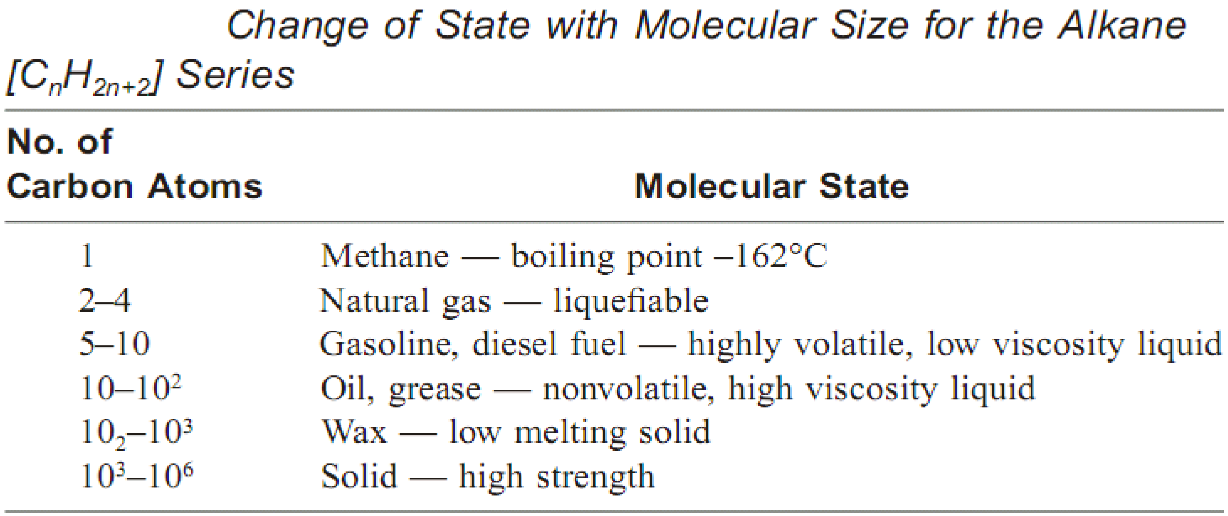
Chemical Bonding and Polymer Structure



Change of State with Molecular Size for the Alkane [C_nH_{2n+2}] *Series*

No. of Carbon Atoms	**Molecular State**
1	Methane — boiling point –162°C
2–4	Natural gas — liquefiable
5–10	Gasoline, diesel fuel — highly volatile, low viscosity liquid
10–10^2	Oil, grease — nonvolatile, high viscosity liquid
10_2–10^3	Wax — low melting solid
10^3–10^6	Solid — high strength

Polymers belong to the high-molecular-weight end of above spectrum. To understand how the unusual properties of high polymers are developed, it will be convenient to consider the **chemical** and **structural** aspects of polymers at three different levels:

1) The chemical structure (atomic composition) of the monomer (primary structure)
2) The single polymer chain (secondary level)
3) Aggregation of polymer chains (tertiary structure)

Chemical Bonding

Primary Bonds

-valence electrons are involved in the formation of primary bond

-They are strong

a) Ionic

b) Covalent

c) Metallic

Secondary Bonds

-valence electrons are not involved in the formation of secondary bonds

-They are weak

a) Dipole

b) Hydrogen

c) Induction

d) van der Waals (dispersion)

Primary Bonds -1

Ionic Bond

In chemical bonds, atoms can either transfer or share their valence electrons. In the extreme case where one or more atoms lose electrons and other atoms gain them in order to produce a noble gas electron configuration, the bond is called an ***ionic bond***

$$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$

The bonding force in sodium chloride is a result of the electrostatic attraction between the two ions.

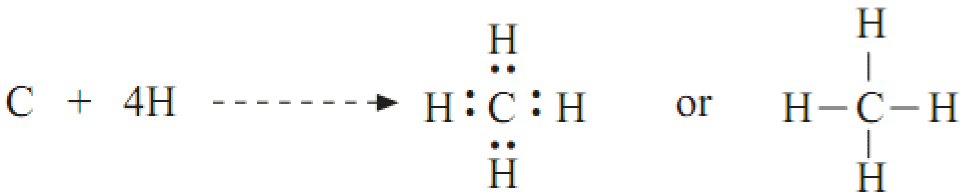
-Not common in polymeric materials
(However, divalent ions are known to act as cross-links between carboxyl groups in natural resins.)

- New class ionomers (contain ionic bond)

Primary Bonds -2

Covalent Bond

Covalent chemical bonds involve the sharing of a pair of valence electrons by two atoms, in contrast to the transfer of electrons in ionic bonds. Such bonds lead to stable molecules if they share electrons in such a way as to create a noble gas configuration for each atom



$$\mathrm{C} + 4\mathrm{H} \dashrightarrow \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H} \quad \text{or} \quad \mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\mathrm{H}$$

.

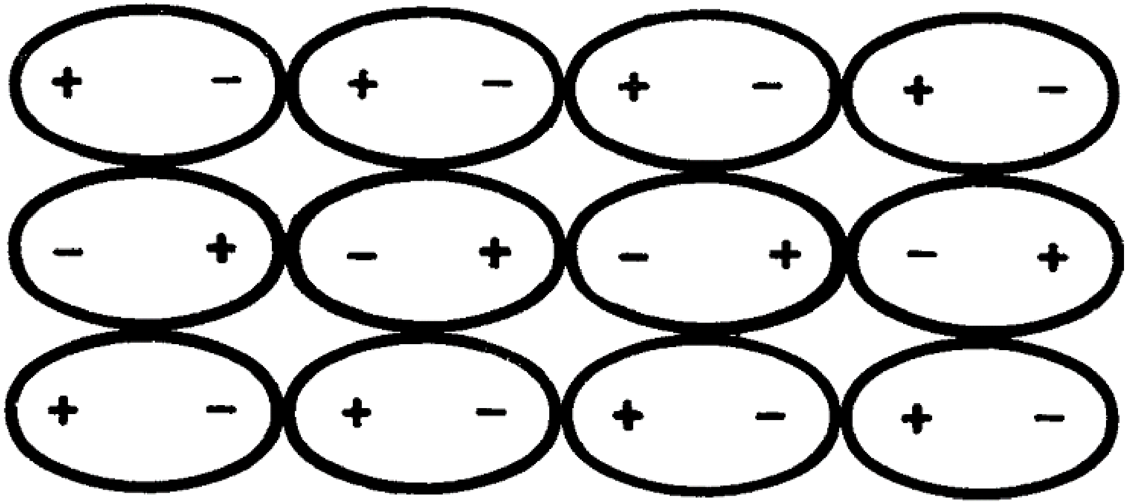
-predominant bond in polymers

-can be single, double or triple depending on the number of electron pairs

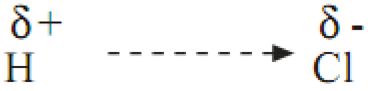
-atoms are free to rotate about single bonds (flexible), they remain spatially fixed (rigid) for double and triple bonds.

Secondary Bonds -1

<u>Dipole-dipole forces</u> are attractive forces between the positive end of one polar molecule and the negative end of another polar molecule. They are much weaker than ionic or covalent bonds and have a significant effect only when the molecules involved are close together.



Dipole–dipole interaction between polar molecules.



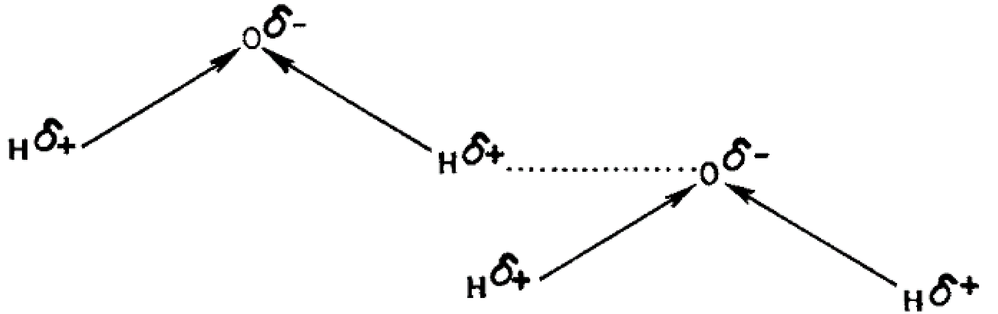
-the dipole–dipole interaction is temperature dependent

-Dipole forces play a significant role in determining the tertiary structure and properties of some polymers.

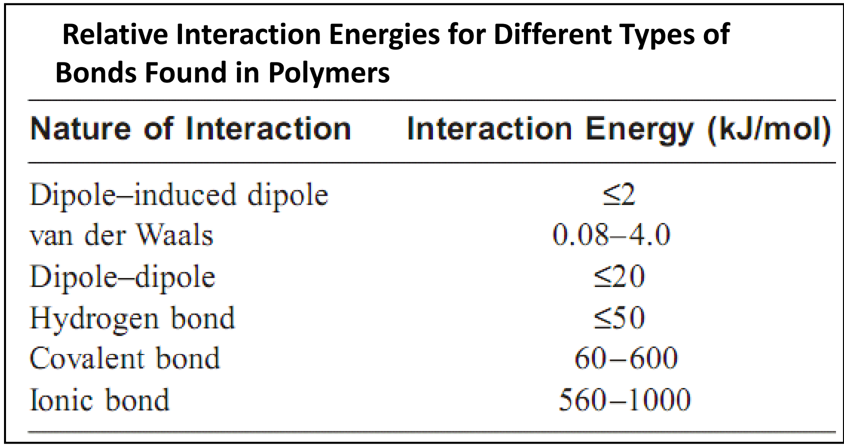
Secondary Bonds -2

HYDROGEN BOND

A particularly important kind of dipole interaction is the hydrogen bond. This is the bond between a positively charged hydrogen atom and a small electronegative atom like F, O, or N.



Hydrogen bonding between two water molecules.



Relative Interaction Energies for Different Types of Bonds Found in Polymers

Nature of Interaction	Interaction Energy (kJ/mol)
Dipole–induced dipole	≤2
van der Waals	0.08–4.0
Dipole–dipole	≤20
Hydrogen bond	≤50
Covalent bond	60–600
Ionic bond	560–1000

➢Hydrogen bonds are relatively stronger than dipole bonds due to the small size of the hydrogen ion

➢ In polymers, hydrogen bonding usually occurs between functional groups in the same or different molecules.

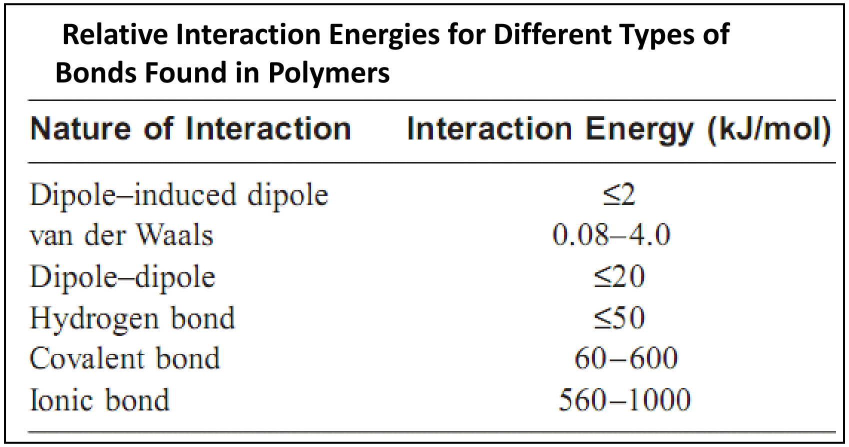
(The hydrogen is generally part of such groups as carboxyl, hydroxyl, amine, or amide, while the other atom in the hydrogen bond is frequently oxygen (in carbonyl, ethers, or hydroxyls) or nitrogen (in amines, amides, urethanes, urea).

➢The hydrogen bond plays a vital role in the structure and properties of polymers, particularly proteins.

Secondary Bonds -3

Induction Forces are intermolecular forces exist between the permanent and induced dipole. Induction forces are weak and temperature independent.

Van der Waals (dispersion Forces): Electrons are usually in constant motion about their nuclei. At any particular instant, the centers of negative charge of the electrons cloud may not coincide with those of the nuclei. Consequently, instantaneous (fluctuating) dipoles exist even in nonpolar materials. If the orientations of fluctuating dipoles in neighboring molecules are in proper alignment, intermolecular attractions occur. These attractive forces are referred to as van der Waals (dispersion) forces. Van der Waals forces are present in all molecules and they contribute significantly to the bonding in polymers.



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Covalent bond	60–600
Ionic bond	560–1000

Primary Structure

Primary structure refers to the atomic composition and chemical structure of the monomer — the building block of the polymer chain.

Basic to understanding the structure of the monomer vis-á-vis the structure and properties of the resulting polymer is a fundamental understanding of;

- The nature of bonds in monomers (chemical bonding)
- The type of monomers that are capable of forming polymers (functionality of monomers)
- The mode of linking of monomers (polymerization mechanisms)
- The chemical composition of monomers and the properties conferred on monomers as a result of their chemical composition

Polarity

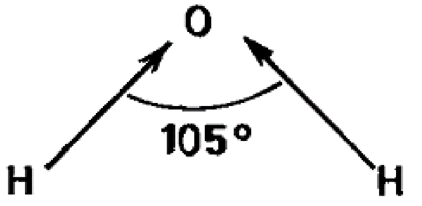
A diatomic molecule with such a pair of equal but opposite charges possesses a permanent dipole moment and is said to be **polar**.

In a diatomic molecule formed from two like atoms (e.g., H_2), the electron pair linking the two atoms is equally shared and the molecule is said to be nonpolar.

Electronegativities of Some Elements

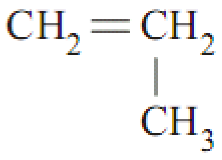
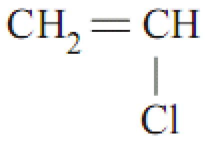
Atom	H	C	N	O	F	Si	S	Cl
Electronegativity	2.1	2.5	3.0	3.5	4.0	1.8	2.5	3.0

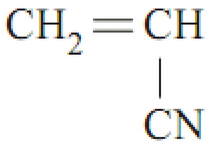
Non-polar; dipoles from polar bonds cancel due to symmetry



Polar; dipoles from polar bonds do not cancel

Polarity of Monomers

Monomer	Polarity
$CH_2=CH_2$ Ethylene	Nonpolar
 $CH_2=\underset{CH_3}{\underset{\vert}{CH_2}}$ Propylene	Nonpolar
 $CH_2=\underset{Cl}{\underset{\vert}{CH}}$ Vinyl chloride	Polar

Monomer	Polarity
$CH_2=CCl_2$ Vinylidene chloride	Nonpolar
 $CH_2=\underset{CN}{\underset{\vert}{CH}}$ Acroylonitrile	Polar
$CF_2=CF_2$ Tetrafluoroethylene (symmetrical)	Nonpolar

Secondary Structure

The secondary structure;

a) the size and b) shape of an isolated single molecule.

The size of the polymer is best discussed in terms of molecular weight.

The shape of the polymer molecule (molecular architecture) will be influenced naturally by the nature of the repeating unit and the manner in which these units are linked together.

