# An introduction to polymer physics

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## 5. Transition AND relaxation





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## 5.1 introduction

**What will happen when temperature or action time changes?**



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**Why temperature or action time have so much effect on the physical properties of polymer material?**

**Because of the long, chain like structure.**



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## Thermal transition of linear amorphous polymer

**Two transitions** **Three states** **Key point**

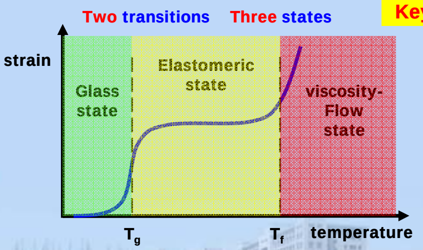


**Fig. 5-1 strain-temperature curve for amorphous polymer**



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## (a) Glass state

1. **crystalline solids**: molecules are ordered in a regular lattice
2. **fluids**: molecules are disordered and are not rigidly bound.
3. **glasses**: molecules are disordered but are rigidly bound.

**Movement of large motion units are frozen**

**How large?**

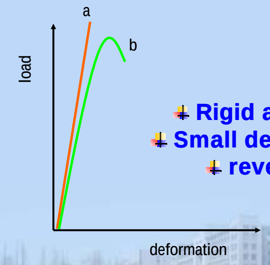
## Motion units

1. **Length and angle** of covalent bonds
2. **Smaller units** – side groups, branched chains……

**Polymer chains ?**



## Mechanical properties

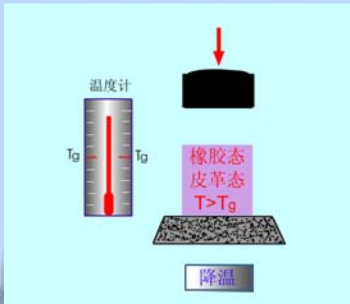



- **Rigid and hard;**
- **Small deformation;**
- **revertible**

**Fig. 5-2 tensile behavior of glass state polymer**

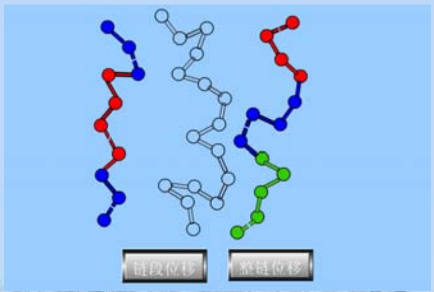


## (b) Rubber state






## Movement of segments

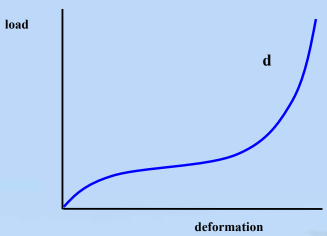


**What can be inferred from this picture?**

1. **Movement of segments is caused by rotation around single bonds**
2. **The mass center of the polymer chain does not move**



## Mechanical properties




- **Soft and elastic;**
- **Large deformation;**
- **revertible**

**Fig. 5-3 tensile behavior of rubber state polymer**



**Table 5.1 comparison between polymer in glass state and rubber state**

| | Modulus (Pa) | strain |
|---|---|---|
| Glass state | $10^{10}$ -$10^{12}$ | 0.01 - 0.1% |
| rubber state | $10^5$ - $10^7$ | 100 – 1000% |

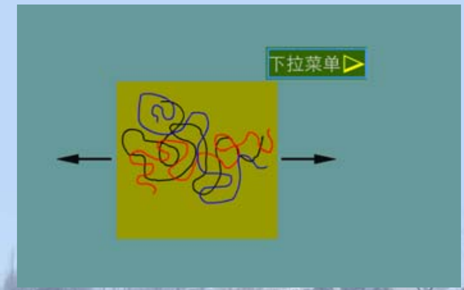
## (c) Viscosity-flow state

动起来

更精彩




## Motion unit – molecular chains






## *Viscosity–flow state*

- Motion of whole molecular chains being activated
- Slippage of chain happens under stress
- Deformation is unrecoverable



## SUMMARY

Glass state $\xleftrightarrow{Tg}$ Rubber state $\xleftrightarrow{T_f}$ Viscosity-flow state

Different motion state

Different deformation ability

Different mechanical state

Different properties

*Attention:*

*1. mechanical states ≠ the thermal dynamic state*

*2. Tg and Tf ≠ the phase transition temperature*



Table 5.2 Summary to the mechanical state of amorphous polymer

| | Motion units | Relaxation time | movement | Temperature range | deformation |
|---|---|---|---|---|---|
| Glass state | | | | | |
| Rubber state | | | | | |
| Viscosity-flow state | | | | | |



## thermal transition of crystalline polymers

难点

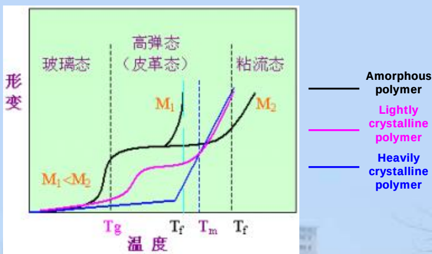
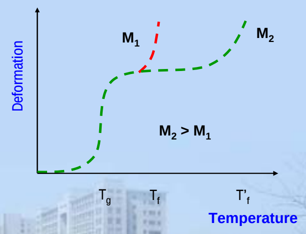



