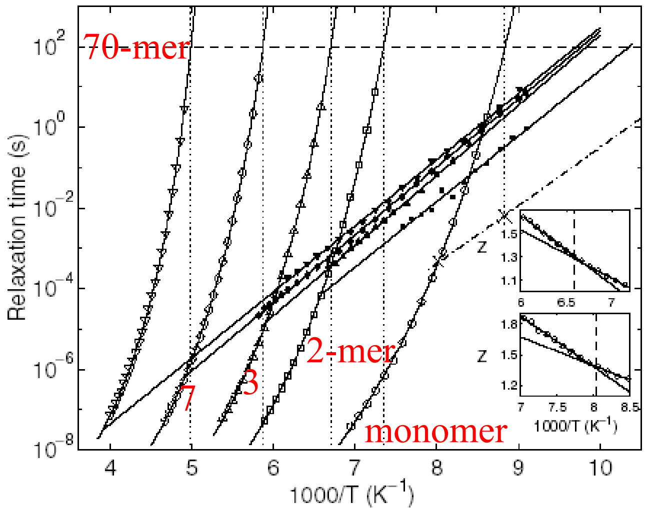




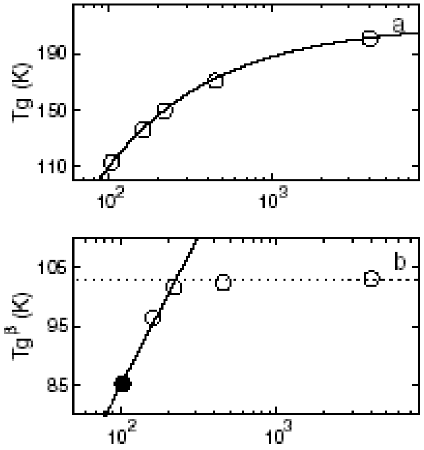
Example of another block-copolymer with flexible cyclohexylene ring that activates only at T~-65°C. γ-relaxation is not active at T~-100°C even in copolymer with 5 monomer blocks. That supports the conclusion that ~7-9 monomers are involved in a single relaxation event in PC.

These results clearly demonstrate intra-molecular nature and strong cooperativity of the γ-relaxation in PC. The authors also note the role of inter-chain interactions because the γ-peak is suppressed by aging. Aging affects inter-chain interactions only.

Influence of molecular weight on secondary relaxation in PPG [Mattson, et al.**PRL 90**, 075702 (2003)]



Analysis of dielectric relaxation spectra in PPG shows that both, α- (segmental) and β- (secondary), relaxations depend on molecular weight. However, secondary relaxation shows much weaker variations with M.



The dependence for the β-process levels off already at a few (~5) monomer length, while it remains visible for the α-process even at ~70 monomers.

The plot shows Tg for each process defined as T at which τ=100 s.

These results support the idea that secondary relaxation processes are more localized than the segmental relaxation. They are more intra-molecular in nature.

Concluding Remarks

1. Structural recovery shows strong non-linearity, asymmetry and a dependence on prehistory. Phenomenological models cannot explain all the details of the recovery.
2. Physical aging shows two characteristic times: relaxation time τ and aging time t_e. τ depends on t_e. No clear model description exists for the aging process.
3. Secondary relaxation is a cooperative process. It is mostly an intra-molecular relaxation. It shows Arrhenius temperature variation and affects significantly ductility of a polymer.

