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$\left.\begin{array}{l}\Delta H_{mix} = 0 \\ \Delta S_{mix} > 0\end{array}\right\}$ $\Delta G = \boxed{\Delta H} - T\Delta S$

Spatial → space

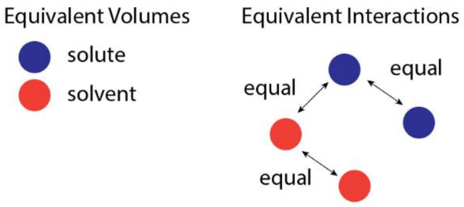
distinguishable spatial arrangement (DSA)

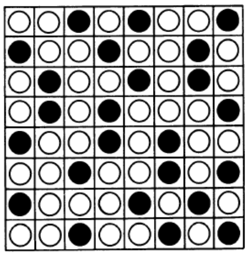
homogeneous

$S = k\ln\Omega$

$S_f = k\ln\Omega_{12}$

$S_i = k\ln\Omega_1 + k\ln\Omega_2$





Ω_1, Ω_2 $\Delta S_{mix} = k[\ln\Omega_{12} - (\ln\Omega_1 + \ln\Omega_2)]$

$\Omega_1 = 1, \Omega_2 = 1$

$\Omega_{12} = \frac{(N_1+N_2)!}{N_1!\,N_2!}$

$\Delta S_{mix} = k\ln\Omega_{12}$

$$\Delta S_{mix} = k\ln\left[\frac{(N_1+N_2)!}{N_1!\,N_2!}\right] = k[\ln(N_1+N_2)! - \ln N_1! - \ln N_2!]$$

Stirling approximation: $\ln N! = N\ln N - N$

$$\Delta S_{mix} = k[(N_1+N_2)\ln(N_1+N_2) - \cancel{(N_1+N_2)} - N_1\ln N_1 + \overset{\checkmark}{\cancel{N_1}} - N_2\ln N_2 + \overset{\checkmark}{\cancel{N_2}}]$$

$$\text{or, } \Delta S_{mix} = k[(N_1+N_2)\ln(N_1+N_2) - N_1\ln N_1 - N_2\ln N_2]$$

$$\text{or, } \Delta S_{mix} = -k[-N_1\overset{\checkmark}{\ln}(N_1+N_2) - N_2\overset{w}{\ln}(N_1+N_2) + N_1\overset{\checkmark}{\ln} N_1 + N_2\overset{w}{\ln} N_2]$$

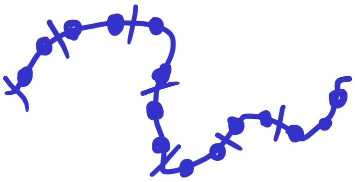
$$\text{or, } \Delta S_{mix} = -k\left[N_1\ln\left(\frac{N_1}{N_1+N_2}\right) + N_2\ln\left(\frac{N_2}{N_1+N_2}\right)\right]$$

$$\Delta S_{mix} = -R\sum_i n_i\ln x_i$$

$n_1 = N_1/N_A$, $n_2 = N_2/N_A$ $\frac{n_1}{n_1+n_2} = x_1$, $\frac{n_2}{n_1+n_2} = x_2$

$$\therefore \Delta S_{mix} = -R[n_1\ln x_1 + n_2\ln x_2]$$

$$\Delta G_{mix} = RT[n_1\ln x_1 + n_2\ln x_2]$$



Flory-Huggins theory

Segments in the polymer chain

no. of segments = x

x defines the size of the polymer molecule.

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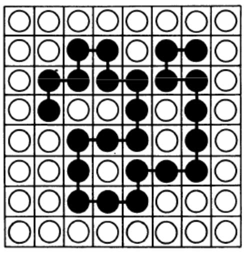
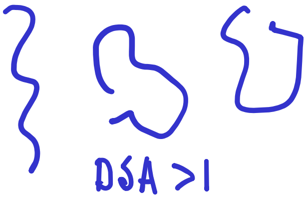


* each lattice cell is either occupied by a solvent molecule or a chain segment.

* each polymer molecule is a continuous series of segments.



DSA > 1

$\therefore \Omega_2 > 1$

$$\Delta S_{mix} = k[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)]$$

$$\Omega_1 = 1$$

$$\Delta S_{mix} = k \ln(\Omega_{12}/\Omega_2)$$

$$\Delta S_{mix} = -k[N_1 \ln \phi_1 + N_2 \ln \phi_2]$$

$$\phi_1 = \text{vol. fraction of solvent} = \frac{N_1}{N_1 + xN_2}$$

$$\phi_2 = \text{'' '' '' solute} = \frac{N_2}{N_1 + xN_2}$$

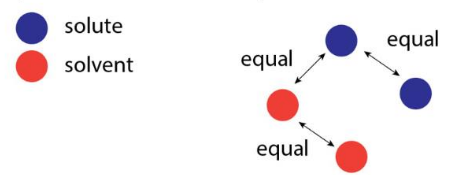
Thermodynamics and Mixing in Polymer Solutions

Now that we have an idea of the various conformations that a polymer may assume in solution, let's consider the thermodynamics of that mixing process. Will the polymer actually dissolve in the solvent? How do the solvent-polymer interactions affect the chain conformations? What about polymer-polymer interactions? We begin to think about the thermodynamics of polymers in solution by starting with a far simpler solution, an ideal solution. This is a simplistic way of thinking of a solution, in which we mix a solute and solvent, but every molecule of solvent and solute is exactly the same in terms of size and intermolecular interactions. This is of course very idealistic and not representative of real solutions, but it's a good place to start in terms of building a framework for thinking about enthalpy and entropy of mixing. From the basic concepts of thermodynamics, for an ideal solution, $\Delta H_{mix} = 0$ (athermal mixing), since all intermolecular interactions are equivalent.

Entropy is a measure of disorder. If we go from two pure substances (solvent and solute) and mix them together, there will be more disorder as now we have to account for all of the different arrangements of the solvent and solute in space.

∴ For an ideal solution, $\Delta S_{mix} > 0$.

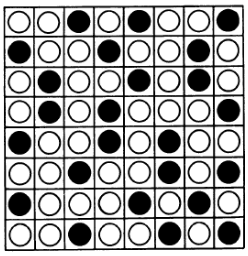
If $\Delta H_{mix} = 0$ and $\Delta S_{mix} > 0$, then by using $\Delta G = \Delta H - T\Delta S$, we know ΔG must be negative and mixing for an ideal solution will always be spontaneous ($\Delta G_{mix} < 0$). So, we know that entropy increases in an ideal solution and this is what drives the spontaneous mixing. But what is the entropy exactly?



How many different **distinguishable arrangements** of the solvent and solute molecules in the array can there be? Note that, ΔS_{mix} depends only upon the combinatorial (or configurational) entropy change which is positive because the number of distinguishable spatial arrangements (DSA) of the molecules increases when they are mixed. From statistical mechanics, entropy, S, is related to the total number Ω of distinguishable degenerate arrangements of the molecules, through the Boltzmann equation,

$$S = k \ln \Omega$$

where k is the Boltzmann constant.