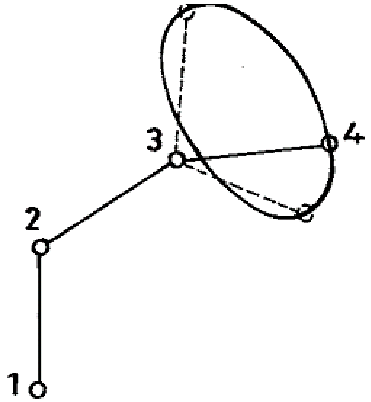
- ***Configuration*** — Arrangement fixed by primary valence bonds; can be altered only through the breaking or reforming of chemical bonds

- ***Conformation*** — Arrangement established by rotation about primary valence bonds

Conformation

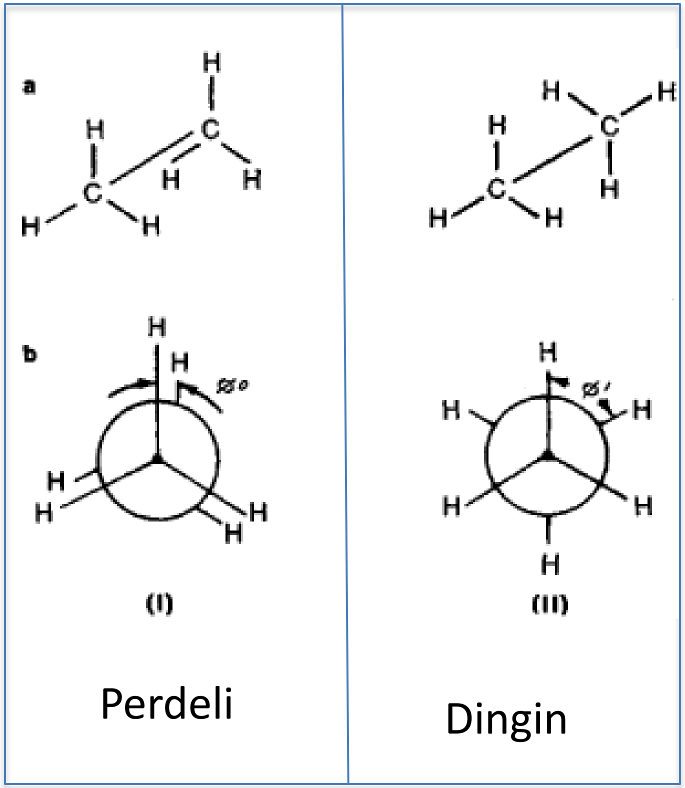
A polymer molecule may assume a large or limited number of conformations depending on:

- Steric factors
- Whether the polymer is amorphous or crystalline
- Whether the polymer is in a solution state, molten state, or solid state



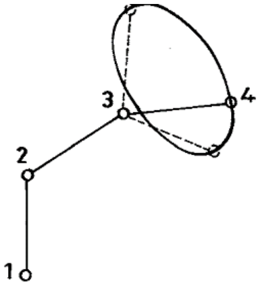
A segment of polymer chain showing four successive chain atoms; the first three of these define a plane, and the fourth can lie anywhere on the indicated circle which is perpendicular to and dissected by the plane.

Konformasyon, bir molekülün bağ kırılması olmadan tek bağlar etrafında dönmeyle alabileceği geometrilerin hepsini kapsar.

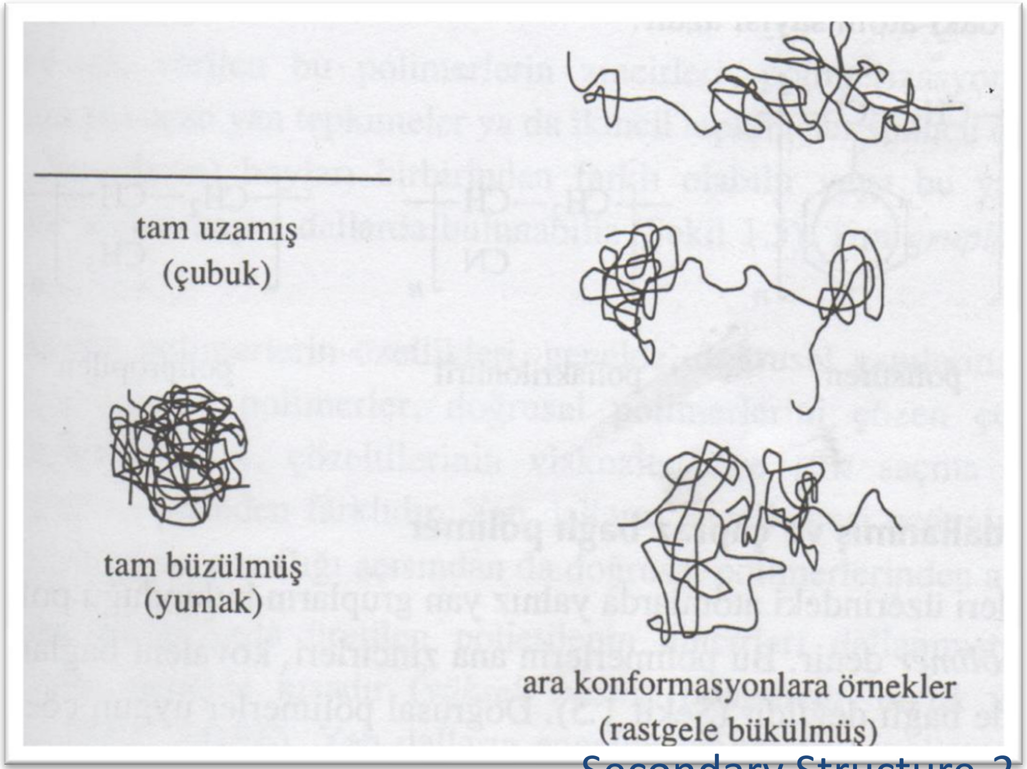


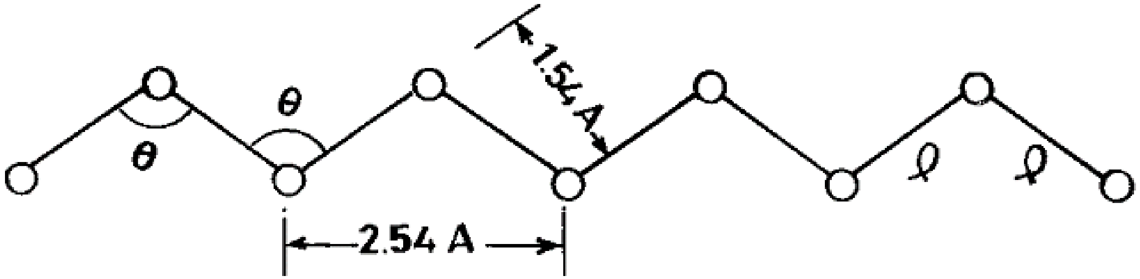
Perdeli

Dingin

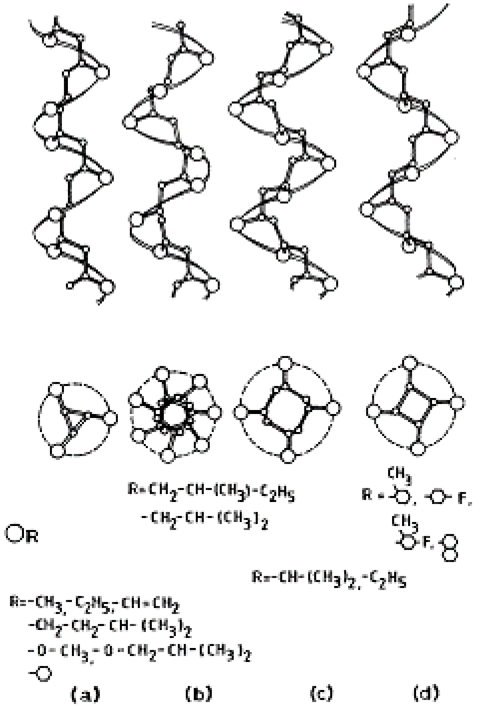


- C-C bağı etrafındaki dönmeler sırasında iki uç konformasyonla karşılaşılır.
- Bunlardan birisi ;her iki karbondaki H atomlarının birbirlerinin tam karşısına geldiği *perdeli* ,diğeri ise birbirlerinden en uzak olduğu *dingin* haldir.
- Dingin konformasyon en kararlı haldir.

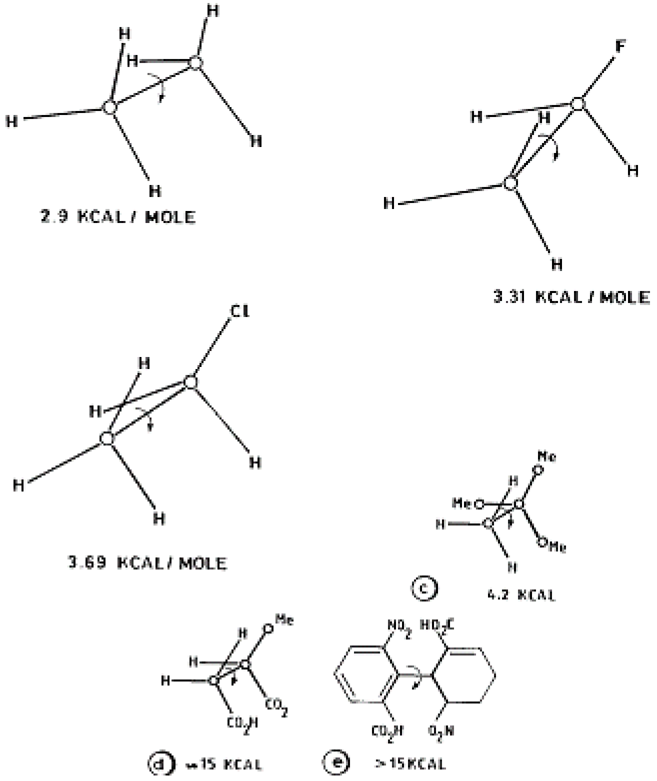




The fully extended all-trans conformation of a carbon–carbon chain.



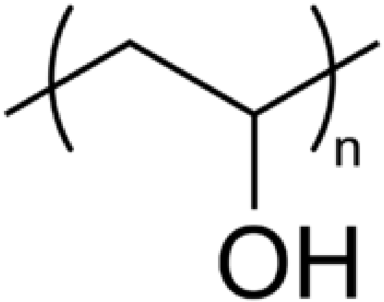
Helical conformations of isotactic vinyl polymers.



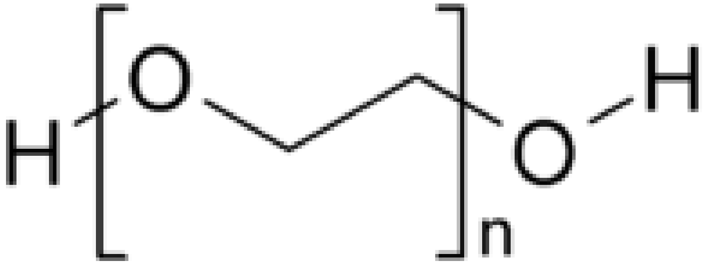
Rotational energy as a function of substitution and interaction of substituent groups.

Configuration

Structural Isomerism

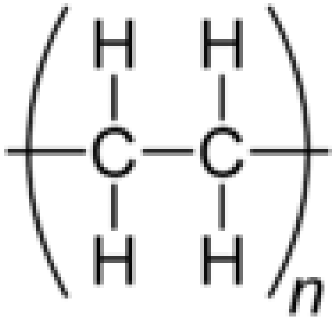


Poly(vinyl alcohol)
T_e= 260 °C



Poly(ethylene oxide)
T_e= 60 °C

Chain Isomerism: Homopolimerlerin; doğrusal, dallanmış ve çapraz bağlı yapılarının yinelenen birimleri aynı kimyasal yapı ile gösterilir.



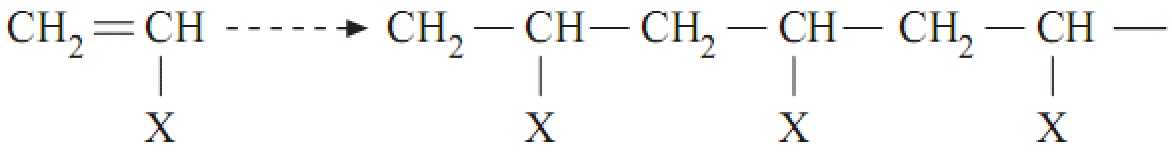
Polyethylene

- HDPE (dallanmanın az olduğu PE) ‘nin yoğunluğu ve kristalinitesi LDPE(dallanmanın çok olduğu PE)’den daha yüksektir.
- Doğrusal, dallanmış ve çapraz bağlı polimerlerin çözünürlük özellikleri birbirinden farklıdır.

Configuration

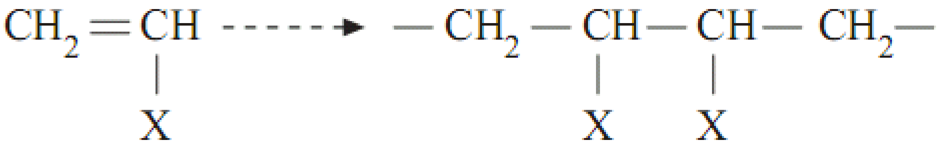
Recurrence regularity refers to the regularity with which the repeating unit occurs along the polymer chain.

Head-to-tail configuration



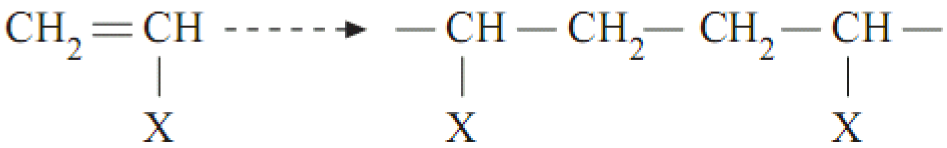
$$\mathrm{CH_2{=}\underset{\underset{X}{|}}{CH}} \dashrightarrow \mathrm{CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH}-}$$

Head-to-head configuration



$$\mathrm{CH_2{=}\underset{\underset{X}{|}}{CH}} \dashrightarrow \mathrm{-CH_2-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-CH_2-}$$

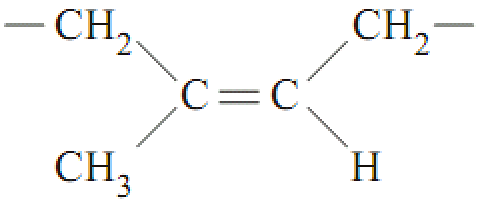
- Tail-to-tail configuration



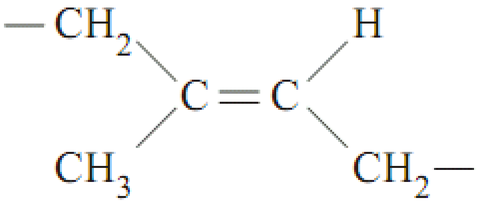
$$\mathrm{CH_2{=}\underset{\underset{X}{|}}{CH}} \dashrightarrow \mathrm{-\underset{\underset{X}{|}}{CH}-CH_2-CH_2-\underset{\underset{X}{|}}{CH}-}$$

Stereoregularity refers to the spatial properties of a polymer molecule.

Diene Polymerization



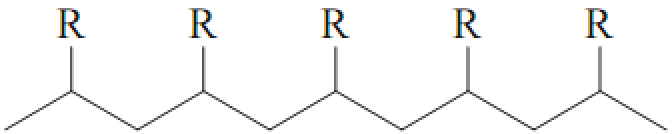
cis-1,4-polyisoprene (natural rubber)

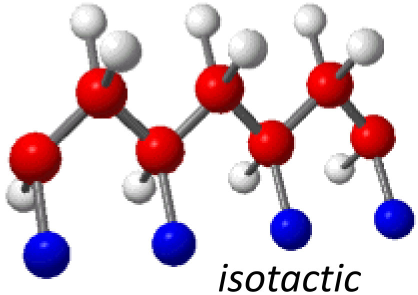


trans-1,4-polyisoprene (gutta-percha)

Tacticity

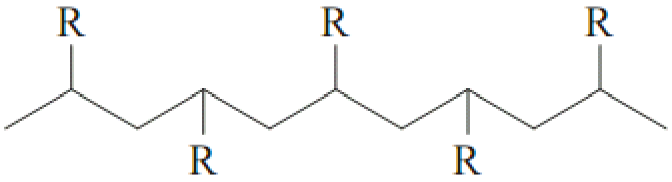
Isotactic — All the substituent groups, R, on the vinyl polymer lie above (or below) the plane of the main chain.

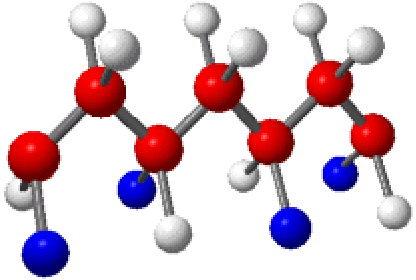




isotactic

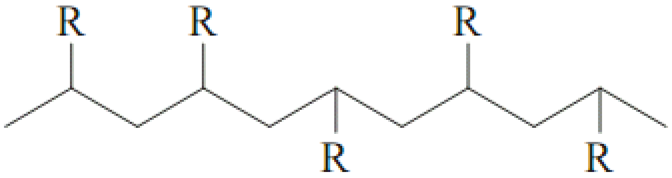
Syndiotactic — Substituent groups lie alternately above and below the plane.