Yield and Fracture in Glassy Polymers

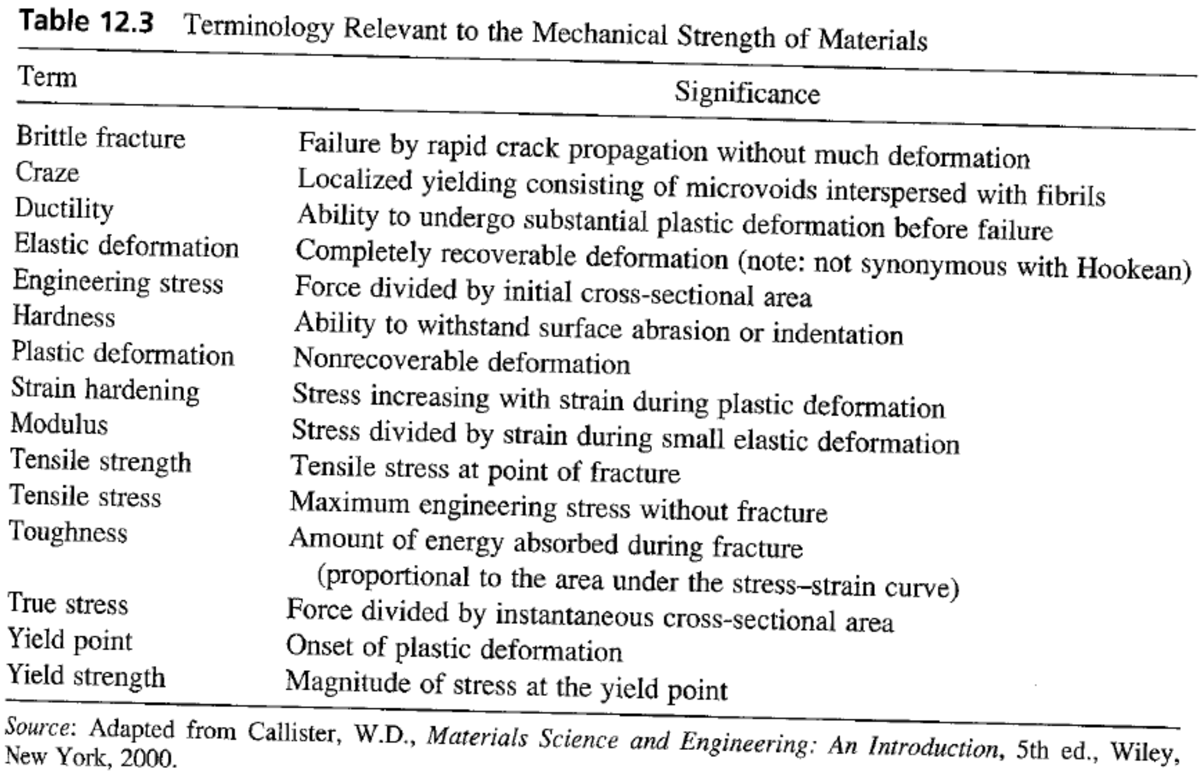
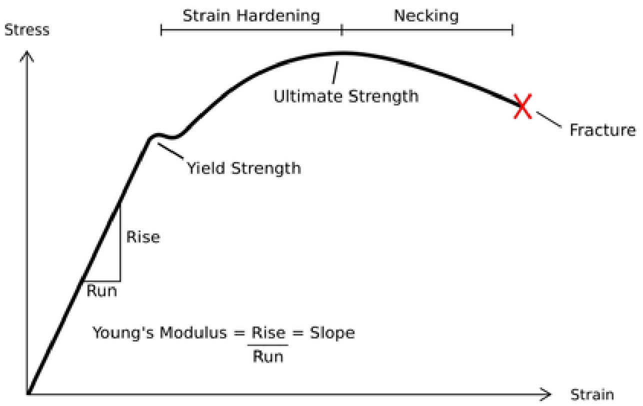


Table 12.3 Terminology Relevant to the Mechanical Strength of Materials

Term	Significance
Brittle fracture	Failure by rapid crack propagation without much deformation
Craze	Localized yielding consisting of microvoids interspersed with fibrils
Ductility	Ability to undergo substantial plastic deformation before failure
Elastic deformation	Completely recoverable deformation (note: not synonymous with Hookean)
Engineering stress	Force divided by initial cross-sectional area
Hardness	Ability to withstand surface abrasion or indentation
Plastic deformation	Nonrecoverable deformation
Strain hardening	Stress increasing with strain during plastic deformation
Modulus	Stress divided by strain during small elastic deformation
Tensile strength	Tensile stress at point of fracture
Tensile stress	Maximum engineering stress without fracture
Toughness	Amount of energy absorbed during fracture (proportional to the area under the stress–strain curve)
True stress	Force divided by instantaneous cross-sectional area
Yield point	Onset of plastic deformation
Yield strength	Magnitude of stress at the yield point

Source: Adapted from Callister, W.D., *Materials Science and Engineering: An Introduction*, 5th ed., Wiley, New York, 2000.