Application of $S = k \ln \Omega$ to the formation of an ideal solution gives

$$\Delta S_{mix} = k[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)]$$

where, $\Omega_1 =$ the total number of DSA in the pure solvent, $\Omega_2 =$ the total number of DSA in the pure solute, and $\Omega_{12} =$ the total number of DSA in the ideal mixture. All the molecules of a pure substance are identical. Since all the molecules of a pure substance are identical, there is only one DSA of them, so that, $\Omega_1 = 1$ and $\Omega_2 = 1$.

$$\therefore \Delta S_{mix} = k \ln \Omega_{12}$$

For ideal mixing of N_1 molecules of solvent with N_2 molecules of solute in a lattice with $(N_1 + N_2)$ cells, the total number of DSA of the molecules is equal to the number of permutations of $(N_1 + N_2)$ objects which fall into two classes containing N_1 identical objects of type 1 and N_2 identical objects of type 2 respectively, that is,

$$\Omega_{12} = \frac{(N_1 + N_2)!}{N_1!\,N_2!}$$

Therefore,

$$\Delta S_{mix} = k \ln \left[\frac{(N_1 + N_2)!}{N_1!\,N_2!}\right]$$

Using Stirling's approximation, $\ln N! = N \ln N - N$, and upon some rearrangement of the above equation we get,

$$\Delta S_{mix} = k[(N_1 + N_2)\ln(N_1 + N_2) - (N_1 + N_2) - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2]$$
$$\text{or, } \Delta S_{mix} = k[(N_1 + N_2)\ln(N_1 + N_2) - (N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2 + (N_1 + N_2)]$$
$$\text{or, } \Delta S_{mix} = k[(N_1 + N_2)\ln(N_1 + N_2) - N_1 \ln N_1 - N_2 \ln N_2]$$
$$\text{or, } \Delta S_{mix} = -k[-N_1 \ln(N_1 + N_2) - N_2 \ln(N_1 + N_2) + N_1 \ln N_1 + N_2 \ln N_2]$$
$$\therefore \Delta S_{mix} = -k\left[N_1 \ln\left(\frac{N_1}{N_1 + N_2}\right) + N_2 \ln\left(\frac{N_2}{N_1 + N_2}\right)\right]$$

Rewriting the above in terms of the numbers of moles, n, and the mole fractions, X,

$$n_1 = N_1/N_A\,,\ n_2 = N_2/N_A\,,\ X_1 = n_1/(n_1 + n_2)\,, X_2 = n_2/(n_1 + n_2)$$

we have,

$$\Delta S_{mix} = -R[n_1 \ln X_1 + n_2 \ln X_2]$$

Therefore,

$$\Delta G_{mix} = RT[n_1 \ln X_1 + n_2 \ln X_2]$$

This important equation provides the fundamental basis from which standard thermodynamic relationships for ideal solutions can be derived (e.g. Raoult's Law). However, since relatively few solutions behave ideally, the simple lattice theory requires modification to make it more generally applicable. For mixtures of small molecules, the non-ideal nature invariably is due to non athermal mixing ($\Delta H_{mix} \neq 0$) and so requires the effects of non-equivalent intermolecular interactions to be taken into account. Polymer solutions show major deviations from ideal solution behaviour, even when $\Delta H_{mix} = 0$. For example, the vapor pressure of solvent above a polymer solution invariably is very much lower than predicted from Raoult's Law.

The failure of the simple lattice theory to give realistic predictions of the thermodynamic properties of polymer solutions arises from

- the assumption that the solvent and solute molecules are identical in size, which is especially wrong in the case of polymer solutions because polymers are very large compared to solvent, and

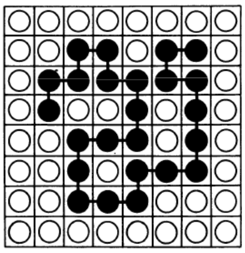
- intermolecular interactions do occur, and they are usually different between solvent-solvent, solute-solute, and solute-solvent.

After all, what if we choose a "bad" solvent for the polymer, like trying to dissolve polyethylene (a hydrophobic polymer) in water? Well, we know that won't work. So, the intermolecular interactions are definitely important in determining whether two components will mix! Paul Flory and Maurice Huggins independently proposed a modified lattice theory which takes account of

- the large differences in size between solvent and polymer molecules, and
- intermolecular interactions.

Flory-Huggins' theory

Attempts to describe the thermodynamics of polymer solutions in a more accurate way than ideal solution theory. How can we account for the fact that polymers are very large in comparison to the size of the solvent? We are going to imagine that a polymer has a bunch of segments (say x in number), where each segment is the size of the solute. The number, x, of segments in the chain defines the size of a polymer molecule. This is given by the ratio of the molecular volumes of polymer and solvent (hence x is not necessarily equal to the degree of polymerization). The theory sets out to predict ΔG_{mix} for the formation of polymer solutions by considering the polymer molecules to be chains of segments, each segment being equal in size to a solvent molecule. On this basis it is possible to think of a (three-dimensional) lattice (which we represent in two dimensions) as before.



On this basis it is possible to place solvent molecules and/or polymer molecules in a 3D lattice consisting of identical cells, each of which is the same size as a solvent molecule and has z cells as first neighbors.

- Each lattice cell is occupied by either a solvent molecule or a chain segment.
- Each polymer molecule is placed in the lattice so that its chain segments occupy a continuous sequence of x cells

We first derive an expression for the ΔS_{mix} when $\Delta H_{mix} = 0$. Just like the mixing of simple compounds, this too involves the application of

$$\Delta S_{mix} = k[\ln \Omega_{12} - (\ln \Omega_1 + \ln \Omega_2)]$$

However, in this case the total number of DSA in the pure solute, $\Omega_2 > 1$, because each molecule in a pure amorphous polymer can adopt many different conformations.

∴ For polymer solutions, $\Delta S_{mix} = k\ln(\Omega_{12}/\Omega_2)$. We will skip the computation of the quantities Ω_{12} and Ω_2. For a system of polymers, therefore,

$$\Delta S_{mix} = -k[N_1 \ln \phi_1 + N_2 \ln \phi_2]$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer respectively, and are given by

$$\phi_1 = N_1/(N_1 + xN_2) \quad \text{and} \quad \phi_2 = N_2/(N_1 + xN_2)$$

In terms of the number of moles, n_1 and n_2, of solvent and polymer in the mixture,

$$\Delta S_{mix}^{Flory-Huggins} = -R[n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

which may be compared to the corresponding expression for ideal mixing,

$$\Delta S_{mix}^{ideal} = -R[n_1 \ln X_1 + n_2 \ln X_2]$$

Thus, the only difference is that for polymer solutions, the mole fractions are replaced by the corresponding volume fractions. The equation for $\Delta S_{mix}^{Flory-Huggins}$ in fact a more general expression for athermal mixing and reduces to the equation for ΔS_{mix}^{ideal} when $x = 1$.