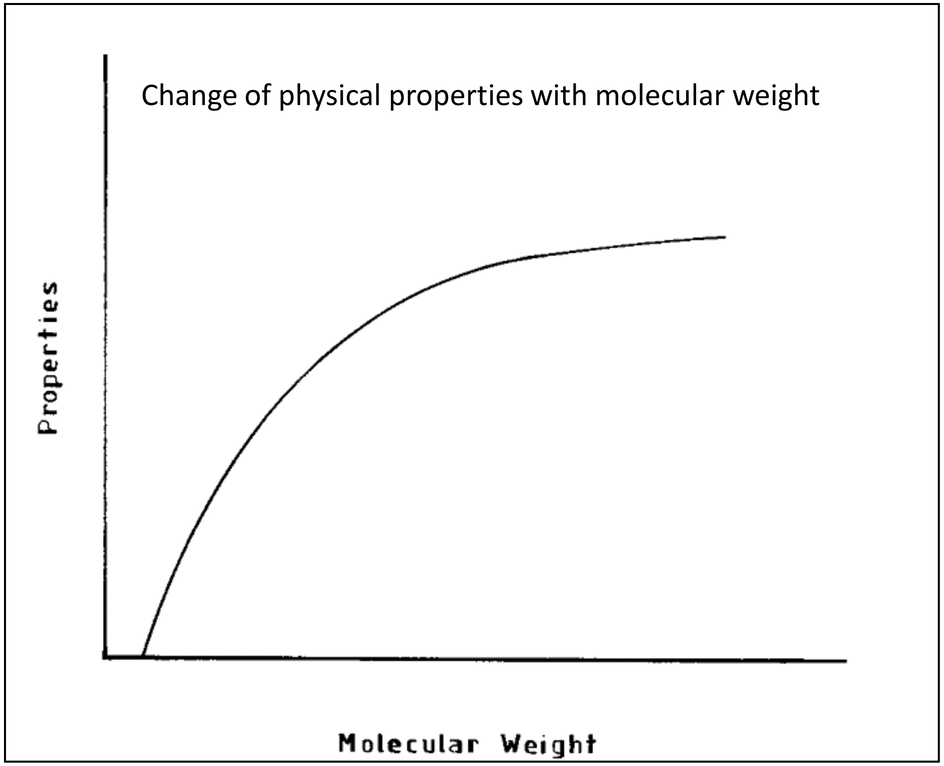


syndiotactic

Atactic — Random sequence of position of substituent occurs along the chain.



Molecular Weight-1



Different average molecular weights exist;

Number average molecular weight ($\overline{M}_n$)

Weight average molecular weight ($\overline{M}_w$)

z-average molecular weight ($\overline{M}_z$)

viscosity average molecular weight ($\overline{M}_v$)

✓Mechanical properties (tensile and compressive strengths, elongation at break, modulus, impact strength)

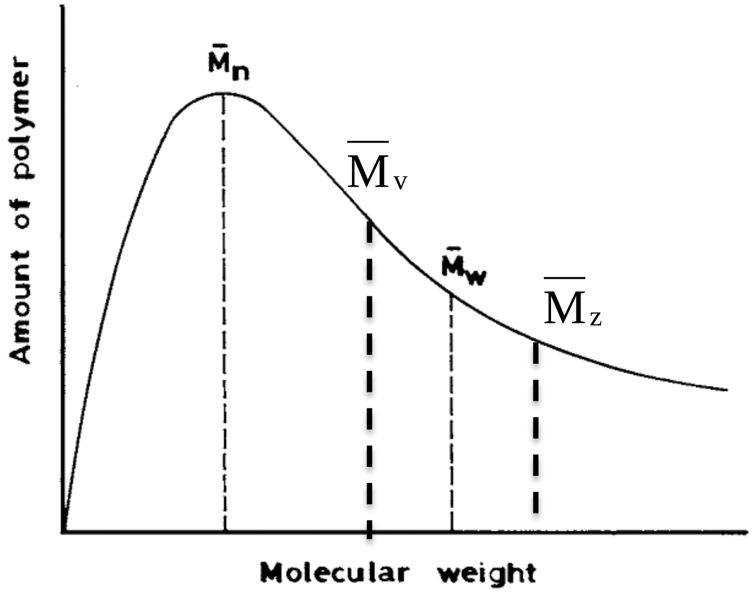
✓Other properties (softening point, solution and melt viscosities, solubility)

Molecular Weight-2

Molecular weight of polymers can be determined by physical and chemical methods;

- End group analysis ($\overline{M}_n$)
- Measurement of colligate properties($\overline{M}_n$)
- Light scattering ($\overline{M}_w$)
- Ultracentrifugation ($\overline{M}_w$)
- Dilute solution viscosity ($\overline{M}_v$)
- Gel permeation chromatography (GPC) ($\overline{M}_n$,$\overline{M}_w$,$\overline{M}_z$)

- Vapor pressure lowering
- Boiling point elevation (ebulliometry)
- Freezing point depression (cryoscopy)
- Osmotic pressure (osmometry)



Molecular weight distribution curve.

Tertiary Structure

- A polymeric solid material is an aggregate of a large number of polymer molecules.

- Depending on the molecular structure, process of molecular arrangement occurs essentially by two possible arrangements of molecules, leading to an ***amorphous*** or ***crystalline*** material.

- The forces for molecular aggregation are intermolecular secondary bonding forces (range from 0.5 to 10 kcal/mol)

- ***Tertiary structure*** is concerned with the nature of the intermolecular secondary bonding forces and with the structure order of the resulting polymer

Cohesive Energy Density (CED)

CED is the total energy per unit volume need to separate all intermolecular contacts and given by,

$$\mathrm{CED} = \frac{\Delta E_{v\delta}}{V_L} \quad \text{where } \Delta E_v = \text{molar energy of vaporization}$$

$$V_L = \text{molar volume of liquid}$$

$$\Delta E_v = \Delta H_V - RT \quad \text{where } \Delta H_V = \text{molar heat of vaporization}$$

$$T = \text{absolute temperature (K)}$$

$$\mathrm{CED} = \frac{\Delta E_V}{V_L} = \frac{\Delta H_V - RT}{V_L}$$

The relation betweeen cohesive energy density and solubility parameter (δ)

$$\mathrm{CED} = \delta^2$$

In the absence of strong interactions, a polymer δ_2 will dissolve in a solvent (δ_1) if;

$$\delta_1 - \delta_2 \leq 1.7 - 2.0$$

Crystalline and Amorphous (Structure of Polymers)

Amorphous- the molecules vitrify, with the polymer chains randomly coiled and entangled. Hard and Glassy

Crystalline- The individual chains are folded and packed in a regular manner characterized by three dimensional long range order

Semicrystalline- containing both crystalline and amorphous regions in the same sample

In polymers, the degree of crystallinity ranges:

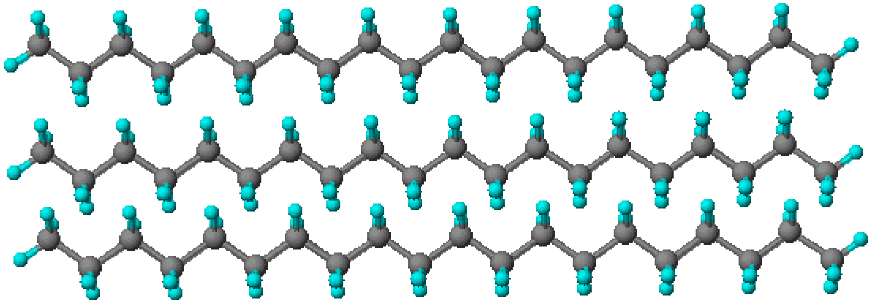
- from 0% (amorphous glasses)
- to >90% (highly crystalline)

Crystallinity is affected by:

- structure
- temperature
- molecular weight
- stereochemistry
- processing conditions

Structural Regularity-1

PE (polyethylene)-nonpolar, intermolecular attraction is due to the van der Waals forces. Planar zigzag conformation, by a sequence of trans bonds.

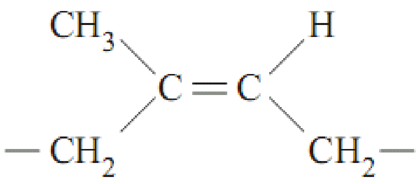
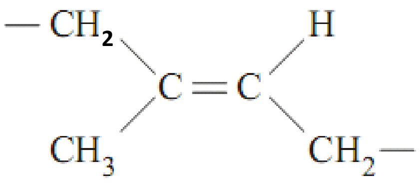


-High melting point (T_m) = 135 °C
-relatively high rigidity
-low room temperature solubility

The irregularities is introduced into the structure, as with low density polyethylene (LDPE).

The crystalline melting point of PE is reduced 20 -25 °C on going from the linear to branched.

Structural Regularity-2

Isomer	Structure	Properties
1,4-*cis*=polyisoprene (heavea rubber)		Soft, pliable, easily soluble rubber; has a high retractive force; used for making vehicle tires
1,4-*trans*-polyisoprene (gutta-percha)		Tough, hard; used as golf ball covers

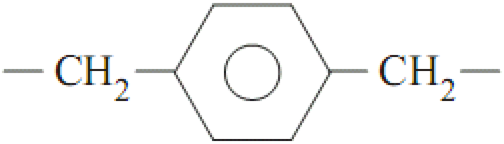
Isotactic, syndiotactic- rigid, crystallizable, high melting and relatively insoluble

Atactic- soft, low melting, easily soluble and amorphous

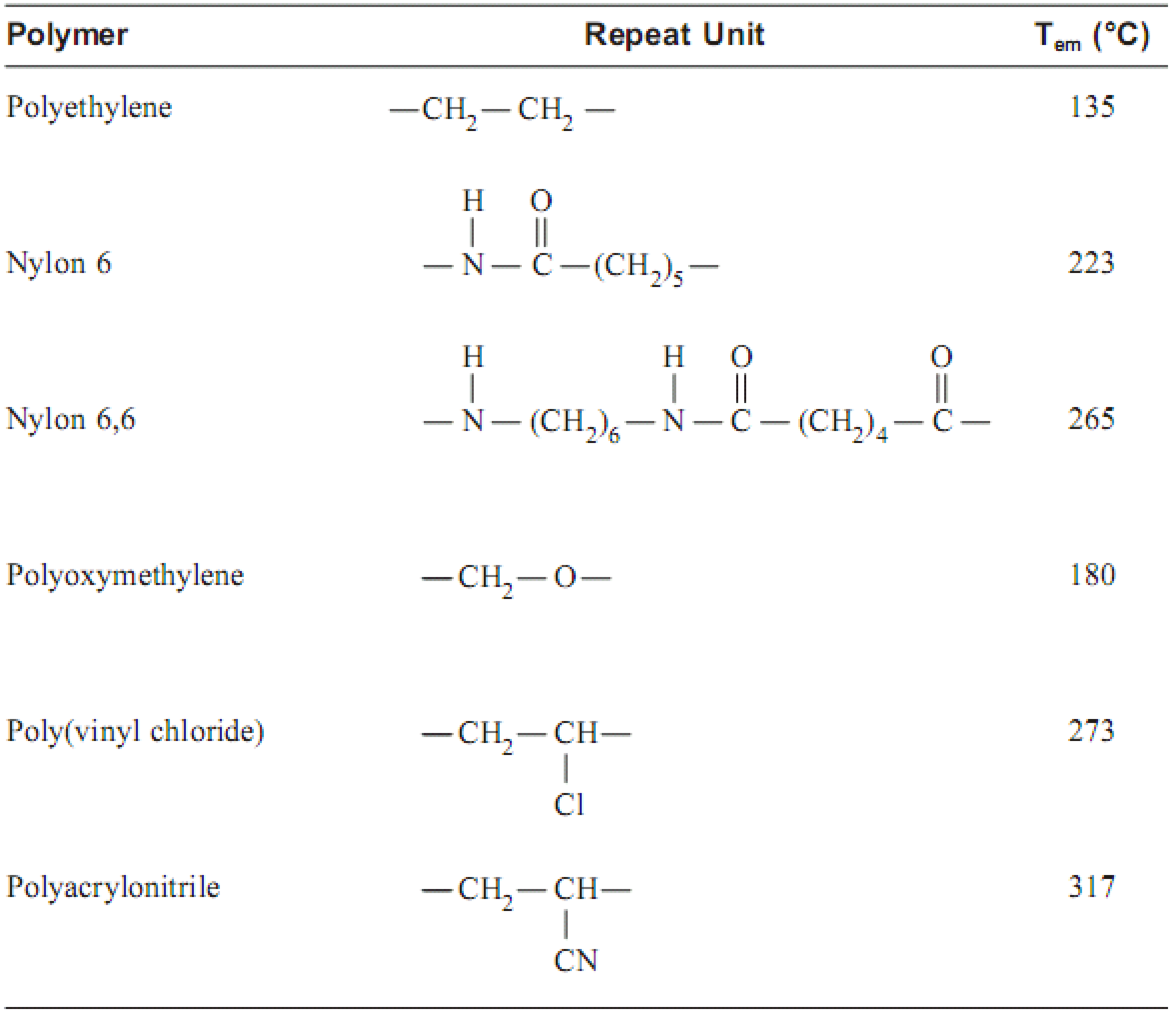
Chain Flexibility

The ***flexibility*** of chain molecules arises from rotation around saturated chain bonds.

Effect of Chain Flexibility of Crystalline Melting Point

Polymer	**Repeating Unit**	**T_m (°C)**
Polyethylene	$-CH_2-CH_2-$	135
Polyoxyethylene	$-CH_2-CH_2-O-$	65
Poly(ethylene suberate)	$-O(CH_2)_2-OCO-(CH_2)_6CO-$	45
Nylon 6,8	$-NH(CH_2)_6NHCO(CH_2)_6CO-$	235
Poly (*p*-xylene)		400

Polarity



Polymer	Repeat Unit	T_{em} (°C)
Polyethylene	$-CH_2-CH_2-$	135
Nylon 6	$-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5-$	223
Nylon 6,6	$-\overset{H}{\overset{\vert}{N}}-(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-$	265
Polyoxymethylene	$-CH_2-O-$	180
Poly(vinyl chloride)	$-CH_2-\underset{Cl}{\underset{\vert}{CH}}-$	273
Polyacrylonitrile	$-CH_2-\underset{CN}{\underset{\vert}{CH}}-$	317

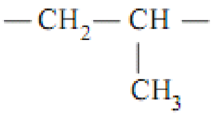
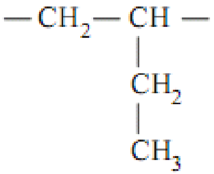
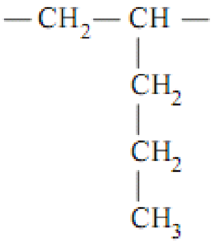
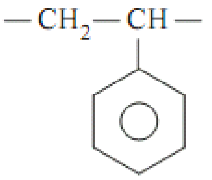
Bulky Substituents

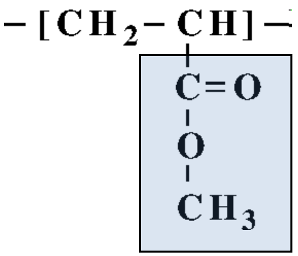
The vibrational and rotational mobility of intrinsically flexible chains can be inhibited by bulky substituents; the degree of stiffening depends on the size, shape, and mutual interaction of the substituents.

-Vinyl polymers, with small substituents PP (-CH_3) and PS (-C_5H_6) can crystallize if they are isotactic or syndiotactic.

-In atactic form, randomly disposed pendant groups prevents the close packing of polymer chains into the crystalline lattice, so atactic forms are amorphous.