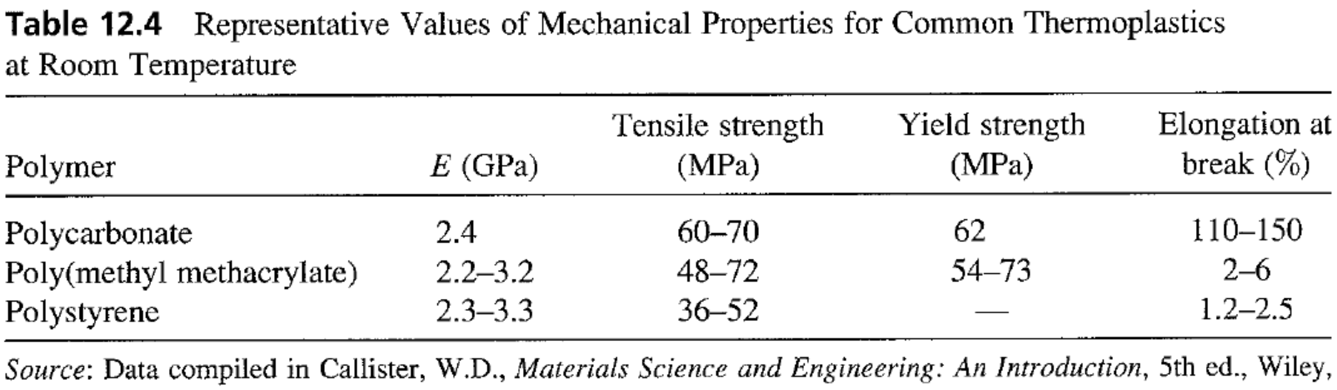
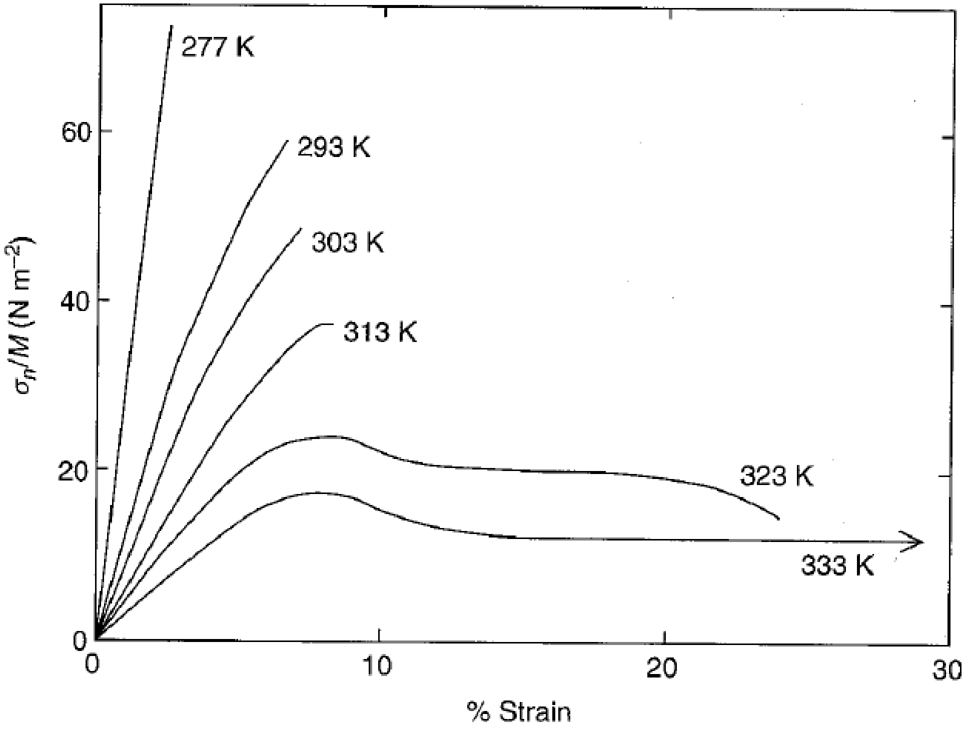


Table 12.4 Representative Values of Mechanical Properties for Common Thermoplastics at Room Temperature

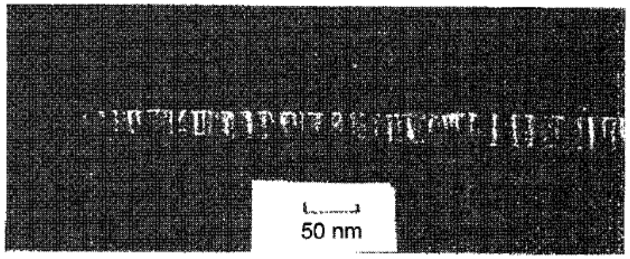
Polymer	*E* (GPa)	Tensile strength (MPa)	Yield strength (MPa)	Elongation at break (%)
Polycarbonate	2.4	60–70	62	110–150
Poly(methyl methacrylate)	2.2–3.2	48–72	54–73	2–6
Polystyrene	2.3–3.3	36–52	—	1.2–2.5

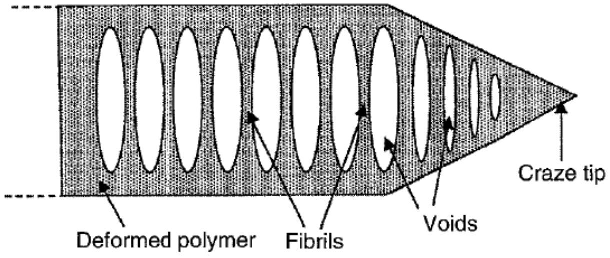
Source: Data compiled in Callister, W.D., *Materials Science and Engineering: An Introduction*, 5th ed., Wiley,

Stress-Strain response of PMMA at T below Tg (~383K).