Fig. 5-4 temperature – deformation curve of crystalline and amorphous polymers

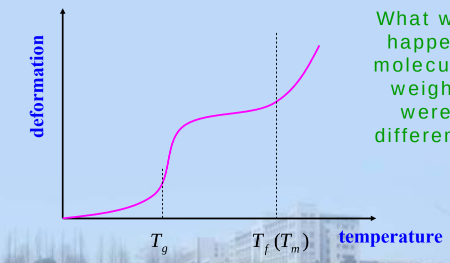
## For amorphous polymer material with different molecular weight

- 3 states and 2 transitions
- Higher molecular weight, higher $T_f$ – due to the **entanglement** of molecules and the **stronger interactions**






## For lightly crystallized polymer material




What will happen molecular weight were different?



## For lightly crystallized polymer material

**Q1. Does crystallization affect the transition?**

**NO, there are still 2 transitions and 3 states. $T_g$ is also obvious.**

**Q2. For small molecular weight material, at which temperature it will transfer into viscosity-state?**

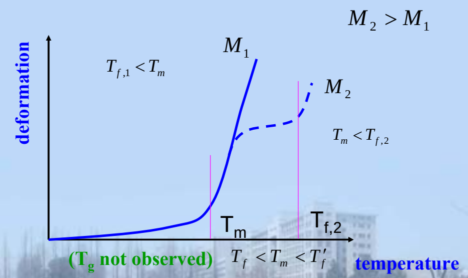
**$T_m$. $T_m$>$T_f$. At $T_f$ it will remaining in rubber state. Crystals are like physical cross-linker.**

**Q3. For large molecular weight material, at which temperature it will transfer into viscosity-state?**

**$T_f$. $T_f$>$T_m$. After crystals being melted, molecules still can not move violently due to strong interactions among the molecules.**



## For heavily crystallized polymer material (>40%)






## For heavily crystallized polymer material (>40%)

**Q1. Why there is no glass transition?**

- **Crystallites form continuous phases.**
- **Motion of Polymer chains is restricted.**
- **Glass transition disappears.**

**Q2. For small molecular weight material, at which temperature it will transfer into viscosity-state?**

**$T_m$. No rubber state.**

**Q3. For large molecular weight material, at which temperature it will transfer into viscosity-state?**

**$T_f$. Has Rubber state.**



## For different molecular weight

Crystallized polymer $\xrightarrow{T_m}$ Crystals destroyed → Amorphous state →

$T_f$<$T_m$ — Low molecular weight → viscosity-flow state (melt)

$T_f$>$T_m$ — High molecular weight → Rubber state $\xrightarrow{T_f}$ Viscosity-flow state

Low crystallinity,
glass state → rubber state → viscosity flow state

High crystallinity,
glass state →
Viscosity-flow state (low molecular weight)
Rubber state → viscosity-flow state

## secondary transition

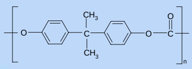
smaller motion units

move ⟷ frozen

- side groups
- branched chains
- functional groups
- local part of the segments



- As we know, polycarbonate (聚碳酸酯) has rigid structure. Why it can be made into feeding-bottles (奶瓶) ?





What is the primary transition?



- Primary transition is usually refer to the glass transition
  - Primary Motion units are larger
  - Secondary Motion units are smaller

What is the largest motion unit?

The molecular chain



## features of molecular motion

Key point

A. Variety (of motion units)

B. Time-dependent

C. Temperature-dependent



## Table 5.2 Variety of motion units

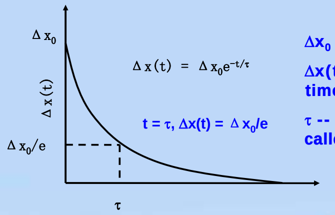
| motion units | Motion | Macro performance | features |
|---|---|---|---|
| Whole molecular chains | Movement of chains | Flow, crystallization | The mass center moves |
| Segments (long and short) | Movement of segments | Transfer from glass state to elastomer state | The mass center does not move |
| Side groups and branched chains | Rotation of side groups, vibration etc | Can not be observed | restricted in small range |



## B. Time-dependence

- ALL the molecular motion of polymers are time-dependent – RELAXATION
- What is RELAXTION
  - Motion units of Polymer transfer from one balance state to another by adjusting themselves

## (a) Relaxation of PVC string (丝)




$\Delta x_0$ – the original length

$\Delta x(t)$ – the length at time t

$\tau$ -- constant, being called relaxation time

τ为常数，不是恒等量，对每个体系均不同

Figure 5-5 relaxation of PVC string

《高分子物理》，p225



## Questions arise

- After the stress is released, the molecules tend to come back from extended state to coil-like state. (why?)
- Why the string can not shrink back immediately ? 收缩
- where does the hindrance come from? 阻力