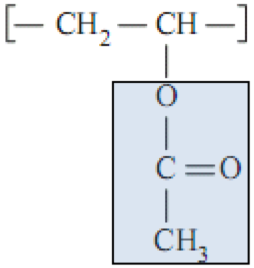
-Large or bulky substituents increase the average distance between chains and prevent the effective and favorable utilization of the intermolecular bonding forces.

Polymer	Repeat Unit	T_m (°C)
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	 $-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-$	176
Poly(1-butene)	 $-CH_2-\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH}-$	125
Poly(1-pentene)	 $-CH_2-\underset{\underset{\underset{\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\vert}}{CH_2}}{\vert}}{CH}-$	75
Polystyrene		240



$-[CH_2-\underset{\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{O}}{|}}{C=O}}{|}}{CH}]-$

Poly(methyl arcylate)

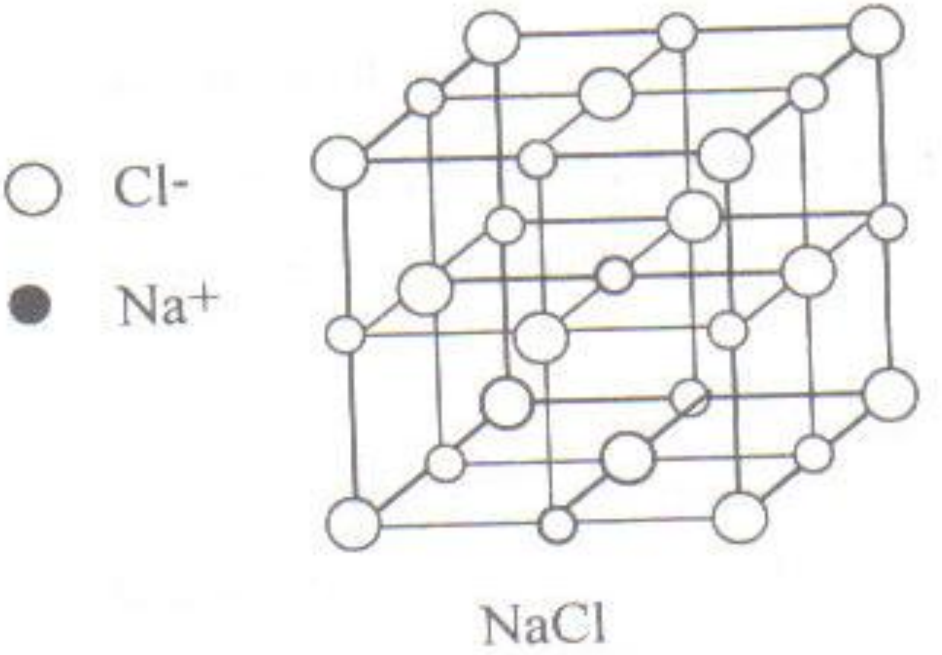


$[-CH_2-\underset{\underset{\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{O}}{|}}{CH}-]$

poly(vinyl acetate)

Can not crystallize even if they are isotactic or syndiotactic

Crystalline Structure of Polymers

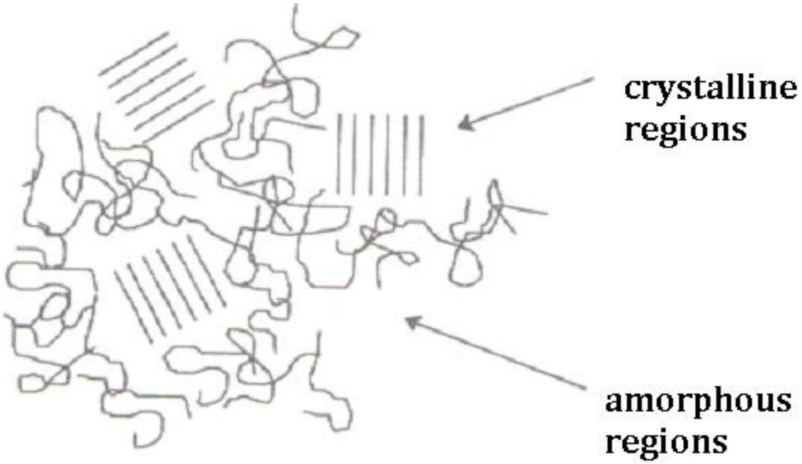


Crystal structure of sodium cloride

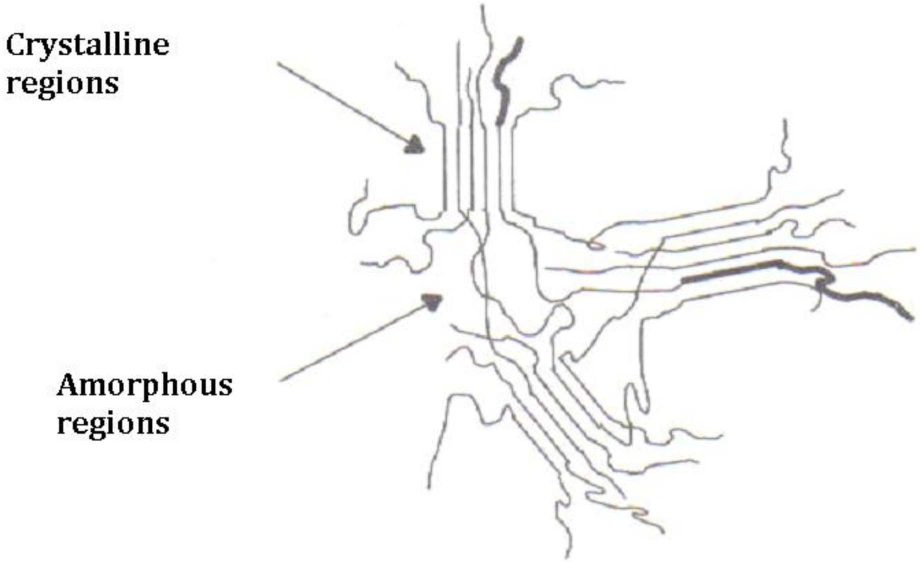
Polimer Kimyası Prof. Dr. Mehmet Saçak (5. Baskı, Gazi Kitapevi)

Morphology of Crystalline Polymers

Semicrystalline Polymers

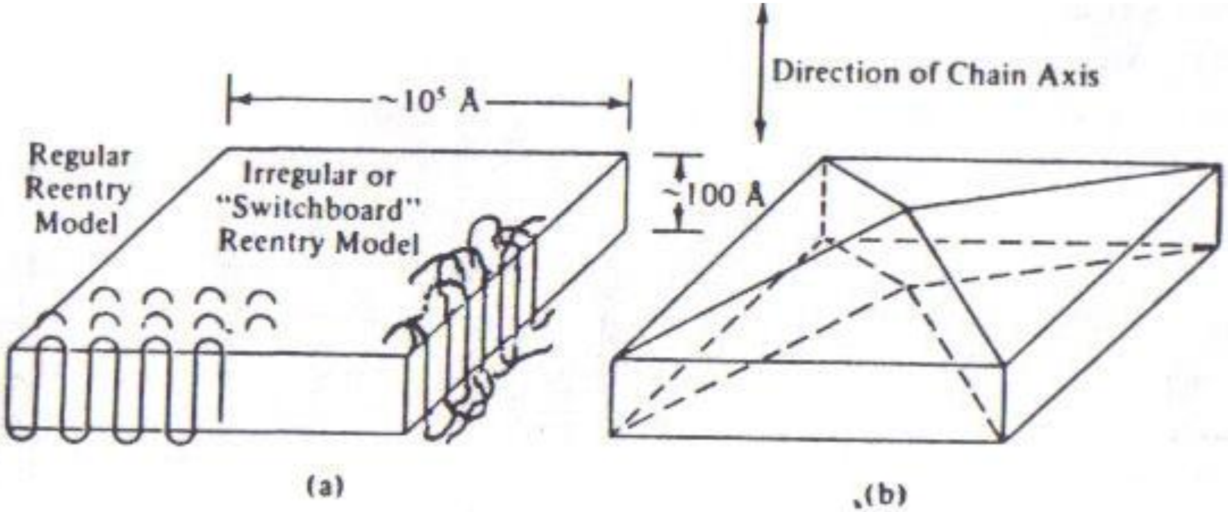


Two phase micelle model



Fringed micelle model

Morphology of Polymer
Single Crystals Grown from Solution -1



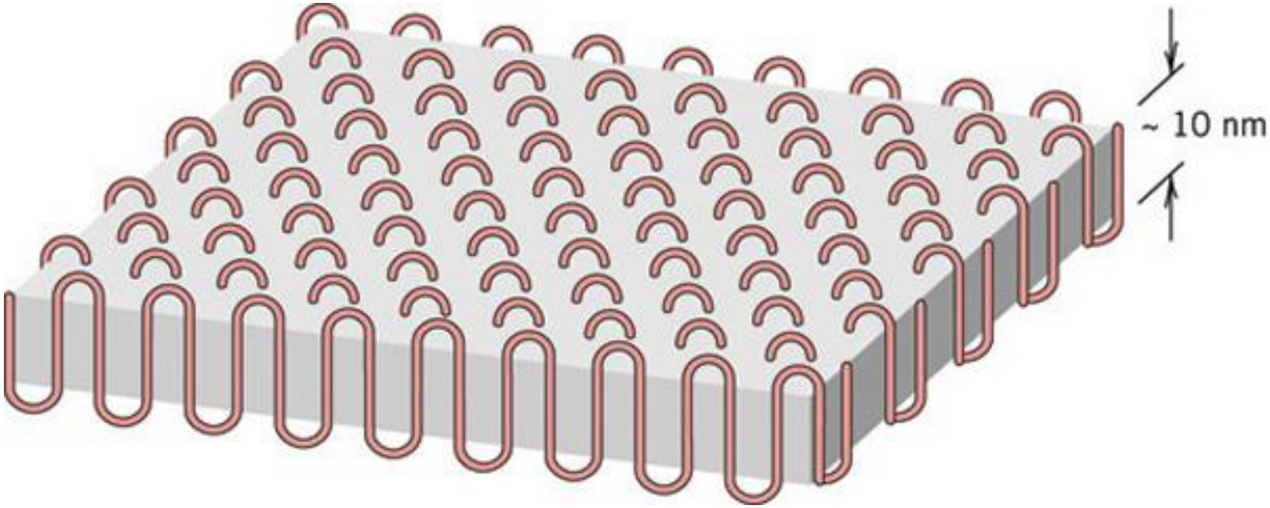
Polymer single crystals: (*a*) flat lamellae; (*b*) pyramidal lamellae. Two concepts of chain reentry are illustrated.

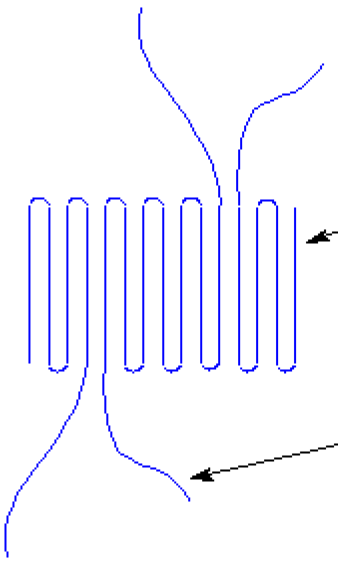
Morphology of Crystalline Polymer Single Crystals Grown from Solution -2

- **Chain folded-model**

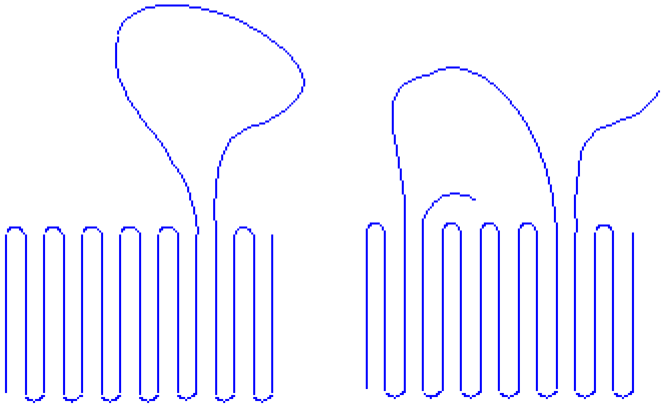
  -Many polymers crystallize as very thin platelets (or lamellae)

  -Idea – the chain folds back and forth within an individual plate (chain folded model)



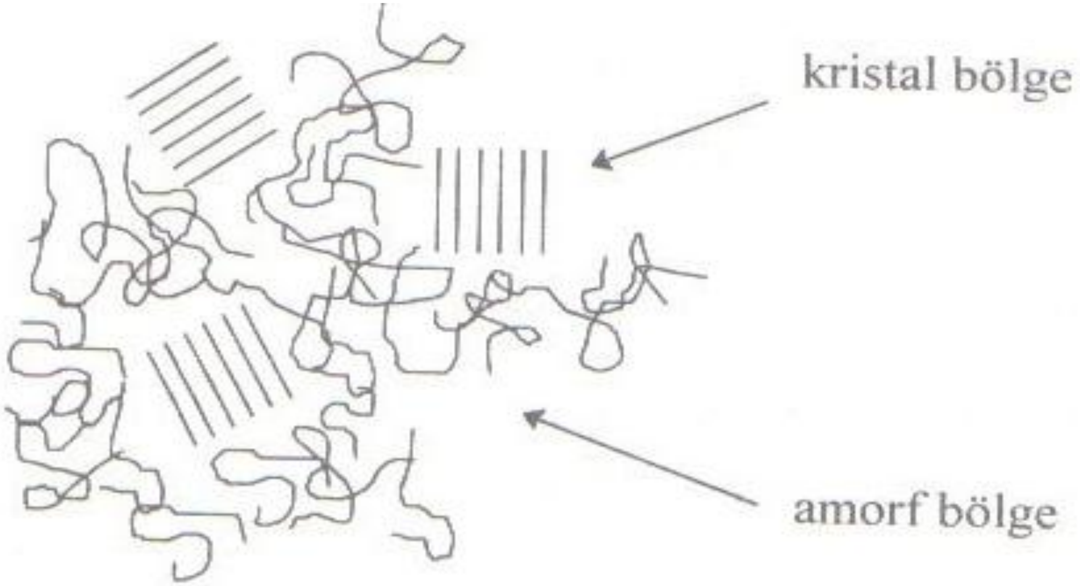


Sometimes a polymer chain is indecisive, and part of it is in the crystalline lamella, but part of it stays outside the lamella, in the amorphous region.

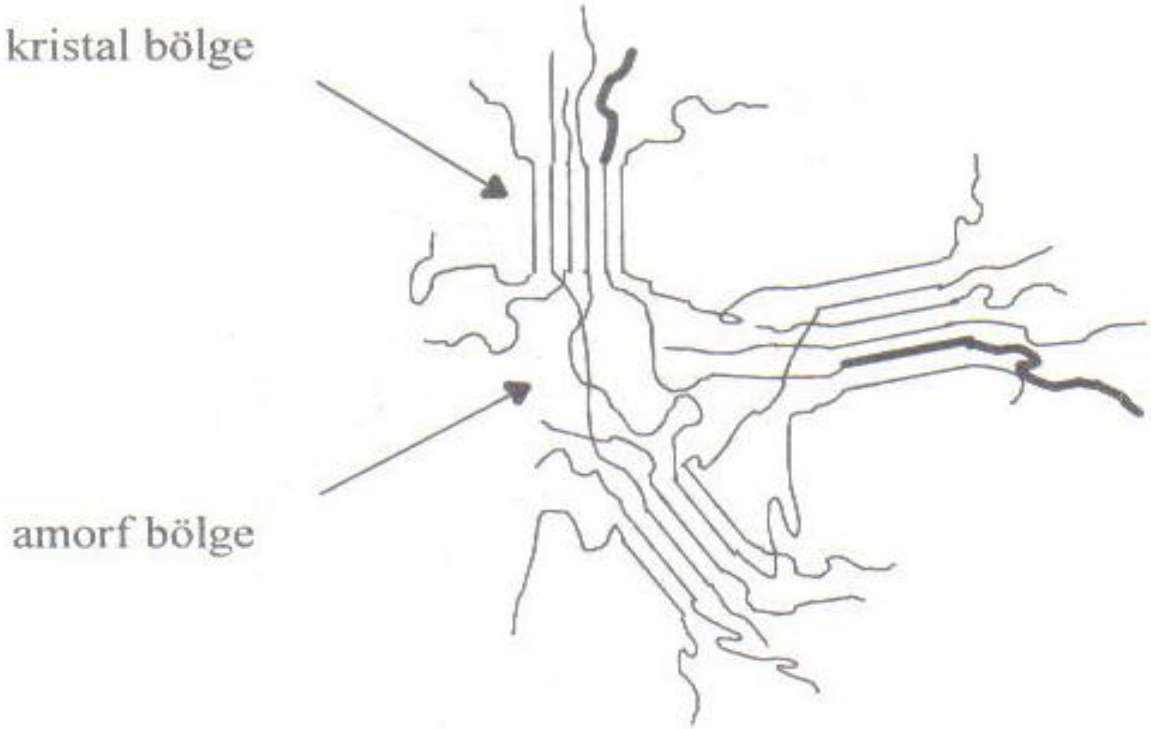


These lamellae have chains that go out for awhile, then come back in. On the left, the chain re-enters the lamellae right next to where it left. On the right our outgoing chain comes back in some distance away from where it left. Both are possible. These two pictures both show what is called the *switchboard model* of a polymer crystalline lamella.