BASICS OF POLYMER CHEMISTRY
(UG SEMESTER-V & DSE-4T UG SEMESTER-VI)

PG SEMESTER-IV 2023-2024 (PHYSICAL CHEMISTRY SPECIALIZATION) / CEM 403 / UNIT-3

GOOGLE MEET LINK: https://meet.google.com/beq-bejw-vqz (CLASS-13, 29/05/2024)

GENERAL INTRODUCTION

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from Greek words, poly= many and mers= parts or units of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words, polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as **polymerization**. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

Polymers have existed in natural form since life began and those such as DNA, RNA, proteins and polysaccharides play crucial roles in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials and other requirements. However, the origin of today's polymer industry is commonly accepted as being the nineteenth century when important discoveries were made concerning the modification of certain natural polymers. In eighteenth century, Thomas Hancock gave an idea of modification of natural rubber through blending with certain additives. Later on, Charles Goodyear improved the properties of natural rubber through vulcanization process with sulfur. The Bakelite was the first synthetic polymer produced in 1909 and was soon followed by the synthetic fiber, rayon, which was developed in 1911. The systematic study of polymer science started only about a century back with the pioneering work of Herman Staudinger. Staudinger has given a new definition of polymer. He in 1919 first published this concept that **high molecular mass compounds were composed of long covalently bonded molecules**.

CLASSIFICATION OF POLYMERS

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymers can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymers can be classified in different ways, which are summarized in the following table, whereas, important and broad classification of polymers are described in the discussion to follow.

Sl.	Basis of Classification	Polymer Type
1.	Origin	Natural, Semi-synthetic, Synthetic
2.	Thermal response	Thermosetting, Thermoplastic
3.	Mode of formation	Addition, Condensation
4.	Line structure	Linear, Branched, Cross-linked
5.	Application and physical properties	Rubber, Plastic, Fiber
6.	Tacticity	Isotactic, Syndiotactic, Atactic
7.	Crystallinity	Amorphous, Semi-crystalline, Crystalline
8.	Polarity	Polar, Non-polar
9.	Chain	Homo-chain, Hetero-chain

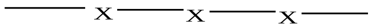
On the basis of their occurrence in nature, polymers have been classified into three types: The polymers which occur in nature are called **natural polymers** (also known as biopolymers). Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc. The **semi-synthetic polymers** are those that are chemically modified natural polymers such as hydrogenated natural rubber, cellulosic, cellulose nitrate, methyl cellulose, etc. The polymers which have been synthesized in the laboratory are known as **synthetic**

polymers. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc.

On the basis of thermal response, polymers can be classified into two groups: The **thermoplastic polymers** are those which can be softened or plasticized repeatedly on application of thermal energy, without much change in properties, if treated with certain precautions. Examples of such polymers are poly-olefins, nylons, linear polyesters and poly-ethers, PVC, sealing wax etc. In contrast, the **thermosetting polymers** are those that undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, phenolic resins, urea, epoxy resins, diene rubbers, etc.

On the basis of mode of formation, polymers can be classified as: The **addition polymers**, which are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene. In contrast to this, the **condensation polymers** are formed from intermolecular reactions between bi-functional or poly-functional monomer molecules having reactive functional groups such as –OH, –COOH, –NH_2, –NCO, etc.

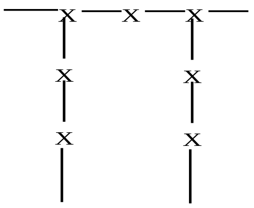
On the basis of structure, polymers are of three types. If the monomer units are joined in a linear fashion, the polymer is said to be a **linear polymer**.



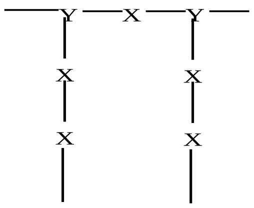
Linear Homo-polymer

Linear Co-polymer

When the monomer units are joined in a branched manner, it is called a **branched polymer**.

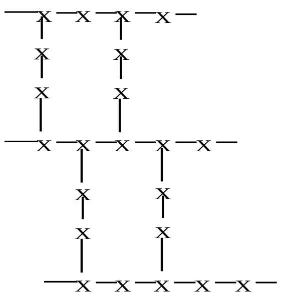


Branched Homo-polymer

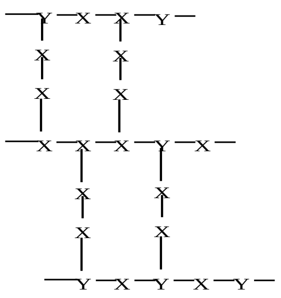


Branched Co-polymer

A polymer is said to be a **cross-linked polymer**, if the monomer units are joined together in a cross-linked manner.



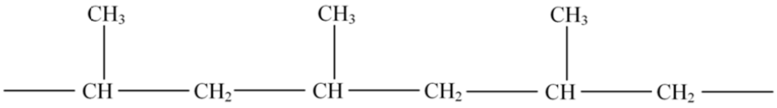
Cross-linked Homo-polymer



Cross-linked Co-polymer

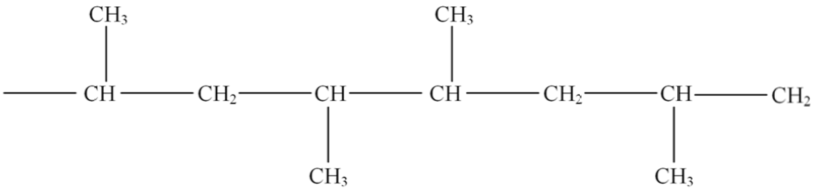
Depending on its ultimate form and use a polymer can be classified as: a **rubber** (or an **elastomer**) which is a high molecular weight polymer with long flexible chains and weak intermolecular forces. They exhibit tensile strength in the range of 300 – 3000 psi (pounds per square inch) and an elongation-at-break 300% – 1000%. Examples are natural and synthetic rubbers. **Plastics** are relatively tough substances with high molecular weights that can be molded with (or without) the application of heat. These are usually much stronger than the rubbers. They exhibit tensile strengths ranging between 40000 – 15000 psi and elongation-at-break ranging usually from 20% – 200%, or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, polystyrene, etc. **Fibers** are long-chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000 – 150,000 psi, are light weight and possess moisture absorption properties.

Tacticity may be defined as the geometric arrangement (or the orientation) of the characteristic group of the monomer unit with respect to the main chain (or the backbone) of the polymer. On the basis of structure, polymers may be classified into three groups: The **isotactic polymers** are those in which the characteristic groups are arranged on the same side of the main chain.



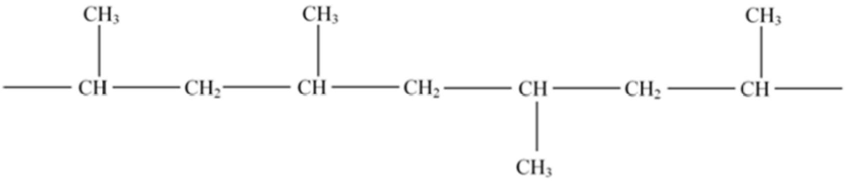
Isotactic polypropylene

A polymer is said to be **syndiotactic** if the side/characteristic groups are arranged in an alternate manner.



Syndiotactic polypropylene

A polymer is said to be **atactic** if the side/characteristic groups are arranged in a random manner around the main chain. Atactic polymers have greater strength and elasticity.



Atactic polypropylene

REACTIONS OF POLYMERS & POLYMERIZATION KINETICS

- **Step growth**: Slow – can use statistical methods and kinetics to describe the molecular weight distributions.
- **Chain polymerization**: Fast – can use statistical methods to analyze the microscopic structure of the products, but not the kinetics of polymerization process and things like molecular weight distributions.