## (b) Relaxation time

Relaxation time $\tau$ is a physical parameter to describe the relaxation speed

$\tau \rightarrow 0$, relaxed very quickly
Example:
$H_2O$ $10^{-9}$ -$10^{-10}$ s

$\tau \rightarrow \infty$, relaxed very slowly
Example:
Creep of polymer chain months - years

蠕变



## (c) Relaxation time spectrum

various motion units

Variety of relaxation time

Being treated as a continuous distribution

relaxation time spectrum



## (d) Time-dependence of properties

**Example I:**
The plastic raincoat will extended a little while it is hung on for a long period of time.

**Example II:**
The melt flow of polymer exhibits to be bristle while being strike.

分子链来不及运动以适应外力，化学键被破坏



## C. temperature-dependence

Mobility ↑ Void space ↑

Temperature ↑ → Relaxation time ↓

## (a) Eyring equation

For small motion units, like side groups or branched chains

$$\tau = \tau_0 e^{\frac{\Delta E}{RT}}$$

T↑, τ↓

$\tau_0$ – constant; R – gas constant

$\Delta E$ – activation energy needed for relaxation



## (b) WLF equation

For large motion units, like segments

$$\ln\left(\frac{\tau}{\tau_s}\right) = -\frac{C_1(T-T_s)}{C_2+(T-T_s)}$$

$C_1$, $C_2$ are constant, s – reference

T↑, τ↓



## 5.2 Glass transition

Key Point

- In general, amorphous polymers change from hard, brittle, 'glassy' materials at low temperatures to soft, deformable, rubbery materials at high temperatures.
- This is known as the 'glass transition' and occurs over a relatively narrow range of temperatures characterised by the glass transition temperature, $T_g$.

**定义**：指非晶态高聚物从玻璃态到高弹态的转变。对晶态高分子来说，玻璃化转变是指其中非晶部分的这种转变。



## Meaning of $T_g$

- That some liquids were solidified to glassy state without crystallization when being cooled was called glass transition.
- The corresponding temperature was called Glass transition temperature, as $T_g$.
- For non-crystalline polymer, it was referred to the transition temperature from rubbery to glassy when being cooled; also the temperature from glassy to rubbery when being heated.



## Technical importance of $T_g$

- It is the upper application temperature of non-crystalline plastics, like PS, PMMA or hard PVC
- It is the lower application temperature of non-crystalline rubber, like NR, SBR etc



## Theoretical importance of $T_g$

➢ To characterize the molecular flexibility

➢ Important feature of polymers

高聚物刚性因子越大，玻璃化转变温度越_____

高　低

## 5.2.1 how to determine $T_g$

- In general, all the properties that will change apparently during glass transition can be used to determine the glass transition temperature



## a. According to the change of mechanical property

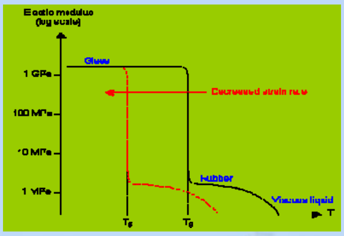



Fig. 5-6 elastic modulus of the polymer as a function of the temperature



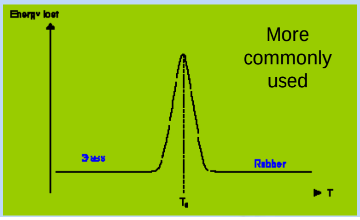
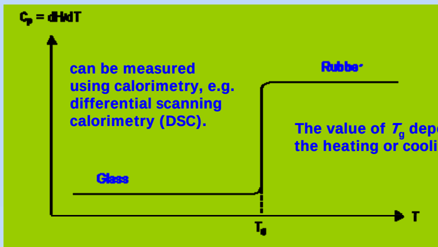



Fig. 5-7 *dynamic mechanical thermal analysis* (DMTA)



## b. According to the thermal analysis




The value of $T_g$ depends on the heating or cooling rate.

Fig. 5-8 The specific heat capacity, $C_p$ – temperature



## c. According to the volume change

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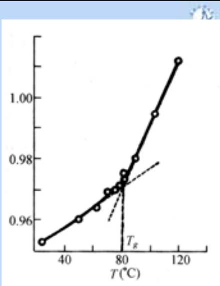


Fig. 5-9 Specific volume – temperature curve for PS



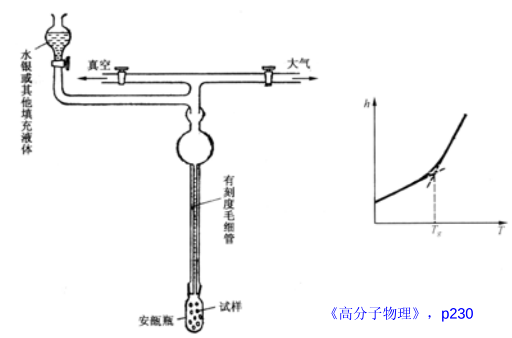


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Fig. 5-10 dilatometer and determination of $T_g$

## d. Dielectric Constant 介电常数

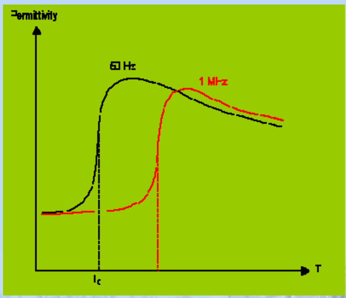


Fig. 5-11 dielectric constant as a function of temperature

If a varying electric field is applied to a polymeric material, any polar groups will align with the field. Below $T_g$ rotation of the bonds is not possible, so the permittivity will be low, with a big increase around $T_g$.
At higher temperatures the increased thermal vibrations cause the permittivity to drop again.
If the frequency of the field is increased, the polar groups have less time to align, so the glass transition occurs at a higher temperature.