Semicrystalline Polymers Grown from Solution



Yarı-kristal bir polimer yapısı için ilk öne sürülen *iki fazlı misel modeli.*



Yarı-kristal bir polimer için öne sürülen *saçaklı misel* modeli. Koyu gösterilen polimer zincirinde olduğu gibi polimer zinciri kristal ve amorf bölgelere katkıda bulunabilir.

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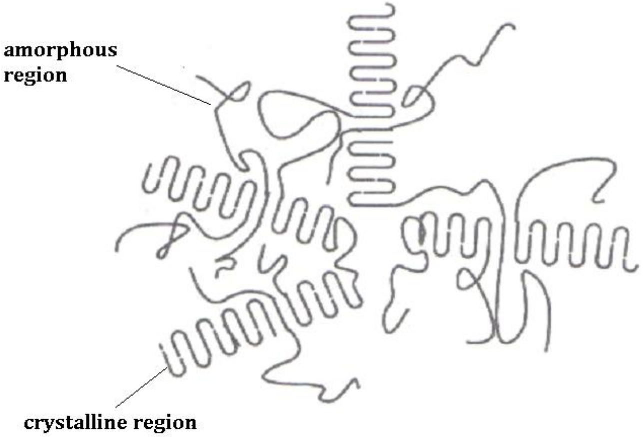
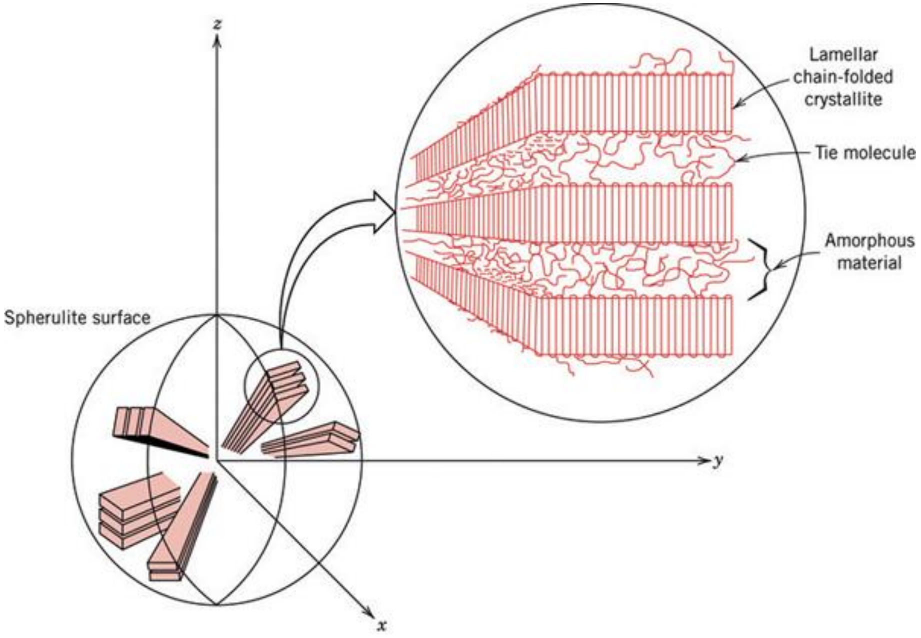
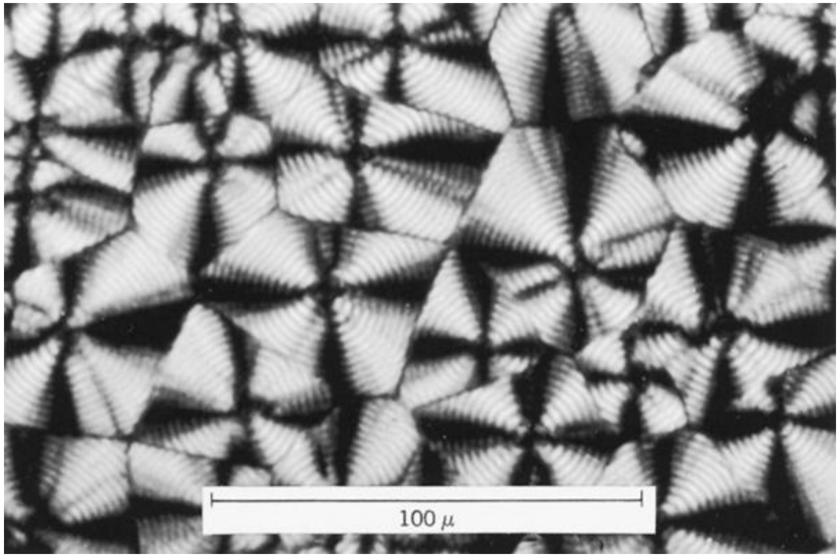
Morphology of Polymers Crystallized from Melt



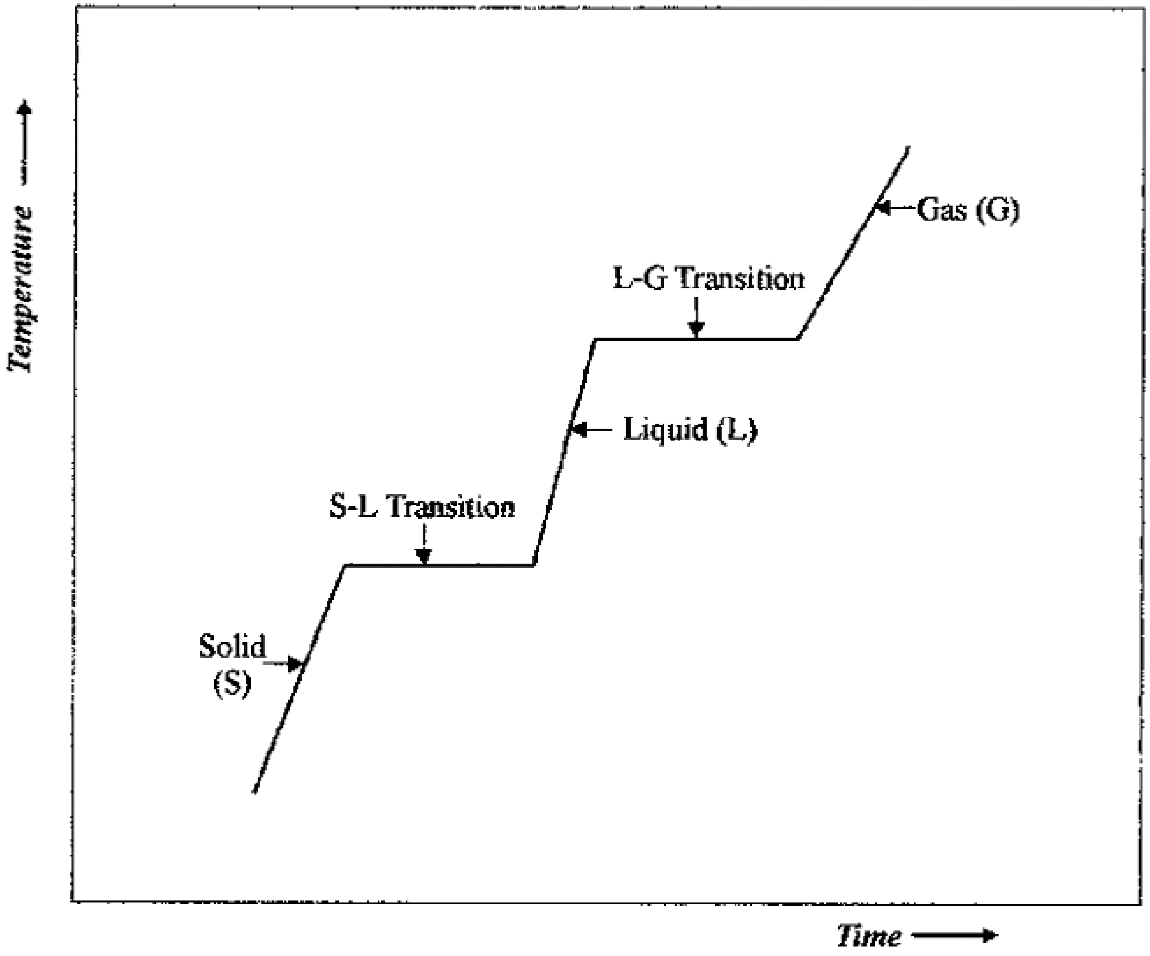
- More commonly, many polymers that crystallize from a melt form ***spherulites***
    - One way to think of these – the chain folded lamellae have amorphous "tie domains" between them
    - These plates pack into a spherical shape
    - Polymer analogues of grains in polycrystalline metals/ceramics

structure of spherulite



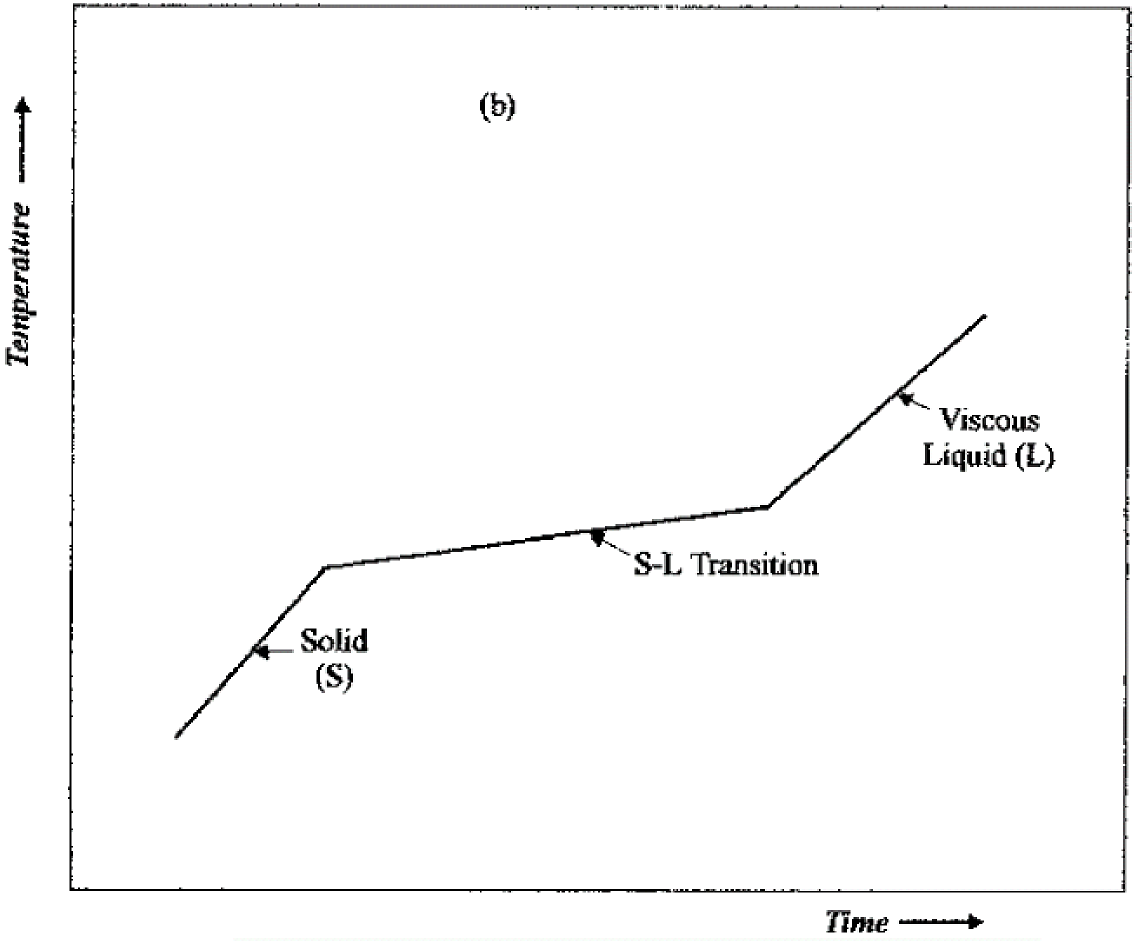


Thermal Responses of Simple Molecules



- Water exists at three distinct physical states-solid, liquid and gas (vapor)
- Transitions between these states occur sharply at constant , well defined temperatures.

Thermal Responses of Polymers-1



- Polymers do not exist in the gaseous state. At high T they decompose.
- The transition between solid and liquid forms of a polymer is rather diffuse and occurs over a temperature range, whose magnitude (of the order of 2-10 °C) depends polydispersity of the polymer

Thermal Responses of Polymers-2

❖The molecular motion in a polymer sample is promoted by its thermal agitation

❖It is opposed by the cohesive forces between structural segments (groups of atoms) along the chain and between neighboring chains.

❖The cohesive forces and thermal transitions in polymers depend on the structure of the polymers.

The glass transition temperature, T_g

The crystalline melting point, T_m

} Temperatures at which physical properties of polymers undergo drastic changes

T_g—transition from the hard and brittle glass into softer rubbery state (amorphous polymer- in the amorphous regions of semicrystalline polymer)

T_m– corresponds to the temperature at which the last crystallite starts melting

depends on the crystallinity and size distribution of crystallites

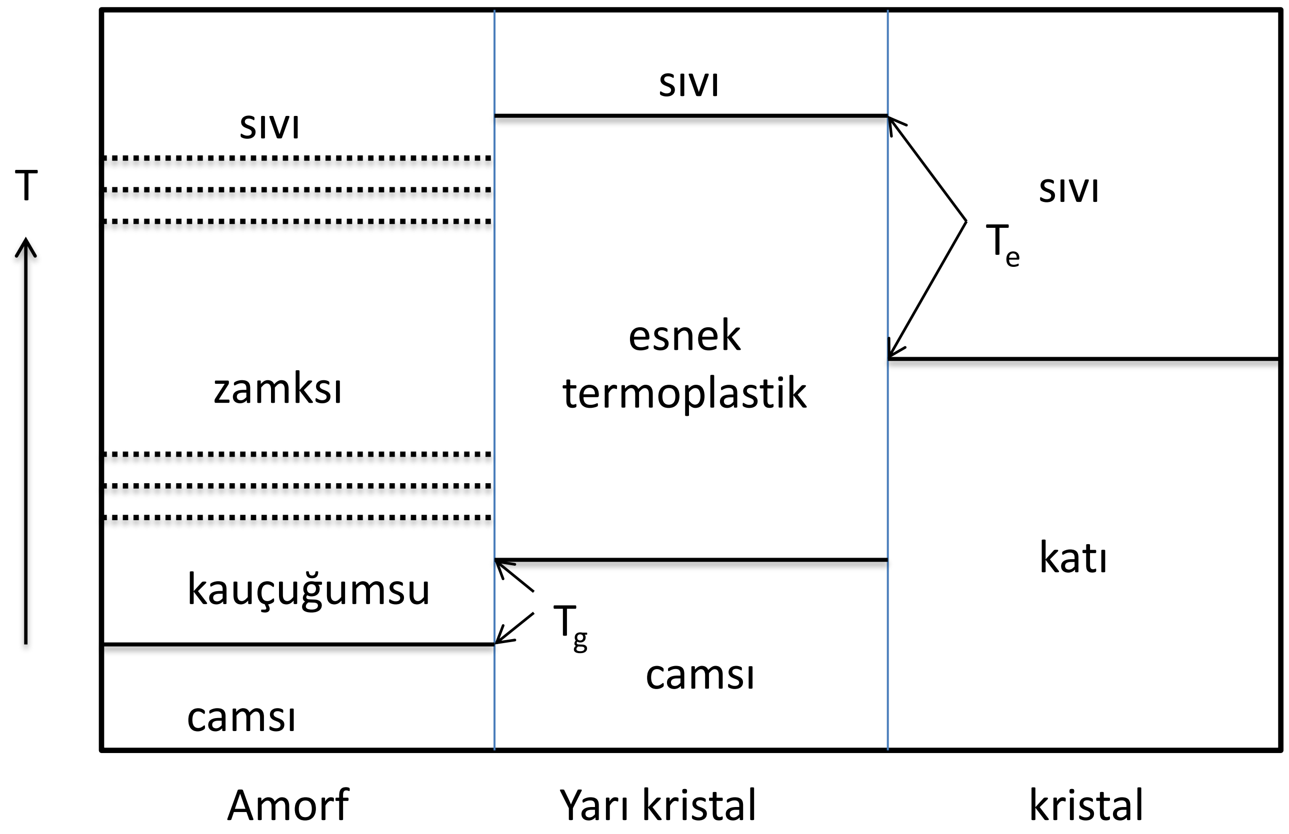
Knowledge of thermal transitions is important in ;

✓The selection of proper processing and fabrication conditions

✓Characterization of physical and mechanical properties of a material

✓Determination of appropriate end uses

Amorf, yarı kristal ve kristal maddelerde ısıl geçişler sırasında gözlenen davranış değişiklikleri



Tam kristal ve yarı kristal maddelerde davranış değişiklikleri belirgin, amorf maddelerde camsı geçiş dışındakiler derecelidir.