We concentrate upon certain issues:

- How long does it take to make a polymer?
- Can we speed up the reaction?
- What is the relationship between kinetics and the molecular weight of the product?

Assumption (Paul J. Flory): the reactivity of a functional group is independent of the length of the chain to which it is attached.

Example: Dibasic acid + Glycol → Polyester

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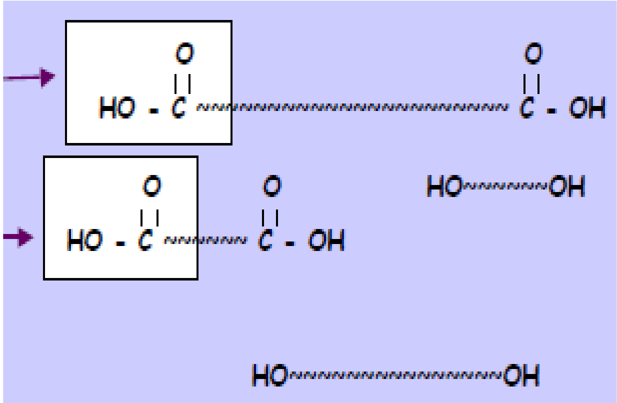
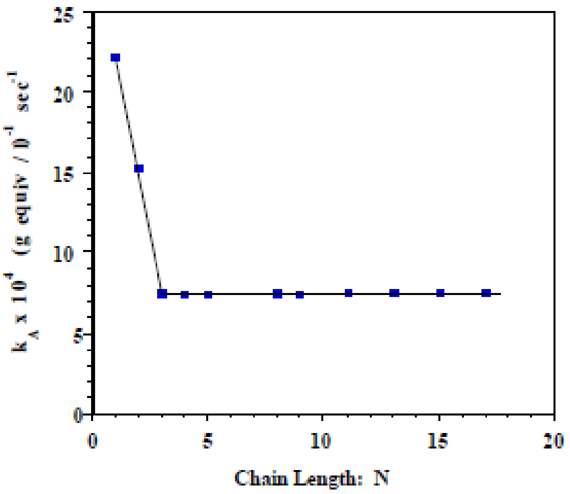


The two groups indicated by arrows react equally readily, irrespective of the chain lengths of the two moieties.



Thus, for the reaction

$$A-A+B-B \rightarrow A-AB-B$$

Kinetic equation for this type of reaction is of the form

$$\text{Rate} = -\frac{d[A]}{dt} = k_2[A][B]$$

$[A]$ and $[B]$ are the concentrations of the functional groups.

Esterification reactions are acid catalyzed, and

(a) In the **absence** of an added strong acid

$$-\frac{d[A]}{dt} = k_3[A]^2[B]$$

If $[A]=[B]=c$, then

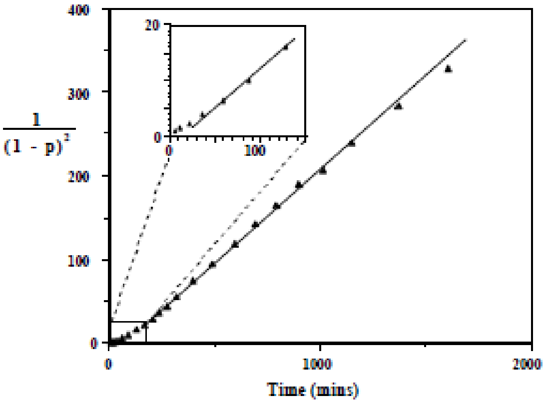
$$-\frac{dc}{dt} = k_3c^3 \Rightarrow -\int_{c_0}^{c}\frac{dc}{c^3} = k_3\int_0^t dt \Rightarrow \left(\frac{1}{c^2}-\frac{1}{c_0^2}\right) = 2k_3t$$

We define the **extent of reaction**, p as

$$p = \frac{\text{No. of} - \text{COOH groups reacted}}{\text{No. of} - \text{COOH groups initially present}}, \text{so that}, c = c_0 - c_0p = c_0(1-p)$$

Substituting the above expression for c in the integrated rate expression (obtained above) and upon some rearrangement, we get

$$\frac{1}{(1-p)^2} = 2c_0^2k_3t + 1$$



The last two graphs have been re-drawn using data from the following sources:

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953, page 71.
2. P. J. Flory, *J. Am. Chem. Soc.*, **61**, 3334 (1939).

(b) In the **presence** of an added strong acid

$$\text{Rate} = -\frac{d[A]}{dt} = k_2'[A][B]$$

k_2' is the pseudo-bimolecular rate constant (includes the concentration term of the strong acid); if $[A]=[B]=c$, then

$$-\frac{dc}{dt} = k_2' c^2 \Rightarrow -\int_{c_0}^{c} \frac{dc}{c^2} = k_2' \int_0^t dt \Rightarrow \left(\frac{1}{c} - \frac{1}{c_0}\right) = k_2' t$$

Hence, with the extent of reaction, p,

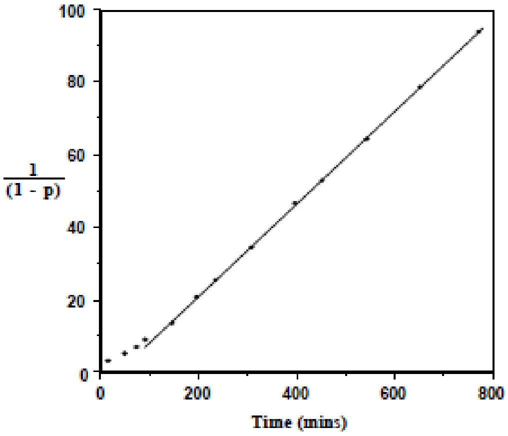
$$\frac{1}{1-p} = c_0 k_2' t + 1$$

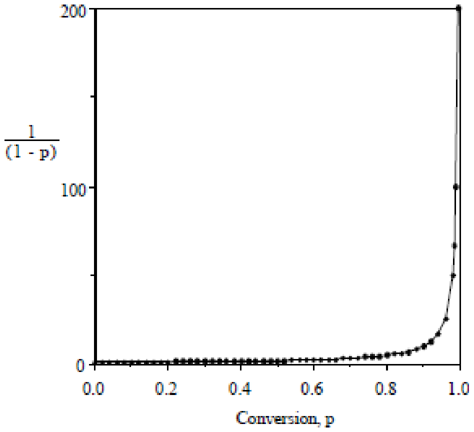
The **number average degree of polymerization**, $\bar{X}_n$, is defined as

$$\bar{X}_n = \frac{N_0}{N} = \frac{c_0}{c} = \frac{c_0}{c_0(1-p)} = \frac{1}{1-p}$$

Hence, the **number average molecular weight** is defined as

$$\bar{M}_n = M_0 \bar{X}_n = \frac{M_0}{1-p}$$





KINETICS OF FREE-RADICAL POLYMERIZATION

Steps: (1) Initiation (via decomposition and addition), (2) Propagation, (3) Termination (via combination and disproportionation) [Note: There can also be a Chain Transfer step between (2) and (3).]