## Important !

- $T_g$ obtained from different methods are usually not the same!
- It is not a phase transition temperature, so that it will be different as testing methods varies.
- As we use them, the testing methods and testing conditions must be mentioned.



## 5.2.2 free volume theory

**1. concept**

Whole volume { free volume / occupied volume

Free volumes are distributed in the whole material as void space for the segments to change conformation

First proposed by Fox and Flory




## 2. Description of free volume theory

- In glass state
  - Movement of segments is frozen
  - Free volume is frozen too, to be a fixed value
  - Size and distribution of Void space are no longer changeable
  - Tg is a critical temperature
  - Under such a temperature there is no extra free space for molecules to adjust their conformation
  - It is a state of constant free volume



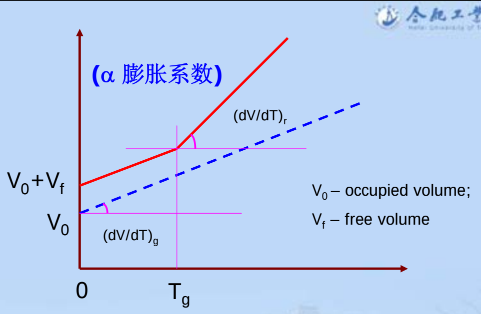


Fig. 5-12 Volume change before and after $T_g$



- Under $T_g$, in glass state
  - Volume expansion is just expansion of molecule themselves
  - Including increment of vibration and bonds length
- At $T_g$
  - Segments get enough energy, space expanded too, begin to move
- Beyond $T_g$, in rubber state
  - Except for the volume expansion of molecules, free volume expands too
  - $\alpha_r > \alpha_g$, (α 膨胀系数)

# 3. more details about free volume theory

The whole volume of polymer at $T_g$

$$V_g = V_f + V_0 + \left(\frac{dV}{dT}\right)_g T_g$$

The whole volume of polymer over $T_g$

$$V_r = V_g + \left(\frac{dV}{dT}\right)_r \left(T - T_g\right)$$

$V_g$ – the whole volume of polymer at $T_g$

$V_r$ – the whole volume of polymer over $T_g$

$V_f$ – the free volume of polymer in glass state

$V_0$ – the volume of polymer occupied in 0 K



$$V_r = V_f + V_0 + \left(\frac{dV}{dT}\right)_g T_g + \left(\frac{dV}{dT}\right)_r \left(T - T_g\right), \quad \left(\frac{dV}{dT}\right)_r = \left(\frac{dV}{dT}\right)_g + \left(\frac{dV}{dT}\right)_f$$

$$V_r = V_f + V_0 + \left(\frac{dV}{dT}\right)_g T_g + \left[\left(\frac{dV}{dT}\right)_g + \left(\frac{dV}{dT}\right)_f\right]\left(T - T_g\right)$$

$V_r =$ 自由体积 + 自身体积



$$\left(V_f\right)_T = V_f + \left(\frac{dV}{dT}\right)_f \left(T - T_g\right)$$

$$= V_f + \left[\left(\frac{dV}{dT}\right)_r - \left(\frac{dV}{dT}\right)_g\right]\left(T - T_g\right)$$

Around $T_g$,

$$\frac{\left(V_f\right)_T}{V_g} = \frac{V_f}{V_g} + \frac{1}{V_g}\left[\left(\frac{dV}{dT}\right)_r - \left(\frac{dV}{dT}\right)_g\right]\left(T - T_g\right)$$

That is,

$$f_T = f_g + \left(\alpha_r - \alpha_g\right)\left(T - T_g\right)$$

$$= f_g + \Delta\alpha\left(T - T_g\right)$$

or

$$f_T = f_g + \alpha_f\left(T - T_g\right)$$



# 5.2.3 WLF equation – talking more

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

$\eta(T)$ – viscosity of polymer at T

$\eta(T_g)$ – viscosity of polymer at $T_g$



$$\eta = A\exp\left(BV_0 / V_f\right)$$

Doolittle Equation

$$\ln\eta(T) = \ln A + B\frac{V_0(T)}{V_f(T)} \qquad \ln\eta\left(T_g\right) = \ln A + B\frac{V_0\left(T_g\right)}{V_f\left(T_g\right)}$$

$$\ln\frac{\eta(T)}{\eta\left(T_g\right)} = B\left[\frac{V_0(T)}{V_f(T)} - \frac{V_0\left(T_g\right)}{V_f\left(T_g\right)}\right]$$