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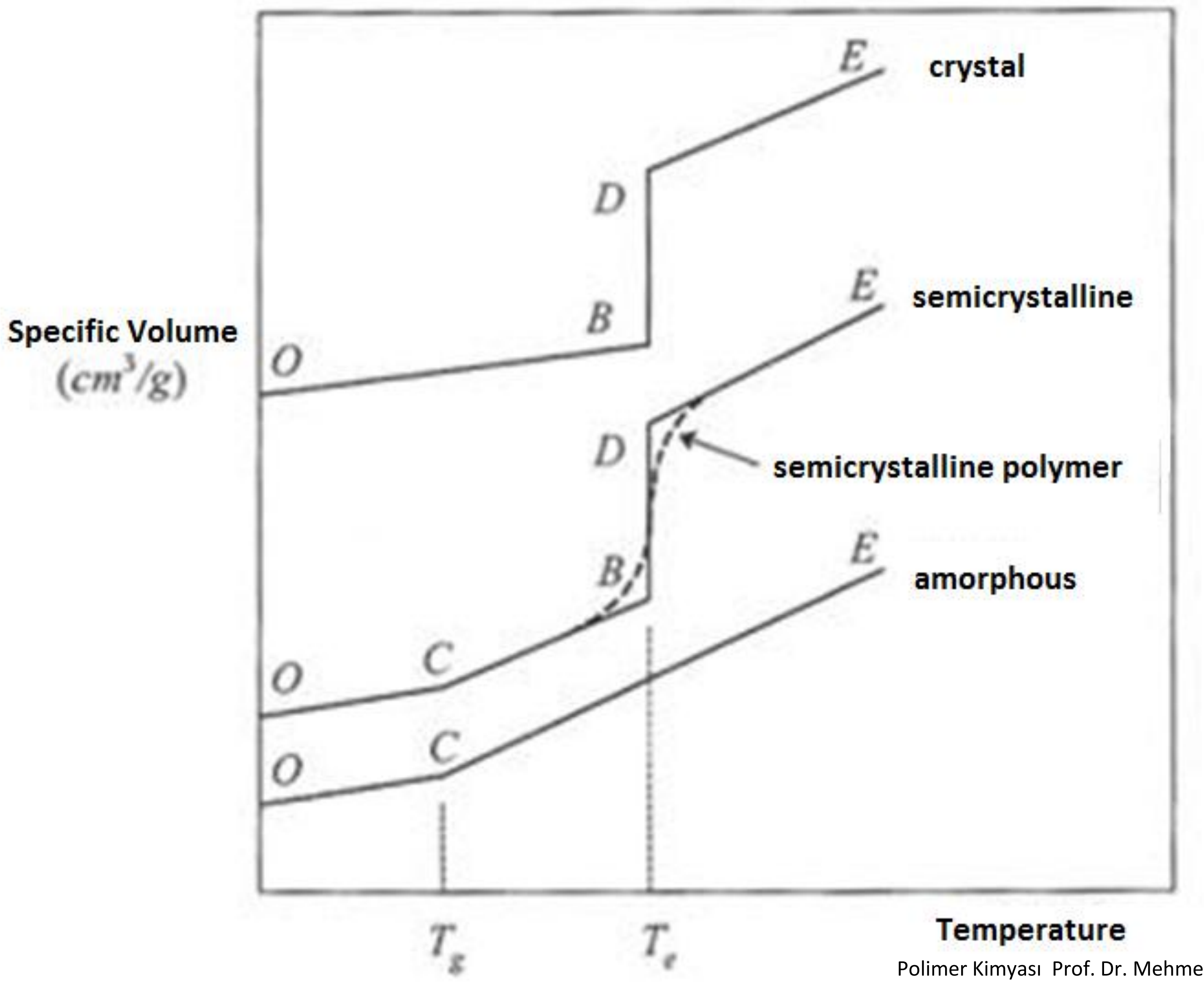
Glass Transition Temperature



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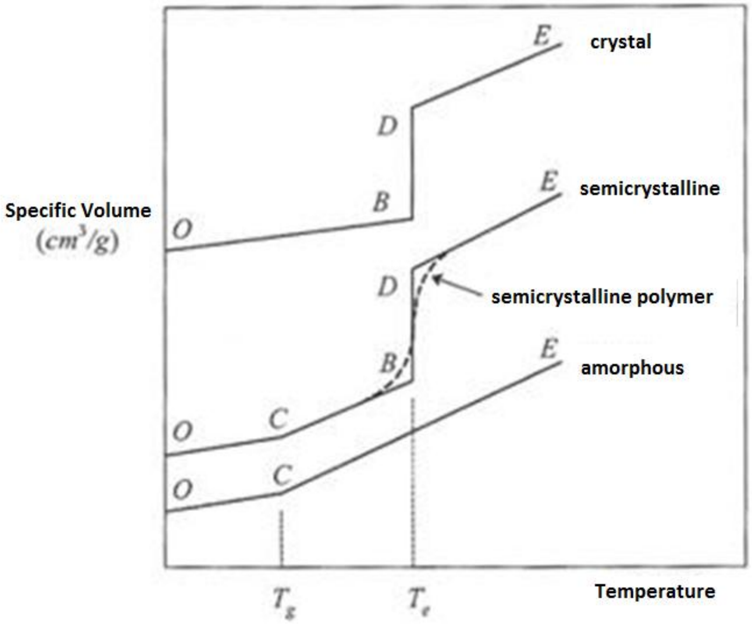
Thermal Transitions

1^{st} order transition

Abrupt change in a fundamental property such as enthalpy (H) and volume (V)

Melting is a first order thermodynamic transition



2^{nd} order transition

First derivative of properties such as enthalpy (H) and volume (V)changes

Heat Capacity

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

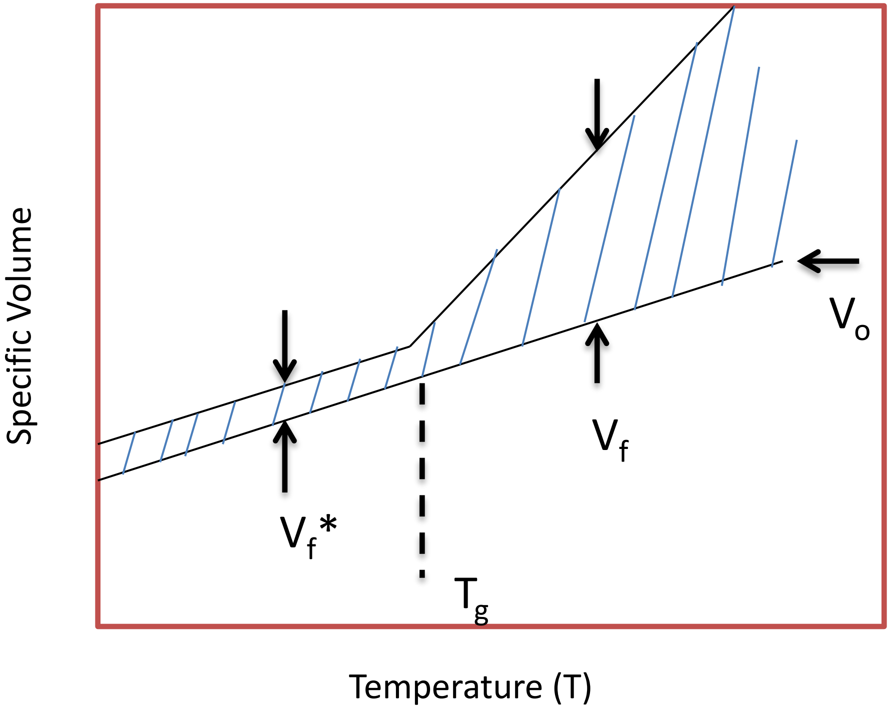
Thermal Expansion Coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Both C_p and α change abruptly at T_g.

Free Volume Theory

This theory considers the free volume (V_f) of a substance as the difference between its specific volume (total volume) (V) and the space actually occupied by the molecules (V_o)



$$V = V_o + V_f$$

$$f = \frac{V_f}{V} \qquad f = \frac{V_f^*}{V} \text{ (constant)}$$

Free Volume Fraction

$$V_f = V_f^* + (T - T_g)\left(\frac{\partial V}{\partial T}\right)$$

$$f = f_g + (T - T_g)\alpha_f$$

$$\alpha_f = \alpha_1 - \alpha_2$$

Thermal expansion coefficient (above Tg)

Thermal expansion coefficient (below Tg)

For whole range of glassy polymers, f_g is remarkably constant and this concept of free volume found important use in the analysis of the rte and temperature dependence of viscoelastic behavior of polymers between T_g and T_g+100K

Glass Transition Temperature

Many important physical properties or polymers (particularly amorphous polymers) change drastically at the glass transition temperature. These variations of properties form a convenient method for determining T_g.

<u>Temperature variation of;</u>

- Specific volume (dilatometry)
- Refractive Index (refractometry)
- Specific heat (calorimetry)
- Changes in vibrational energy level (Infrared Spectroscopy)
- Changes in proton environment (Nuclear Magnetic Resonanse or NMR)
- Changes in dipole moment (Dielectric constant and loss)
- Changes in elastic modulus (creep and stress relaxation)
- Changes in mechanical energy absorption (Dynamic Mechanical Analysis or DMA)

Factors Affecting T_g

Structural Features;

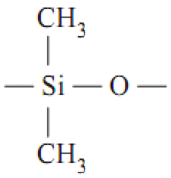
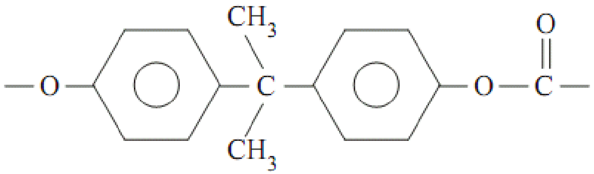
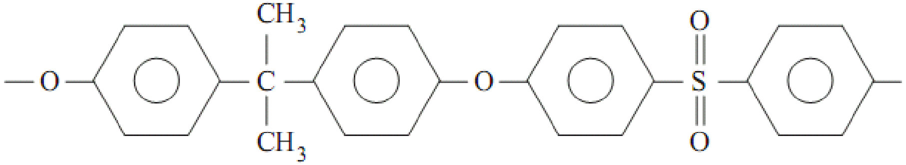
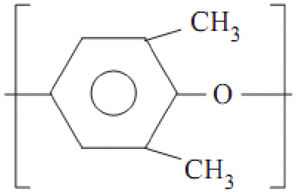
- Chain Flexibility (stiffness, polarity, steric hindrance)
- Interchain Attractive Forces
- Geometric Factors
- Copolymerization
- Molecular Weight
- Branching and Crosslinking
- Crystallinity

External Variables;

- Plasticization
- Pressure
- Rate of Testing

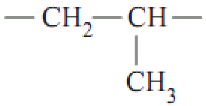
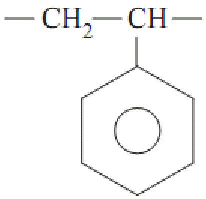
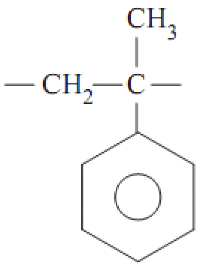
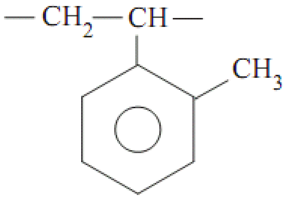
Chain Flexibility

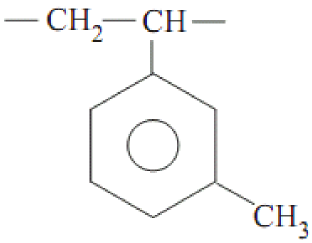
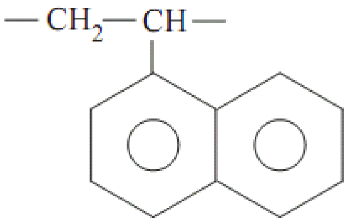
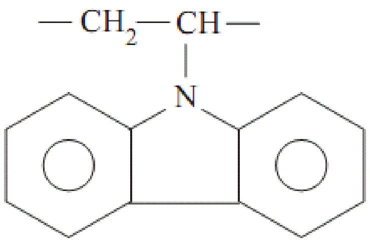
Chain flexibility is determined by the ease with which rotation occurs about primary valence bonds. Polymers with low hindrance to internal rotation have low T_g values

Polymer	Repeat Unit	T_h (°C)
Polyethylene	$-CH_2-CH_2-$	–120
Polydimethylsiloxane	 $-\overset{CH_3}{\underset{CH_3}{Si}}-O-$	–123
Polycarbonate		150
Polysulfone		190
Poly(2,6-dimethyl-1,4-phenylene oxide)		220

- ➢Long-chain aliphatic groups (ether-ester linkages) enhance flexibility
- ➢Cyclic structures stiffen the backbone

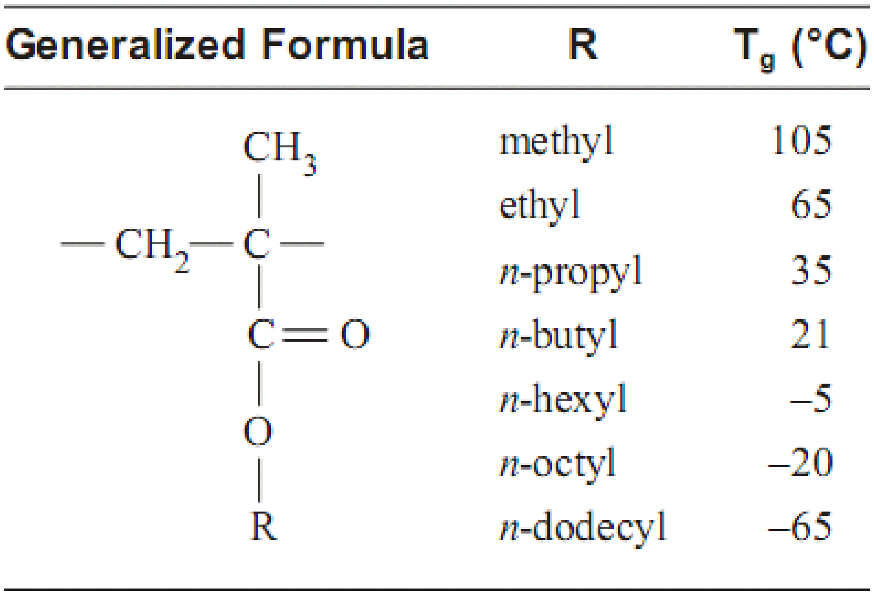
Chain Flexibility

Polymer	Repeat Unit	T_g(°C)
Polyethylene	$-CH_2-CH_2-$	–120
Polypropylene	 $-CH_2-CH(CH_3)-$	–10
Polystyrene		100
Poly(α-methylstyrene)		192
Poly(*o*-methylstyrene)		119