(1) Initiation:

(a) Decomposition: $R_2 \xrightarrow{k_d} 2\dot{R}$

(b) Addition: $\dot{R} + M \xrightarrow{k_a} \dot{M}$

Assuming the decomposition to be the RDS, that is, $k_a \gg k_d$, then

$$-\frac{d[R_2]}{dt} = \frac{1}{2}\frac{d[\dot{M}]}{dt} = k_d[R_2]$$

However, only a fraction f of the radicals initiate chain growth. Therefore,

$$r_{\text{initiation}} = \frac{d[\dot{M}]}{dt} = 2fk_d[R_2]$$

(2) Propagation:

$$\dot{M} + M \xrightarrow{k_p} \dot{M}_2$$
$$\dot{M}_2 + M \xrightarrow{k_p} \dot{M}_3$$
$$\cdots$$

Therefore, in general,

$$\dot{M}_X + M \xrightarrow{k_p} \dot{M}_{X+1}$$
$$\therefore r_{\text{propagation}} = -\frac{d[M]}{dt} = k_p[M][\dot{M}]$$

[Assumption: The reactivity is independent of chain length (Flory); hence, all propagation rate constants, k_p's are equal.]

(3) Termination:

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(a) Combination: $\dot{M}_X + \dot{M}_Y \xrightarrow{k_{tc}} M_{X+Y}$

(b) Disproportionation: $\dot{M}_X + \dot{M}_Y \xrightarrow{k_{td}} M_X + M_Y$

Both combination and disproportionation reactions are of second order; the rate of removal of the chain radicals is equal to the sum of the rates of the two termination reactions.

$$r_{\text{termination}} = -\frac{d[\dot{M}]}{dt} = 2k_t[\dot{M}][\dot{M}] = 2k_t[\dot{M}]^2, \text{where } k_t = k_{tc} + k_{td}$$

Use the steady-state approximation to determine $[\dot{M}]$ (radicals are consumed at the same rate as they are generated, that is, $[\dot{M}]$ is a constant). Hence,

$$r_{\text{initiation}} = r_{\text{termination}} \Rightarrow [\dot{M}] = \left(\frac{fk_d[R_2]}{k_t}\right)^{1/2}$$

We also note that the rate of propagation, $r_{\text{propagation}}$ is equal to the rate of polymerization, $r_{\text{polymerization}}$. Now,

$$r_{\text{propagation}} = -\frac{d[M]}{dt} = k_p[M][\dot{M}] = k_p\left(\frac{fk_d[R_2]}{k_t}\right)^{1/2}[M] = r_{\text{polymerization}}$$

The rate constant of the propagation reaction, k_p, is for most monomers in the range of $10^2 - 10^4$ liters/mole.sec, whereas k_t is in the range of $10^6 – 10^8$ liters/mole.sec, and therefore larger than k_p by a few orders of magnitude. This fact does not prevent the polymerization to take place because the concentration of the radical species is much lower than the concentration of the monomer. Moreover, the rate of polymerization depends only on $1/\sqrt{k_t}$. It is also interesting to note that doubling the rate of initiation does not double the rate of polymerization, rather increases it only by a factor of $\sqrt{2}$. From the last equation one might conclude that the rate of polymerization decreases as long as the polymerization proceeds as a consequence of the decrease of $[M]$. However, exactly the contrary is very often observed. At a certain point the rate of polymerization increases with the conversion, or with the reaction time.

But $[R_2]$ is not a constant, rather,

$$-\frac{d[R_2]}{dt} = k_d[R_2] \Rightarrow [R_2] = [R_2]_0 e^{-k_d t}$$

$$\therefore r_{\text{polymerization}} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][R_2]_0^{1/2}e^{-k_d t/2}$$

Note that $r_{\text{polymerization}}$ increases when $[M]$ or $[R_2]$ or both are increased (changing $[R_2]$, however changes the molecular weight). Also, $r_{\text{polymerization}} \sim k_p/\sqrt{k_t}$.

We define a quantity called conversion, C as

$$C = \frac{[M]_0 - [M]}{[M]_0} = \frac{\text{Amount of monomer used up}}{\text{Amount of monomer at start}}$$

At the initial stages of the reaction ($t \to 0$), $[R_2] = [R_2]_0 = \text{constant}$.

$$\frac{d[M]}{dt} = -k_p[M][\dot{M}] = -k_p\left(\frac{fk_d[R_2]}{k_t}\right)^{1/2}[M] \Rightarrow \frac{d[M]}{[M]} = -k_p\left(\frac{fk_d[R_2]}{k_t}\right)^{1/2}dt$$

$$\therefore \int_{[M]_0}^{[M]}\frac{d[M]}{[M]} = -k_p\left(\frac{fk_d}{k_t}\right)^{1/2}\int_0^t [R_2]^{1/2}dt = -k_p\left(\frac{fk_d}{k_t}\right)^{1/2}\int_0^t [R_2]_0^{1/2}e^{-k_d t/2}dt$$

The integrations lead to

$$\ln\frac{[M]}{[M]_0} = -\frac{2k_p}{k_d}\left(\frac{fk_d[R_2]_0}{k_t}\right)^{1/2}\left(1 - e^{-k_d t/2}\right)$$

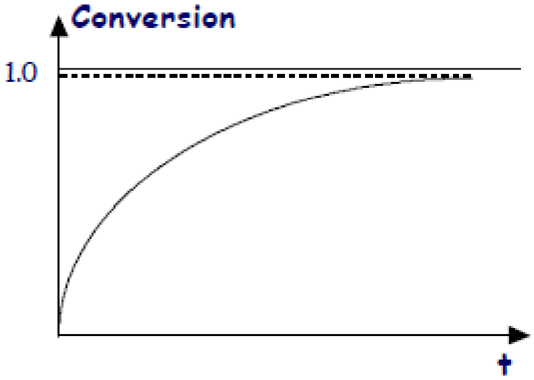
Hence,

$$C = \frac{[M]_0 - [M]}{[M]_0} = 1 - \frac{[M]}{[M]_0} = 1 - \exp\left\{-\frac{2k_p}{k_d}\left(\frac{fk_d[R_2]_0}{k_t}\right)^{1/2}\left(1 - e^{-k_d t/2}\right)\right\}$$

Maximum conversion, $C_{\max}$ is defined as the value of C when $t \to \infty$.

$$\therefore C_{\max} = 1 - \exp\left\{-2k_p\left(\frac{f[R_2]_0}{k_d k_t}\right)^{1/2}\right\}$$

Considering the equation for $r_{\text{polymerization}}$ one might conclude that the rate of polymerization decreases as long as the polymerization proceeds as a consequence of the decrease of $[M]$. However, exactly the contrary is very often observed. At a certain point the rate of polymerization increases with the conversion, or with the reaction time. This is shown qualitatively in the figure above, giving the expected and the actual trends of the increase of the conversion with the reaction time.



This phenomenon is commonly known in the scientific literature as **Trommsdorff effect** or gel effect. The latter term is mostly used in the literature, but it is quite inappropriate because this phenomenon has got nothing to do with the formation of a gel.