**According to the concept of $f_T$**

$$f_T = \frac{V_f(T)}{V_0(T) + V_f(T)} \approx \frac{V_f(T)}{V_0(T)}$$

$$\ln\frac{\eta(T)}{\eta\left(T_g\right)} = B\left[\frac{1}{f_T} - \frac{1}{f_g}\right]$$

$$f_T = f_g + \alpha_f\left(T - T_g\right)$$

$$\lg\frac{\eta(T)}{\eta\left(T_g\right)} = \frac{-B}{2.303 f_g}\,\frac{T - T_g}{\dfrac{f_g}{\alpha_f} + \left(T - T_g\right)}$$

$$\frac{-B}{2.303 f_g} = -17.44 \qquad f_g / a_f = 51.6$$

Usually, B≈1

$$f_g = 0.025 = 2.5\%, a_f = 4.8\times10^{-4} / K$$



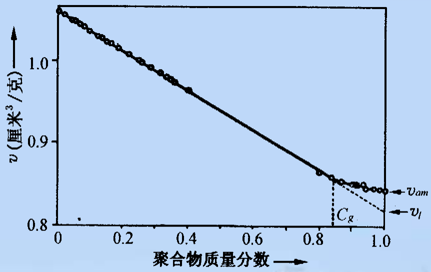


图 6－19　PMMA 与 MMA 混合物的比容和聚合物重量分数的关系图

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- 聚甲基丙烯酸甲酯（高分子固体）与甲基丙烯酸甲酯（小分子液体）--相似又不同
- 混合物比体积随聚合物浓度提高而降低，但在较高浓度下，混合物的粘度变得很大，聚合物的链段不再能自由运动
- 由于这种冻结，非晶态聚合物的比体积大于同一温度下外推得到的比体积
- 自由体积可以定义为

$$f_{WLF} = \frac{v_{am} - v_l}{v_{am}}$$

- 实验测得$v_{am}$=0.842cm³/g，$v_l$=0.820cm³/g，因而聚甲基丙烯酸甲酯的自由体积分数为0.026，等于2.6%，与WLF方程预言的自由体积分数很接近



## 5.3 Factors affecting $T_g$

**Key point**

- 5.3.1 Chemical structures
- 5.3.2 Other factors
- 5.3.3 environmental factors



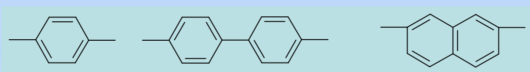
## 5.3.1 Chemical structures
### A. main chain structure

- **$A_1$ saturated bonds**
  - **Flexibility: -C-C- < -C-O- < –Si-O-**
  - **Rotate easily, $T_g$ ↓**
  - **PE: -68 ℃; POM: -83 ℃; PDMS: -123 ℃**
  - **The more flexible, the lower the $T_g$**



## 5.3.1 Chemical structures.
### A. main chain structure

- **$A_2$ Introduction of phenyl group, biphenyl group, naphthyl group (萘基) will increase the $T_g$**
- **Molecular chain turns to be rigid, rotation is more difficult**



phenyl group　biphenyl group　naphthyl group

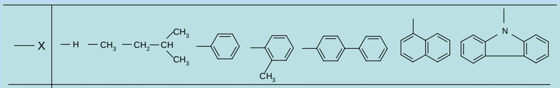
## 5.3.1 Chemical structures.
## A. main chain structure

- $A_3$ isolated double bonds
  - Flexible, $T_g$ is low
    - Natural rubber: $T_g$ = -73 ℃
    - cis-PB, -108℃; trans, -83℃
    - cis-polyisoprene, -73℃; trans, Tg = -60℃
    - By the way, Trans-polyisoprene is more likely to compact together and form ordered structure



## 5.3.1 Chemical structures
## B. stereo-hindrance of substitutes

- $B_1$. For $-(CH_2\text{-}CHX)_n-$, size of X ↑, rotation ability ↓, then $T_g$ ↑ .




| Tg | -68 | -20 | 29 | 100 | 119 | 138 | 162 | 208 |
|---|---|---|---|---|---|---|---|---|

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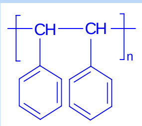
## 5.3.1 Chemical structures
## B. stereo-hindrance of substitutes

- $B_2$. For polyacenaphthylene(聚苊烯)

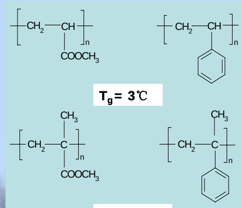



  - Rotation is hindered seriously, $T_g$ reaches 264 ℃



## 5.3.1 Chemical structures
## B. stereo-hindrance of substitutes

- $B_3$. For $-(CH_2\text{-}CXY)_n-$,
  - X ≠ Y, stereo hindrance ↑, Tg ↑



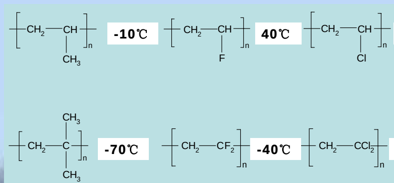

$T_g$= 3℃ $T_g$= 100℃

$T_g$= 115℃ $T_g$= 192℃



## 5.3.1 Chemical structures
## B. stereo-hindrance of substitutes

- $B_4$. For $-(CH_2\text{-}CXY)_n-$,
  - X = Y, stereo hindrance ↓, even less than single bond rotation barrier, $T_g$ ↓