Polymer	Repeat Unit	T_g(°C)
Poly(*m*-methylstyrene)		72
Poly(α-vinyl naphthalene)		135
Poly(vinyl carbazole)		208

- ➢Bulky side groups that are stiff and close to the backbone cause steric hindrance , decrease chain mobility and hence raise T_g

Chain Flexibility

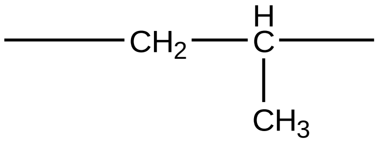
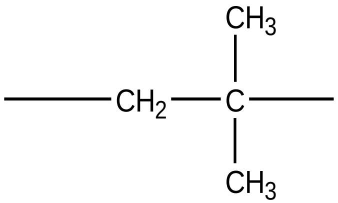
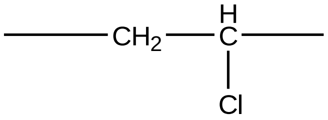
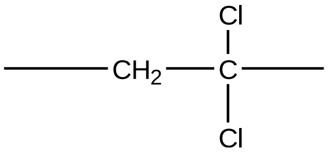


Generalized Formula	R	T_g (°C)
$-CH_2-\overset{CH_3}{\underset{\underset{\underset{R}{\mid}}{\underset{O}{\mid}}}{\underset{C=O}{\mid}}}{\overset{\mid}{C}}-$	methyl	105
	ethyl	65
	n-propyl	35
	n-butyl	21
	n-hexyl	–5
	n-octyl	–20
	n-dodecyl	–65

The influence of the side group in enhancing chain stiffness depends on the flexibility of the group and not its size.
In fact, side groups that are fairly flexible have little effect within each series; instead polymer chains are forced further apart.
This increases the free volume, and consequently T_g drops.

Geometric Factors

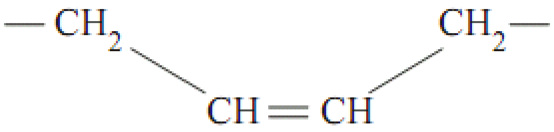
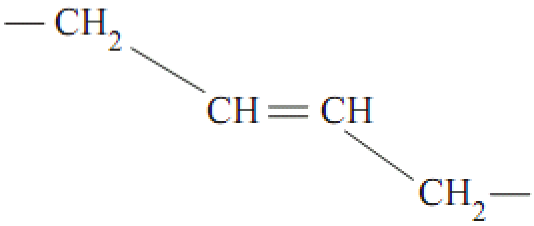
Effect of Symmetry of T_g

Polymer	**Repeat Unit**	**T_g(°C)**
Polypropylene	 $-CH_2-\overset{H}{\underset{CH_3}{C}}-$	–10
Polyisobutylene	 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$	–70
Poly(vinyl chloride)	 $-CH_2-\overset{H}{\underset{Cl}{C}}-$	87
Poly(vinylidene chloride)	 $-CH_2-\overset{Cl}{\underset{Cl}{C}}-$	–17

- ➢Polymers that have symmetrical structure have lower T_g than those with asymmetric structures.
- ➢The additional groups near the backbone can be accommodated in a conformation with a "loose" structure. The increased free volume results in a lower T_g.

Geometric Factors

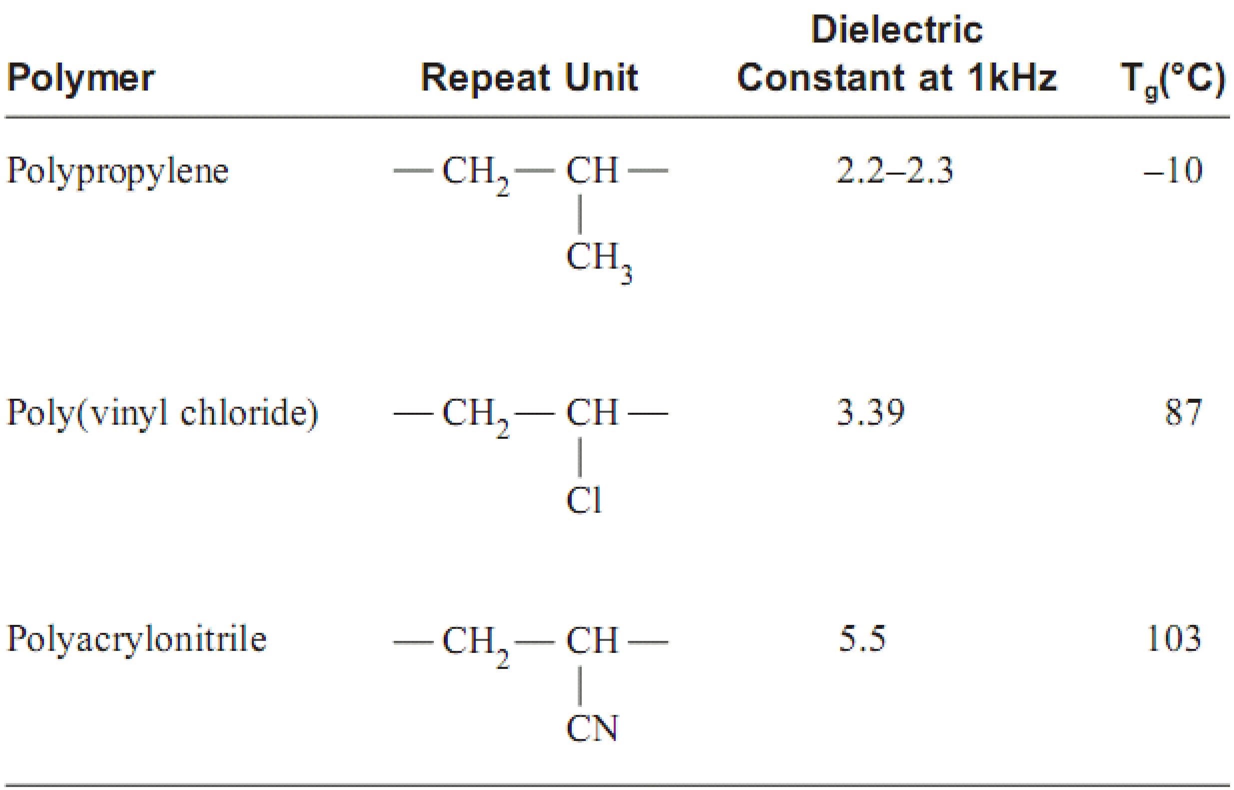
Relative Effects of cis–trans Configuration on T_g

Polymer	**Repeat Unit**	**T_g(°C)**
Poly(1,4-*cis*-butadiene)		–108
Poly(1,4-*trans*-butadiene)		–83

Double bonds in the cis form reduce the energy barrier for rotation of adjacent bonds, “soften” the chain, and hence reduce T_g

Interchain Attractive Forces

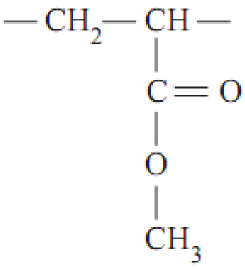
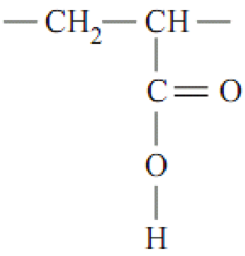
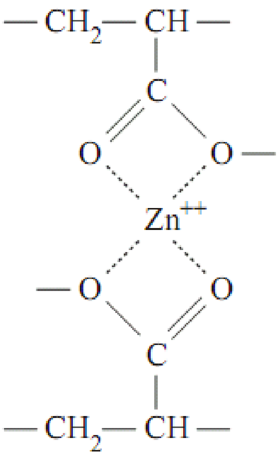
The effect of polarity

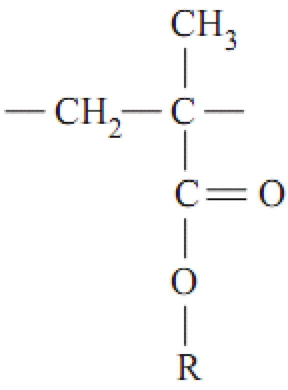


Polymer	Repeat Unit	Dielectric Constant at 1kHz	T_g(°C)
Polypropylene	$-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	2.2–2.3	–10
Poly(vinyl chloride)	$-CH_2-\underset{Cl}{\underset{\vert}{CH}}-$	3.39	87
Polyacrylonitrile	$-CH_2-\underset{CN}{\underset{\vert}{CH}}-$	5.5	103

The steric effects of the pendant group in series (CH_3, Cl, CN) are similar but the polarity increases so T_g increases.

Interchain Attractive Forces

Polymer	**Repeat Value**	**T_g(°C)**
Polymethylacrylate	 $-CH_2-CH(C{=}O-O-CH_3)-$	3
Poly(acrylic acid) Hydrogen Bonding	 $-CH_2-CH(C{=}O-O-H)-$	106
Poly(zinc acrylate) Ionic Bonding		>400

Generalized Formula	**R**	**T_g (°C)**
 $-CH_2-C(CH_3)(C{=}O-O-R)-$	methyl	105
	ethyl	65
	n-propyl	35
	n-butyl	21
	n-hexyl	–5
	n-octyl	–20
	n-dodecyl	–65

- ➢Any structural feature that tends to increase the distance between polymer chains decreases the cohesive energy density and hence reduces T_g.
- ➢In the polyacrylate series shown above, the increased distance between chains due to the size of the alkyl group, R, results in reduced T_g.

Copolymerization

To be able to control the T_g and T_m independent of each other is very difficult, but it is solved to some extent by copolymerization of polyblending.

A copolymer system may be characterized by:

- geometry of the resulting polymer (random, alternating, graft or block)
- The compatibility (miscibility) of two monomer

Isomorphous Systems (Homogeneous Copolymers or Compatible Polyblends

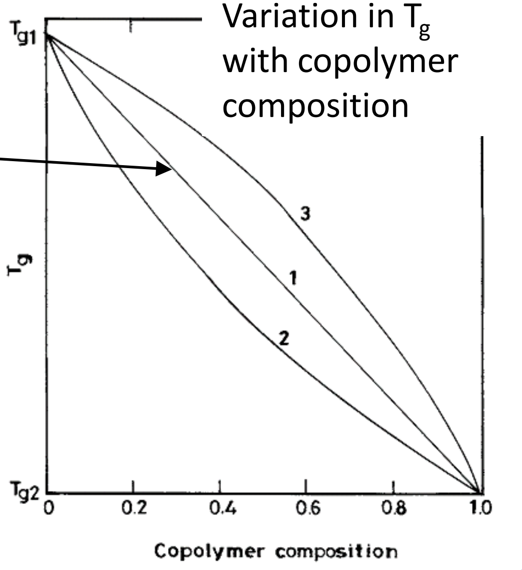
- In isomorphous systems, the component monomers occupy similar volumes and are capable of replacing each other in the crystal system.
- Copolymerization merely shifts the T_g to the position intermediate between those of the two homopolymers; it does not alter the temperature range or the modulus within the transition region

$$T_g = V_1 T_{g1} + V_2 T_{g2} \quad (1)$$

where;

T_{g1} and T_{g2} are T_g of individial homopolymers

V_1 and V_2 are volume fractions of components 1 and 2



Variation in T_g with copolymer composition

Copolymerization

Nonisomorphous Systems In nonisomorphous systems, the specific volumes of the monomers are different. In this case, the geometry of the resulting polymer becomes important.

Random and Alternating: The increased disorder resulting from the random or alternating distribution of monomers enhances the free volume and consequently reduces T_g below that predicted by Equation 1.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (2)$$

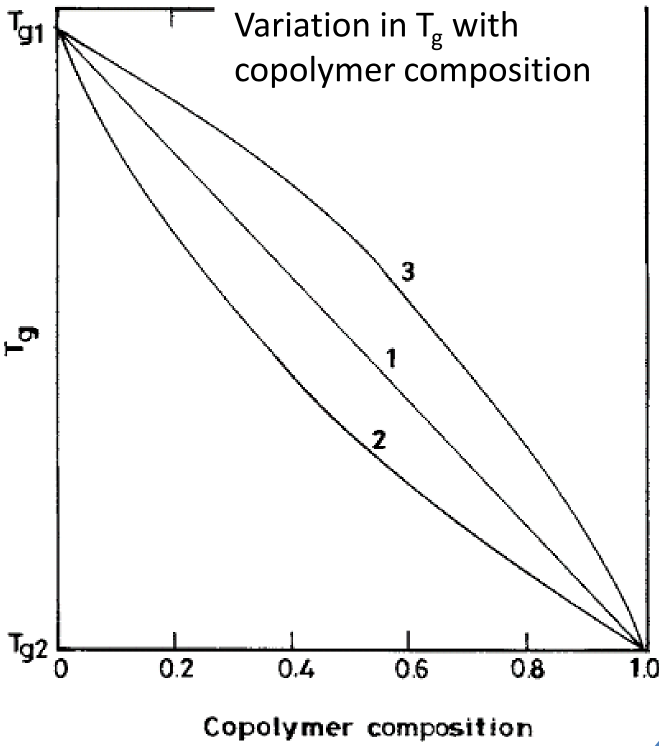
where;

T_{g1} and T_{g2} are T_g of individial homopolymers

W_1 and W_2 are weight fractions of components 1 and 2

Examples of this type are methyl methacrylate–acrylonitrile, styrene–methyl methacrylate, and acrylonitrile–acrylamide copolymers. (Line 2-next graph)

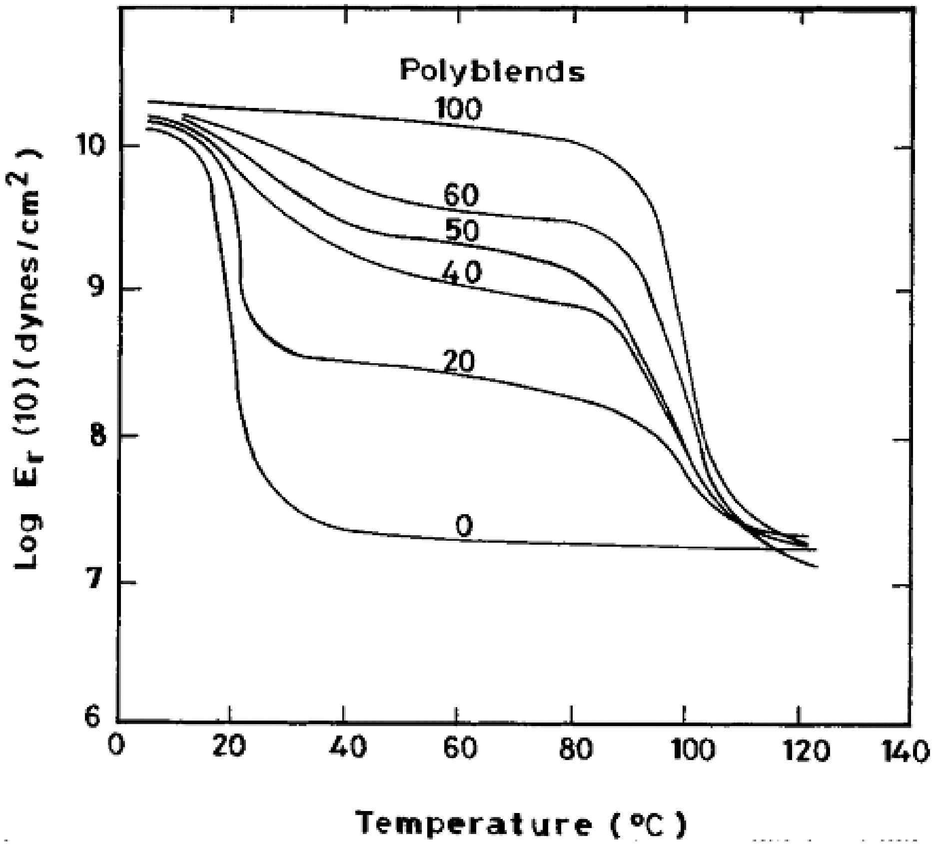
It is also possible that monomers involved in the copolymerization process (as in the copolymers methylacylate–methylmethacrylate and vinylidene chloride–methylacrylate) introduce significant interaction between chains. In this case the T_g will be enhanced relative to the predicted value (line 3 –next graph)



Variation in T_g with copolymer composition

Copolymerization

Block or Graft Copolymers (incompatible Copolymers): For block or graft copolymers in which the component monomers are incompatible, phase separation will occur. Depending on a number of factors — for example, the method of preparation — one phase will be dispersed in a continuous matrix of the other. In this case, two separate glass transition values will be observed, each corresponding to the T_g of the homopolymer.