MOLECULAR WEIGHT OF POLYMERS

If we think about the molecular weight (MW) of any molecule, we can calculate the same from their molecular formulae. But what about the MW of a polymer? During the polymerization process, the growth of the chain is random in nature and the product contains a mixture of chain of different lengths. Every polymer molecule in a collection has its own formula. As in a polymer, there is a spread/distribution of different polymer molecules of different chain length, hence the MW of the polymer is given as an average MW. Different methods of determination of MW provide different average MW. Regarding the MW of a polymer, we will discuss three types of MW

- Number average MW: $\langle M_n \rangle$
- Weight average MW: $\langle M_w \rangle$
- Viscosity average MW: $\langle M_v \rangle$

The Number Average Molecular Weight, $\langle M_n \rangle$

A polymer solution of known concentration is made by dissolving a weight of amount of polymer in its solvent. The colligative properties of this solution are then determined which counts the number of molecules in a given volume or mass. Each molecule makes an equal contribution to the colligative properties regardless of its weight or mass. Hence this method depends on the number of the molecule present. The MW obtained by colligative property measurement is known as the number average MW and denoted by $\langle M_n \rangle$. If a sample contains N_i molecules of MW M_i, the number average MW is given by

$$\langle M_n \rangle = \frac{\sum_i M_i N_i}{\sum_i N_i}$$

Usually, $\langle M_n \rangle$ is determined by employing any one of the following: osmometry (osmotic pressure measurement), ebulliometry (elevation of b. p. measurement), cryoscopy (depression of freezing point measurement) and end group analysis. A sample of an ordinary chemical compound contains molecules, each of which has the same molecular formula and naturally has the same molecular weight (a monodisperse system). Whereas a polymer sample contains molecules, each of which can have different molecular weights (a polydisperse system).

The Weight Average Molecular Weight, $\langle M_w \rangle$

Certain optical experiments (light scattering experiments) on polymeric systems show that the amplitude of the scattered light is proportional to the polarizability and hence to the mass of the scattering particle.

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∴ The intensity of scattering is proportional to the square of the particle mass. If the solute is polydisperse (as the polymers really are), the heavier molecules contribute more to the scattering as compared to the light ones. From such experiments one can define the weight average MW of a polymer as,

$$\langle M_w \rangle = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

The significance of $\langle M_n \rangle$ and $\langle M_w \rangle$ is noteworthy. The quantity $\langle M_w \rangle$ is always greater than $\langle M_n \rangle$ for a polydisperse system. The ratio $\langle M_w \rangle / \langle M_n \rangle$ is a measure of the polydispersity (often termed as polydispersity index, PDI) of the system. Not all polymers are polydisperse. Natural polymers and synthetic polymers made by anionic polymerization are monodisperse, so that their $PDI = 1$, that is, $\langle M_w \rangle = \langle M_n \rangle$. While $\langle M_w \rangle$ is particularly sensitive to the presence of high MW species, $\langle M_n \rangle$ is influenced more by species at the lower end of the MW distribution.

The Viscosity Average Molecular Weight, $\langle M_v \rangle$

The intrinsic viscosity, $[\eta]$, of a species is related to its molecular weight, M, by equation

$$[\eta] = K' M^a$$

where both K' and a are constants. (Staudinger, 1930, proposed that the reduced viscosity of a polymer is proportional to M). Measurement of intrinsic viscosity of polymer systems leads to the definition of the viscosity average MW as

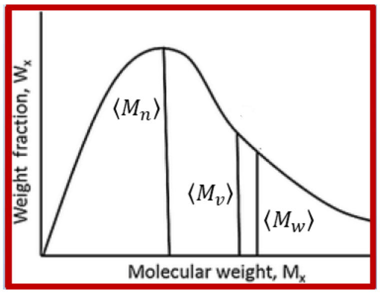
$$\langle M_v \rangle = \left(\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i} \right)^{1/a}, a = \text{constant}$$

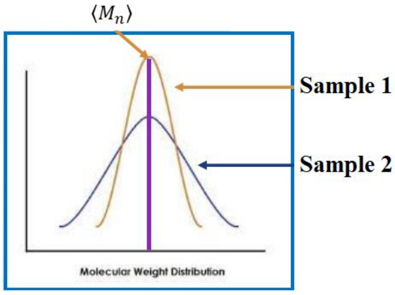
Thus, $\langle M_v \rangle$ depends on a, as well as on the distribution of molecular species. For many polymers, $\langle M_v \rangle$ is $10 - 20\%$ below $\langle M_w \rangle$. For $a = 1$, $\langle M_v \rangle = \langle M_w \rangle$. Let us clarify some of the terms related to the solution viscosity. The intrinsic viscosity, $[\eta]$, is also known as Staudinger index or limiting viscosity index (having a dimension of reciprocal of concentration). For calculating the intrinsic viscosity of a polymer sample in solution we need not know the absolute viscosities of solvent and solution, but only the flow time of constant volume of solvent and the solution through a particular tube. This principle is used in viscometry of molecular weight determination.

Common Name	Recommended Name	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_{rel} = \eta/\eta_0 \approx t/t_0$
Specific viscosity	–	$\eta_{sp} = \eta_{rel} - 1 = (\eta - \eta_0)/\eta_0$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity no.	$\eta_{inh} = (\ln \eta_{rel})/c$
Intrinsic viscosity	Limiting viscosity no.	$[\eta] = (\eta_{sp}/c)_{c=0}$

Molecular Weight Distribution of Polymers

We recall that a sample of ordinary chemical compounds contains molecules, each of which has the same MW (a monodisperse system), whereas a polymer contains molecules, each of which can have different MWs (a polydisperse system). Polydisperse nature of the polymer is the basis of the concept of average MW. To know a polymer property, we must have a knowledge of the both – the average MW and its dispersion pattern. This dispersity with respect to the lowest and to the highest MW homologues is expressed by a simple MW distribution curve.





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Such a curve for a polymer sample is drawn by plotting the number/weight fraction of the molecules having a particular molecular weight against the corresponding MW. Two samples having same $\langle M_n \rangle$, but different polydispersity values. Sample 1 obviously has a narrower dispersion pattern and hence a lower polydispersity than sample 2. Polydispersity gives an idea of the lowest and highest MW species as well as the distribution pattern of the intermediate molecular species.