## 5.3.1 Chemical structures
## C. the length of side chains

- Important! – with the length of side chains ↑, $T_g$ ↓
- For PAA series(聚丙烯酸酯系列)

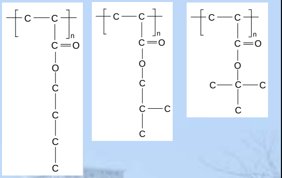
| n | 1 | 2 | 3 | 4 | 6 | 8 | 12 | 18 |
|---|---|---|---|---|---|---|---|---|
| $T_g$(℃) | 105 | 65 | 35 | 21 | -5 | -20 | -65 | -100 |

- The longer the side chains, the flexible of side chains, and the lower the $T_g$
- In fact, side chains function as plasticizing agent (增塑剂)

《高分子物理》, p245

## 5.3.1 Chemical structures
### C. the length of side chains

- **Another example**
  - 聚丙烯酸丁酯
    - 正丁酯 Tg = -56 ℃ 柔性最大
    - 仲丁酯 Tg = -22 ℃ 柔性次之
    - 叔丁酯 Tg = 43 ℃ 柔性最小



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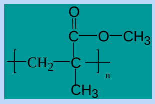
## 5.3.1 Chemical structures
### D. Configuration

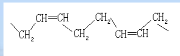
全同$T_g$ < 间同$T_g$ PMMA

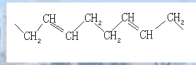


Isotactic, $T_g$= 45 ℃ < Syndiotactic, $T_g$= 115 ℃

顺式$T_g$ < 反式$T_g$ Poly(1,4-butadiene)

Cis-顺式, $T_g$= -102 ℃ < Trans-反式, $T_g$= -48 ℃





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## 5.3.1 Chemical structures
### E. interaction between polymer chains

- **Polarity of side chains**
  - **The higher the polarity, the higher the $T_g$**

| polymer | —C—C— | —C—C(C)— | —C—C(Cl)— | —C—C(CN)— |
|---|---|---|---|---|
| $T_g$ ℃ | -68 | -20 | 87 | 104 |

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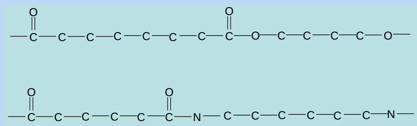
## 5.3.1 Chemical structures
### E. interaction between polymer chains

- **H-bonds**
  - 聚辛二酸丁二酯 VS. 尼龙66



  - 原子总数目相同，$T_g$ 不同，氢键作用
  - -57℃ ↔ +50℃

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## 5.3.1 Chemical structures
### F. effect of ion on polyelectrolyte

- **Addition of ion into polyelectrolyte, such as polyacrylic acid, will increase the Tg remarkably**
  - **Addition of $Na^+$, $T_g$ 106℃ → 280℃**
  - **Addition of $Cu^{2+}$, $T_g$ → 500℃**

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## 5.3.1 Chemical structures
### G. $T_m$ and $T_g$

- **For symmetrical polymer**
  - $T_g / T_m \approx 1/2$
- **For non-symmetrical polymer**
  - $T_g / T_m \approx 2/3$

- ***Kelvin* temperature scale!**

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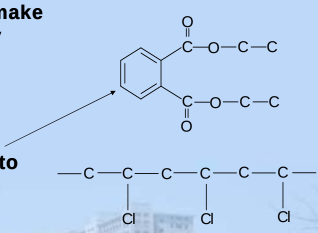
## Table 5.6 approximate relationship between $T_m$ and $T_g$ for some typical polymers

| polymer | $T_m$ ℃ | $T_g$ (calculated) ℃ | $T_g$ (experimental) ℃ |
|---|---|---|---|
| Nylon-6 | 225 (498K) | 59 (332K) | 50 |
| PET | 267 (540K) | 87 (360K) | 69 |
| PE | 137 (410K) | -68 (205K) | -68 |
| PVDC | 198 (471K) | -37.5 (235.5K) | -17 |



## 5.3.2 other factors
### A. plasticizer (plasticizing agent)

- Plasticizing is to make polymer soften by adding small molecules into it.
- Example – adding diethyl phthalate to PVC





## 5.3.2 other factors
### A. plasticizer (plasticizing agent)

- 常见PVC增塑剂品种
  - 邻苯二甲酸二丁酯 (DBP)
  - 邻苯二甲酸二辛酯 (DOP)
  - 癸二甲酸二辛酯
  - 磷酸三苯酯
  - 磷酸三甲酚酯
  - 烷基磺酸苯酯

| Content of DOP | $T_g$ of PVC |
|---|---|
| 0 | 78 |
| 10 | 50 |
| 20 | 29 |
| 30 | 3 |
| 40 | -16 |
| 45 | -30 |



## 5.3.2 other factors
### A. plasticizer (plasticizing agent)

- Effect of plasticizer
  - enlarge the space between polymer chains (SO WHAT?)
  - inactivate the polar substitutes
  - In summary – lower the $T_g$ of polymers