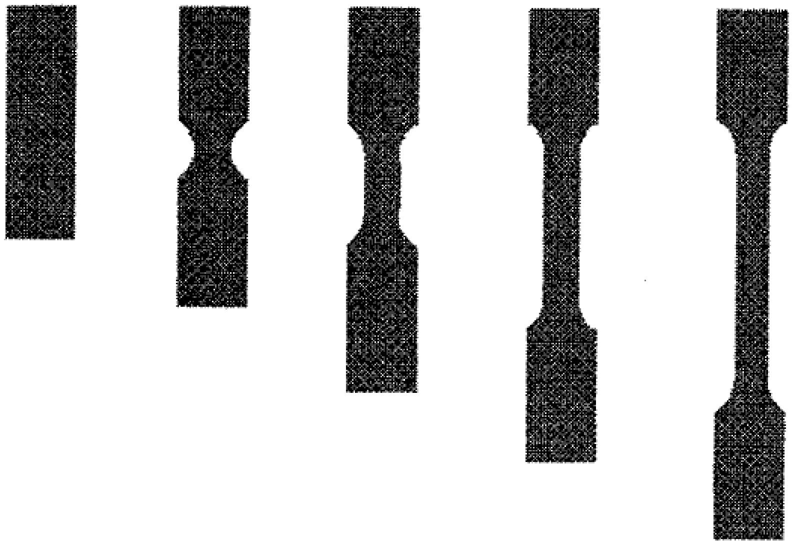


- Ductile-to-brittle transition upon cooling is common for polymers. Temperature of the transition differs for different polymers.
- It also depends on the rate of deformation and happens at higher T with increase of the rate.
- Macroscopic failure of polymeric material is related to rupture of chains.
- Crack propagation is the main mechanism of the brittle failure. Crack propagation in polymers is different from other materials.

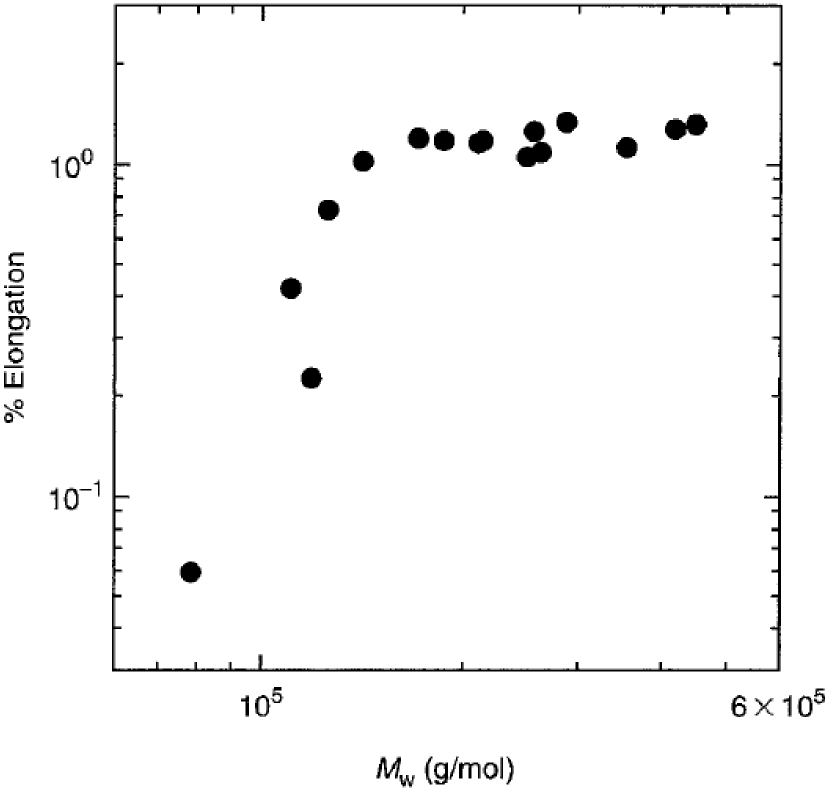




A craze is formed by a cavitation process. Crazes propagate perpendicular to the direction of strain. They dissipate significant amount of energy and in this way enhance mechanical strength of the material. Crazing also allows significant deformation (several %) before fracture.



Significant deformation of the material without crazing is *yielding*. Yielding appears as necking. Neck is getting longer with extension.



Yielding and crazing depend on molecular flexibility and also on entanglements between chains. The more entangled the chain the larger elongation at break can be achieved. It saturates at ~10 M_e.