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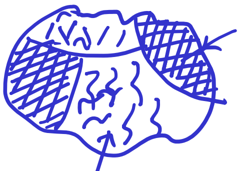
Crystallinity of polymers

$\text{NaCl (molten state)} \xrightarrow[p\uparrow]{T\downarrow} \text{NaCl(s) (FCC)}$

Na^+, Cl^- perfect crystal

$$\begin{tikzcd}
\text{polymer (molten state)} \arrow[rr, "T\downarrow", "p\uparrow"'] \arrow[d] & & \text{polymer(s)} \arrow[dl] \arrow[d] \\
\text{chain entanglement} & \text{crystalline} & \text{amorphous}
\end{tikzcd}$$



degree of crystallinity

v, m : total vol. and mass of the solidified polymer.

v_c, m_c : total vol. and mass of the crystalline portion of the polymer.

v_a, m_a : total vol. and mass of the amorphous portion of the polymer

ρ_c, ρ_a, ρ

$v = v_c + v_a$ or, $v_a = v - v_c$

$m = m_c + m_a$

$\rho v = \rho_c v_c + \rho_a v_a \rightarrow \rho v = \rho_c v_c + \rho_a (v - v_c)$

or, $\rho v = \rho_c v_c + \rho_a v - \rho_a v_c$

or, $\rho = \rho_c \dfrac{v_c}{v} + \rho_a - \rho_a \dfrac{v_c}{v}$

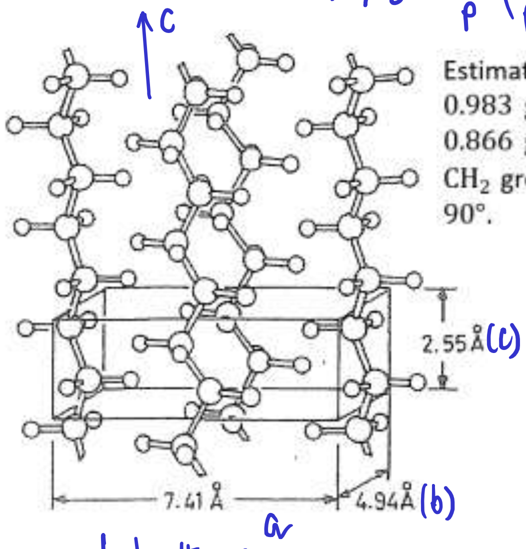
or, $\rho - \rho_a = (\rho_c - \rho_a)\dfrac{v_c}{v}$

or, $\dfrac{v_c}{v} = \dfrac{\rho - \rho_a}{\rho_c - \rho_a}$

$\dfrac{v_c}{v} = \epsilon_c$ = vol. fraction of the crystalline component $= \dfrac{\rho - \rho_a}{\rho_c - \rho_a}$

mass fraction of the crystalline component, $\mu_c = \dfrac{m_c}{m} = \dfrac{\rho_c v_c}{\rho v}$

or, $\mu_c = \dfrac{\rho_c}{\rho}\left(\dfrac{\rho - \rho_a}{\rho_c - \rho_a}\right)$



polyethene

Estimate the fraction of crystalline material in a sample of polyethene of density 0.983 gm/cm^3. Given the density of amorphous polyethene to be 0.866 gm/cm^3. The unit cell dimensions of polyethene crystal (containing four CH$_2$ groups) are $a = 7.41$ Å, $b = 4.94$ Å, c(fibre axis) $= 2.55$ Å; $\alpha = \beta = \gamma = 90°$.

fibre axis = c

vol. of the unit cell $= 7{\cdot}41 \times 4{\cdot}94 \times 2{\cdot}55 \times 10^{-24}\ cm^3$
$= 93{\cdot}34 \times 10^{-24}\ cm^3$

a unit cell of polyethene, contains 4 CH_2 groups.

$\equiv \dfrac{4 \times 14\ gm\ mol^{-1}}{6{\cdot}02 \times 10^{23}\ mol^{-1}} = 9{\cdot}3 \times 10^{-23}\ gm$

$\therefore$ density of the crystalline material, $= \dfrac{9{\cdot}3 \times 10^{-23}\ gm}{93{\cdot}34 \times 10^{-24}\ cm^3} = 0{\cdot}966\ gm\ cm^{-3}$

$\mu_c = \dfrac{\rho_c}{\rho}\left(\dfrac{\rho - \rho_a}{\rho_c - \rho_a}\right)$ = mass fraction

degree of crystallinity ≡ percentage of crystalline material

% of crystallinity $= 100 \times \dfrac{0{\cdot}996}{0{\cdot}983}\left(\dfrac{0{\cdot}983 - 0{\cdot}866}{0{\cdot}996 - 0{\cdot}866}\right) = 91\%$.

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Thermal transitions in polymers

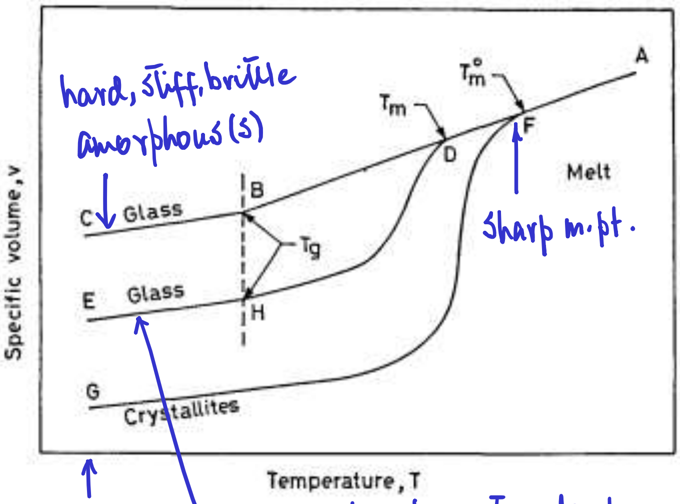
↓

change of state due to the change in the T of the system.

Specific vol. = vol. per unit mass of the substance.

↓

reciprocal of density



hard, stiff, brittle amorphous (s)

Sharp m.pt.

hard, rigid solid

partially crystalline

T_g : glass transition temp.

thermoplastic polymer

↓T↑

Softened, allow the polymer chains to move freely

↓T↑

highly viscous liquid (provided that there is no degradation)

T_m : m.pt. of the crystalline portion

heat deflection temp.

CRYSTALLINE NATURE OF POLYMERS

Polymers crystallized from melt are never completely crystalline. This is because there are extensive chain entanglements in the melt making it impossible for the polymer chains to be fully aligned to form a 100% crystalline polymer during crystallization. The degree of crystallinity is of considerable importance as it influences the properties, and hence the applications, of polymers. The crystalline regions in the polymer have a higher density than the non-crystalline (amorphous) regions and this difference in densities, which is quite large (up to 20%), provides the basis of the density method for the determination of the degree of crystallinity. An expression relating the degree of crystallinity of a semi-crystalline polymer to the sample density and the densities of the crystalline and amorphous components may be derived as follows.

Let v_c, v_a and v be the total volumes of the crystalline, amorphous and the overall specimen, respectively. Say, m_c, m_a and m be the corresponding masses, and ρ_c, ρ_a and ρ be the respective densities. Then,

$$v = v_c + v_a \tag{1}$$

$$m = m_c + m_a \tag{2}$$

$$\Rightarrow \rho v = \rho_c v_c + \rho_a v_a \tag{3}$$

Substituting v_a in Eq. (3) from Eq. (1) and rearranging leads to

$$\epsilon_c = \frac{v_c}{v} = \left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \tag{4}$$

where ϵ_c is the volume fraction of the crystalline components. The mass fraction of the crystalline components, μ_c, is similarly defined as

$$\mu_c = \frac{m_c}{m} = \frac{\rho_c v_c}{\rho v} \tag{5}$$

Combination of Eqs. (4) and (5) then gives

$$\mu_c = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \tag{6}$$

In terms of specific volumes (volume per unit mass, or, the reciprocal of density), $\bar{v}_c$ and $\bar{v}_a$, of the crystalline and amorphous components, respectively, Eq. (6) takes the form