## 5.3.2 other factors
### B. copolymerization

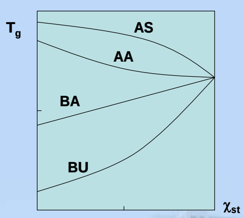



Fig. 5-17 $T_g$ of styrene copolymers VS. content of styrene



## 5.3.2 other factors
### B. copolymerization

- Effect of copolymerization – continuously change of $T_g$ of copolymer
- For random copolymer
- One $T_g$ available

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

## 5.3.2 other factors
### B. copolymerization

- For alternative copolymer
- -A-B-A-B-A-B-A-B-A-B-
- Can be seen as -(AB)-(AB)-(AB)-(AB)-
- Only one $T_g$ available



## 5.3.2 other factors
### B. copolymerization

- For block copolymer
  - -AAAAA-BBBBBBB-AAAAA-
- There are two phases formed by A segments and B segments
  - If the two phases are compatible, then only one $T_g$ appears
  - If the two phases are not compatible, then two Tg appears (phase separation can be observed)



## 5.3.2 other factors
### B. copolymerization

- In fact, $T_g$ appearing or not depends on the size of phase formed by the polymer chain segments
- If the phase size is large enough, movement of segments can be detected, then $T_g$ can be observed
- On the other hand, $T_g$ can not be observed
- Such a conclusion is suitable for blends too.



## 5.3.2 other factors
### C. crosslinking

- In general, crosslinking will restrict the movement of segments
- And it will raise $T_g$ of original polymer

Table 5.8 Content of Diethyl-benzene on the Tg of crosslinked styrene copolymer

| Diethyl-benzene % | Tg (℃) | Average chain links between two crosslinking points |
|---|---|---|
| 0 | 87 | - |
| 0.6 | 89.5 | 172 |
| 0.8 | 92 | 101 |
| 1.0 | 94.5 | 92 |
| 1.5 | 97 | 58 |



## 5.3.2 other factors
### D. molecular weight

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

The lower the molecular weight is, the more the chain ends will be

Free space around the chain ends is larger than that around the middle parts of polymer chain

Lower molecular weight will result in lower $T_g$

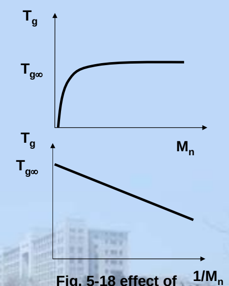



Fig. 5-18 effect of molecular weight on Tg



## 5.3.3 environmental factors
### A. heating rate

难点

- Heating rate or Cooling rate ↑, apparent $T_g$ ↑
- Heating rate or Cooling rate ↓, apparent $T_g$ ↓

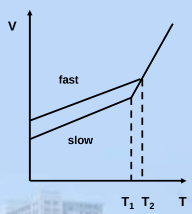



Fig. 5-19 effect of heating/cooling rate on Tg

## 5.3.3 environmental factors
## B. exogenic forces

- Exogenic forces will force the segments to move, so that $T_g$ will be lowered.
  - As PVC was under tensile force of 200 kg/cm², $T_g$ was lowered from 78 ℃ to 50 ℃.
- 外力作用降低了链段运动势能位垒，从而使链段活动能力增强，玻璃化转变温度降低（强迫高弹形变现象）



## 5.3.3 environmental factors
## C. surrounding pressure

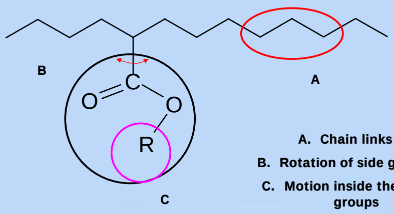
- Surrounding pressure will lower the free volume and increase the motion hindrance
- Need more energy input to make the segments move
- And will increase $T_g$
- 压力会增加链段运动位垒，需要更多热量，更高温度才能实现链段运动



## 5.4 molecular motion of glass state polymer

- secondary molecular motions in glass state polymer.
  - Motion of chain links (链节)
  - Rotation of side groups
  - Motion inside side groups






A. Chain links
B. Rotation of side groups
C. Motion inside the side groups

Fig. 5-20 examples of motion units causing secondary transition



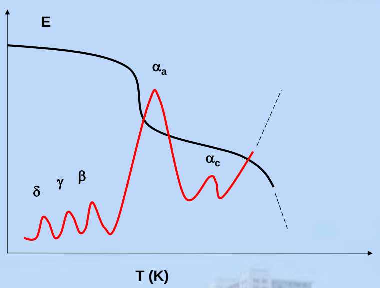



Fig. 5-21 Typical dynamic mechanical analysis spectrum



## 5.4.2 crank (曲柄) motion

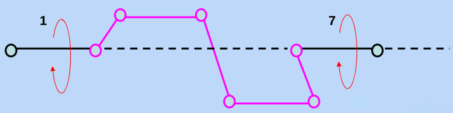
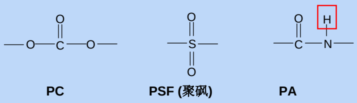