Polyblends of polystyrene (100) and 30/70 butadiene- styrene copolymer

Molecular Weight

At a given temperature, therefore, chain ends provide a higher free volume for molecular motion. As the number of chain ends increases (which means a decrease in M_n), the available free volume increases, and consequently there is a depression of T_g. The effect is more pronounced at low molecular weight, but as M_n increases, T_g approaches an asymptotic value.

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

$$\text{where } T_g^{\infty} = T_g \text{ of an infinite molecular weight}$$

$$K = \text{a constant}$$

Crosslinking and Branching

Crosslinking involves the formation of intermolecular connections through chemical bonds, and this results in chain mobility and T_g increases.

For lightly crosslinked systems like vulcanized rubber, T_g shows a moderate increase over the un crosslinked polymer.

For the highly crosslinked systems like phenolics and epoxy resins, the T_g is virtually infinite.

Like long and flexible side chains, branching increases the separation between chains , enhances free volume and decreases T_g

Cristallinity

In semicrystalline polymers, the crystallites may be regarded as the physical cross-links that to reinforce or stiffen the chain. So T_g will increase with increasing crystallinity.

$$\frac{T_g}{T_m} = \left\{ \begin{matrix} 1/2 \text{ for symmetrical polymers} \\ 2/3 \text{ for unsymmetrical polymers} \end{matrix} \right\}$$

where T_g and T_m are in degrees Kelvin

Plasticization

Plasticity is the ability of material to undergo plastic or permanent deformation.

Plasticity is the process of inducing plastic flow in a material. In polymers, this can be achieve by addition of low molecular weight organic compounds (plasticizers).

Plasticizers are nonpolymeric, organic liquids of high boiling points. They are miscible with the polymer, and should remain in the polymer. (Very low T_g between -50 °C and -160 °C)

Addition of a small amount of plasticizer drastically reduces the T_g of polymer.

Effect of plasticizer in reducing T_g

- Plasticizers function through a solvating action by increasing intermolecular distance, thereby decreasing intermolecular bonding forces.
- The addition of plasticizers results in a rapid increase in chain ends and hence an increase in free volume.
- A plasticized system may also be considered as a polyblend, with the plasticizer acting as the second component

Crystalline Melting Point

Melting represents a true first order thermodynamic transition characterized by the discontinuities in the primary thermodynamic values (heat capacity, specific volume (density), refractive index and tranparency.

$$\Delta G_m = \Delta H_m - T_m \Delta_m = 0$$

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

$$\text{where } \Delta H_m = \text{enthalpy change during melting}$$

$$\Delta S_m = \text{entropy change during melting}$$

Factors that determine crystallization tendency;

- Structural regularity
- Chain Flexibility
- Intermolecular Bonding

Melting in crystalline polymeric systems.

- The macromolecular nature of polymers and the existence of molecular weight distribution (polydispersity) lead to a broadening of T_m.
- The process of crystallization in polymers involves chain folding. This creates inherent defects in theresulting crystal. Consequently, the actual melting point is lower than the ideal thermodynamic melting point.
- Because of the macromolecular nature of polymers and the conformational changes associated with melting, the process of melting in polymer is more rate sensitive than that in simple molecules.
- No polymer is 100% crystalline.

Factors Affecting The Crystalline Melting Point T_m

Pesudoequilibrium process

$$T_m = \frac{\Delta H_m}{\Delta S_m}$$

where

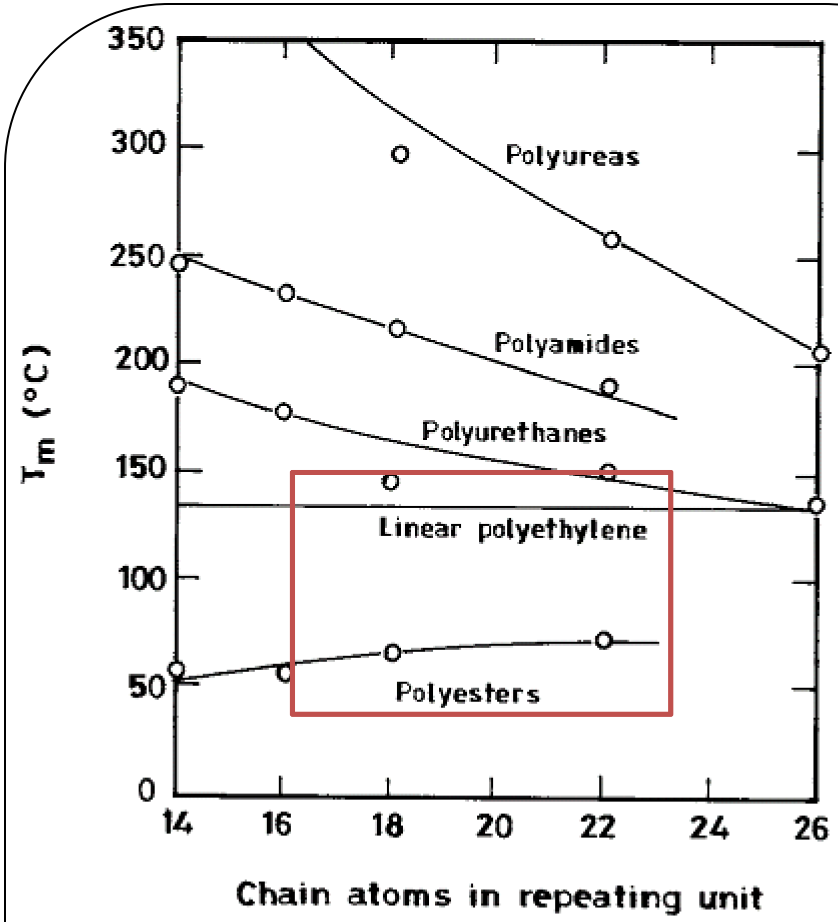
$\Delta \mathrm{H}_\mathrm{m}$ = the difference in the cohesive energies between chains in the crystalline and liquid states

$\Delta \mathrm{S}_\mathrm{m}$ = difference in degree of order between molecules in the two states

ΔH_m is independent of molecular weight. Polar groups on the chain would enhance the magnitude of ΔH_m

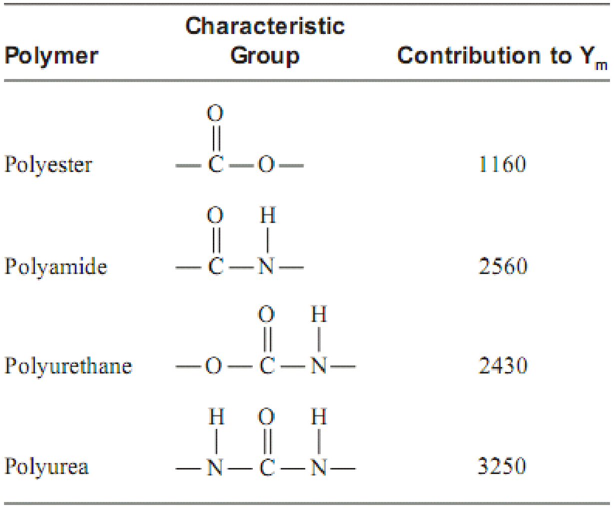
ΔS_m depends not only molecular weight, but also on structural factors like chain stiffness. Chains that are flexible in the molten state (large number of conformations than stiff chains) result in a large ΔS_m

Intermolecular Bonding-1



Trend of crystalline melting point in homologous series of aliphatic polymers.

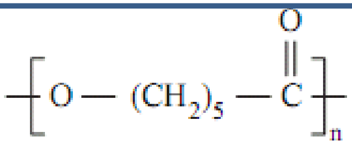
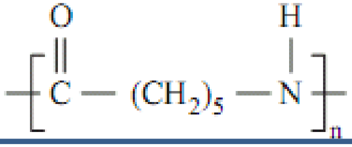
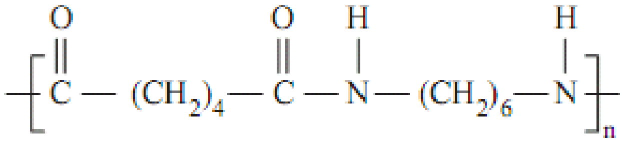
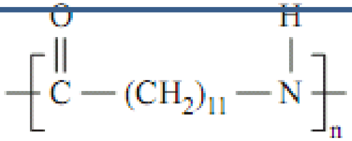
- ➢The melting points approach that of polyethylene as the spacing between polar groups increases.
- ➢For the same number of chain atoms in the repeat unit, polyureas, polyamides, and polyurethanes have higher melting points than polyethylene, while polyesters have lower.



Polymer	Characteristic Group	Contribution to Y_m
Polyester	$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$	1160
Polyamide	$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\|}}{N}-$	2560
Polyurethane	$-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\|}}{N}-$	2430
Polyurea	$-\overset{\overset{\displaystyle H}{\|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\|}}{N}-$	3250

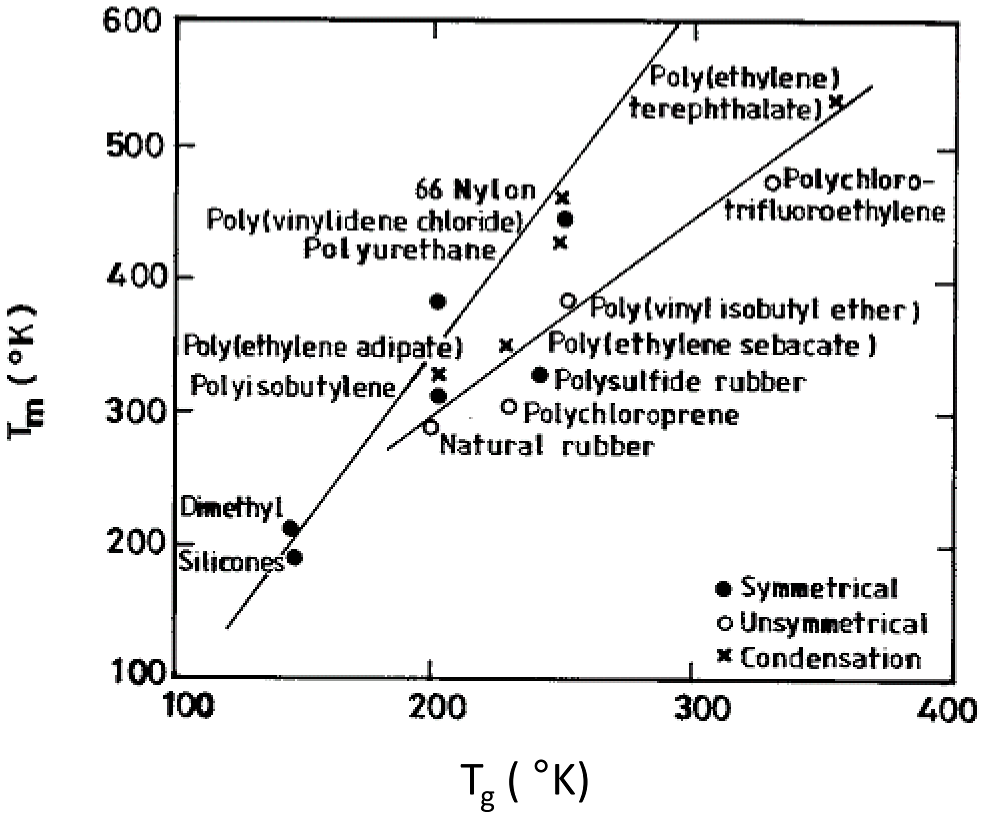
Y_m =molar melt transition function

Intermolecular Bonding-2

Polymer	**Characteristic Group**	**Melting Temperature (T_m)(°C)**
Polycaprolactone	 $\left[O-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C} \right]_n$	61
Polycaprolactam (nylon 6)	 $\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_5-\overset{\overset{\displaystyle H}{\vert}}{N} \right]_n$	226
Poly(hexamethylene adipamide) (nylon 6,6)	 $\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{\vert}}{N}-(CH_2)_6-\overset{\overset{\displaystyle H}{\vert}}{N} \right]_n$	265
Nylon 12	 $\left[\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_{11}-\overset{\overset{\displaystyle H}{\vert}}{N} \right]_n$	179

- The melting points of the nylons reflect the density of hydrogen forming amide linkages.
- The densities of interunit linkages in polycaprolactone (ester units) and polycaprolactam (amide units) are the same, but the amide units are more polar than the ester units.

Effect of Structure

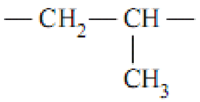
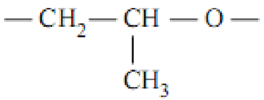
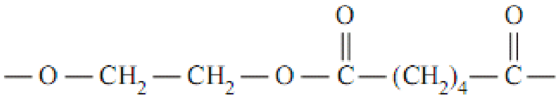
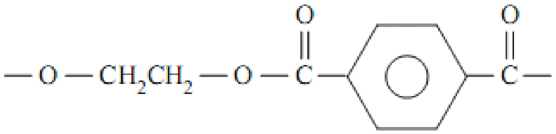


$$\frac{T_g}{T_m} = \left\{ \begin{array}{l} 1/2 \text{ for symmetrical polymers} \\ 2/3 \text{ for unsymmetrical polymers} \end{array} \right\}$$

where T_g and T_m are in degrees Kelvin

Chain Flexibility

- Polymers with rigid chains would be expected to have higher melting points than those with flexible molecules
- On melting, polymers with stiff backbones have lower conformational entropy changes than those with flexible backbones.
- Chain flexibility is enhanced by the presence of such groups as –O– and –(COO)– and by increasing the length of $(-CH_2-)$ units in the main chain.
- Insertion of polar groups and rings restricts the rotation of the backbone and consequently reduces conformational changes of the backbone

Polymer	**Repeat Unit**	**T_m(°C)**
Polyethylene	$-CH_2-CH_2-$	135
Polypropylene	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-$	165
Polyethylene oxide	$-CH_2-CH_2-O-$	66
Poly(propylene oxide)	 $-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-O-$	75
Poly(ethylene adipate)	 $-O-CH_2-CH_2-O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-$	50
Poly(ethylene terephthalate)		265

Copolymerization

The effect of colpolymerization on T_m depends on the value of compatibility of conmonomers.

- If the comonomers have similar specific volumes, they can replace each other in the crystal lattice (isomorphous systems), and T_m will vary smoothly over the entire composition range.
- If the copolymer is made from monomers each of which forms a crystalline homopolymer, the degree of crystallinity and the crystalline melting point decreases as the second constituent is added to either of the homopolymers.

The T_m of the copolymer (in the second case);

$$\frac{1}{T_m} = \frac{1}{T_m^{\circ}} - \frac{R}{\Delta H_m} \ln X$$

$$where;$$

$$\Delta \mathrm{H_m} = heat\ \text{heat of fusion}$$

$$\mathrm{X} = \text{mole fraction of the homopolymer or crystallizing (major) component}$$

Block and graft copolymers with sufficiently long homopolymer chain sequences crystallize and exhibit properties of both homopolymers and have two melting points, one for each type of chain segment.