Fig. 5-22 illustration of crank motion of chain links

## 5.4.3 motion of non-carbon atoms

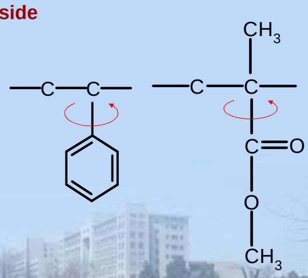



- For PA-6, the relaxation peak at -40°C will be enlarged if the H was replaced by $-CH_3$ group. (?)
- It means that the relaxation is caused by amido groups (酰胺基)



## 5.4.4 motion of side groups or side chains

- A. rotation of large side groups
  - PS
  - PMMA
- β-relaxation





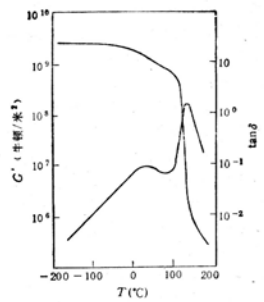



Fig. 5-23 DMA (1 Hz) spectrum of PMMA



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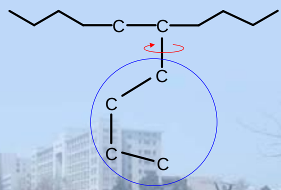
## 5.4.4 motion of side groups or side chains

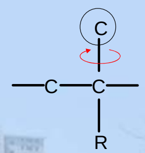
- B. Crank motion of long side chains ( $CH_2 \geq 4$)





## 5.4.4 motion of side groups or side chains

- C. Motion of α-methyl groups
- γ-relaxation
- For PMMA, -173°C, DMA (1Hz)





## 5.4.4 motion of side groups or side chains

- D. Motion of the other methyl groups
  - In PMMA, rotation of $-CH_3$ group in $-COOCH_3$,
  - δ relaxation peak
    - Very low test frequency, 4K, no extremum (极值)
    - $10^4$ Hz, 6K
    - 50 MHz, 90K
- Higher frequency used, higher transition temperature observed

Table 5.9 DMA value (50 MHz)

for different methyl groups

| 甲基位置 | 50 兆赫时的内耗峰温度（K） | 松弛活化能 ΔE（千焦耳/摩尔） | 实 例 |
|---|---|---|---|
| $-O-CH_3$ | 90 | 10 | PMMA |
| $-CH_2-CH_3$ | 150 | 16.3 | 石蜡 |
| $H-C(C)(C)-CH_3$ | 190 | 18.4 | 天然橡胶 |
| $C-C(C)(C)-CH_3$ | 270 | 26.8 | PMMA |

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## 5.5 molecular motion of crystalline polymers

- Although the segments of polymers are restricted in the crystalline regions, there are still some kinds of molecular motion available.



## 5.5 molecular motion of crystalline polymers

- For small molecules, crystalline structure is very stable, molecular motion is vibration of atoms at their equilibrium position
- For polymers, it is quite different.
  - Molecular motion in the non-crystalline region is like that of non-crystalline material, but affected by crystalline region
  - Various molecular motion patterns available inside the crystalline region



## 5.5.1 melting of crystalline polymer

- It refers to the viscosity-flow transition of polymers
- Molecule moves as a whole, it flows
- Some structural factors will affect $T_m$
  - Interaction or intra-action of molecules will affect the value of ΔH
  - Flexibility will affect the value of ΔS

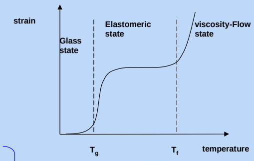


Fig. 5.2 strain-temperature curve for amorphous polymer

$$T_m = \frac{\Delta H}{\Delta S}$$



## 5.5.2 conversion of crystalline pattern

- Under $T_m$, crystallites can change crystalline pattern from one to another one
- For polypropylene, $\alpha \leftrightarrow \beta \leftrightarrow \gamma$ is available under some certain circumstance
  - γ crystallites are obtained under pressure, but is not stable
  - When heating to 150°C, γ crystallites will turn to α crystallites spontaneously



## 5.5.3 double $T_g$ phenomenon

- $\alpha_a$ – major transition near amorphous region
- $\alpha_c$ – major transition near crystalline region
  - For PTFE, $T_g(\alpha_c)$ = 315K, $T_g(\alpha_a)$ = 253K
  - As crystallinity → 0, $T_g(\alpha_c) \rightarrow T_g(\alpha_a) \equiv T_g$

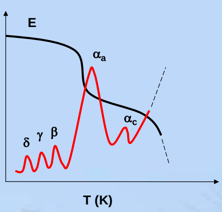


Fig. 5-21 Typical dynamic mechanical analysis spectrum

## 5.5.3 double $T_g$ phenomenon

★

- **Notice!**
  - It is different from the double $T_g$ phenomenon observed in blends of non-compatible polymers
    - Which is related to the super-molecular structures (phase separation)



## 5.5.4 motion inside the crystalline region

- Caused by the molecular motion of defects inside the crystalline region
- or by side groups
- Or maybe by interaction between crystalline region and amorphous region (need more evidence)