$$\mu_c = \frac{\bar{v}_a - \bar{v}}{\bar{v}_a - \bar{v}_c} \tag{7}$$

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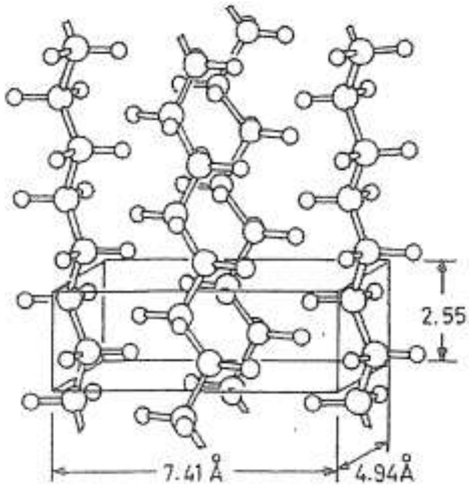
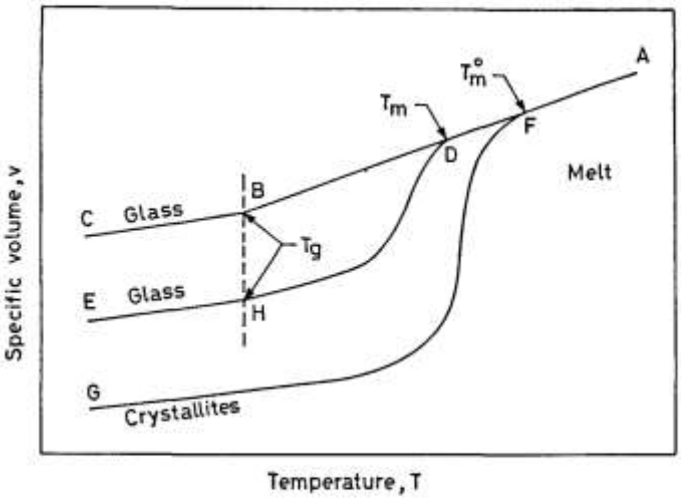
We will use this idea to quantitatively estimate the fraction of crystalline material in a sample of polyethene which has a density of 0.983 gm/cc. The unit cell of semicrystalline polythene is as given below.



Thermal Transitions in Polymers

The term "transition" refers to a change of state induced by changing the temperatures or pressure. Two major thermal transitions are the glass transition and the melting, the respective temperatures being called T_g and T_m.

All polymers are hard rigid solids at sufficiently low temperatures but as the temperature rises a thermoplastic polymer eventually acquires sufficient thermal energy to enable its chains to move freely enough for it to behave like a viscous liquid (assuming there is no degradation). There are several ways in which a polymer can pass from the solid to the liquid phase, depending on the structure of the polymer chains and their arrangement in the sample. The different types of thermal response in this transition from a rigid solid to an eventually liquid state can be illustrated in several ways. One of the simplest and most satisfactory is to trace the change in specific volume, as shown schematically in the figure below.



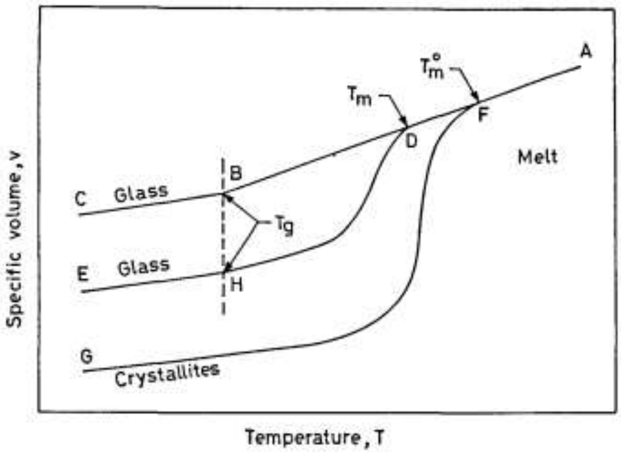
A thermoplastic polymer may be completely amorphous in the solid state, which means that the polymer molecular chains in the specimen are arranged in a totally random fashion. The volume change in amorphous polymers follow the curve ABC. In the region C-B, the polymer is a glassy solid and has the characteristics of glasses, including hardness, stiffness, and brittleness. In the glassy region, the available thermal energy (RT energy units/mol) is insufficient to allow rotation about single bonds in the polymer backbone overcoming intramolecular energy barriers, and movements of large (some 10-50 consecutive chain atoms) segments of the polymer chain cannot take place. But as the sample is heated, it passes through a temperature T_g, called the glass transition temperature, above which it softens and becomes rubberlike. This is an important temperature and marks the onset of extensive molecular motion, which is reflected in marked changes in properties, such as specific volume, refractive index, stiffness, and hardness. Above T_g, the material may be more easily deformed. A continuing increase in temperature along B-A leads to a change of the rubbery polymers to a viscous liquid without any sharp transition. In a perfectly crystalline polymer, all the chains would be contained in regions of three-dimensional order, called crystallites, and no glass transition would be observed, because of the absence of disordered chains in the sample. A perfectly crystalline polymer, on heating, would thus follow curve G-F-A, melting at T_m^0 to become a viscous liquid.

Perfectly crystalline polymers are, however, not encountered in practice and real polymers may instead contain varying proportions of ordered and disordered regions in the sample. These semicrystalline polymers usually exhibit both T_g and T_m (not T_m^0) corresponding to the disordered and ordered regions, respectively, and follow curves similar to E-H-D-A. As T_m^0 is the melting temperature of a perfectly crystalline polymer of high molecular weight, T_m is lower than T_m^0 and more often represents a melting range, because the semicrystalline polymer contains crystallites of various sizes with many defects which act to depress the melting temperature. Both T_g and T_m are important parameters that serve to characterize a given polymer. While T_g sets an upper temperature limit for the use of amorphous thermoplastics like poly(methyl methacrylate) or polystyrene and a lower temperature limit for rubbery behaviour of an elastomer-like SBR rubber or 1,4-cis-polybutadiene, T_m or the onset of the melting range determines the upper service temperature. Between T_m and T_g, semicrystalline polymers tend to behave as a tough and leathery material. As a general rule, however, semicrystalline polymers are used at temperatures between T_g and a practical softening temperature, which lies above T_g and below T_m. The onset of softening is usually measured as the temperature required for a particular polymer to deform a given amount under a specified load. These values are known as *heat deflection temperatures*. Such data do not have any direct relation with T_m, but they are widely used in designing with plastics.

In addition to the main or primary glass transition discussed above, many polymers also exhibit secondary glass transitions. The primary glass transition occurs in the temperature region where long segments of the polymer chain backbone become free to move. The secondary glass transitions occur in the temperature ranges where short sections of the main chain or side chains become free to move or oscillate. Since these groups are small compared to the polymer chain, they require less volume and energy than the longer chain segments for movement. Secondary glass transitions therefore occur at lower temperatures than primary glass transitions. The transitions are sometimes denoted α, β, γ etc., in order of descending temperature, the transition of highest temperature α being called T_g, which thus refers to the primary glass transition.

First- and Second-Order Transitions

In first-order transitions, such as melting, there is a discontinuity at the transition temperature in the volume-temperature plot or the enthalpy-temperature plot as shown below.



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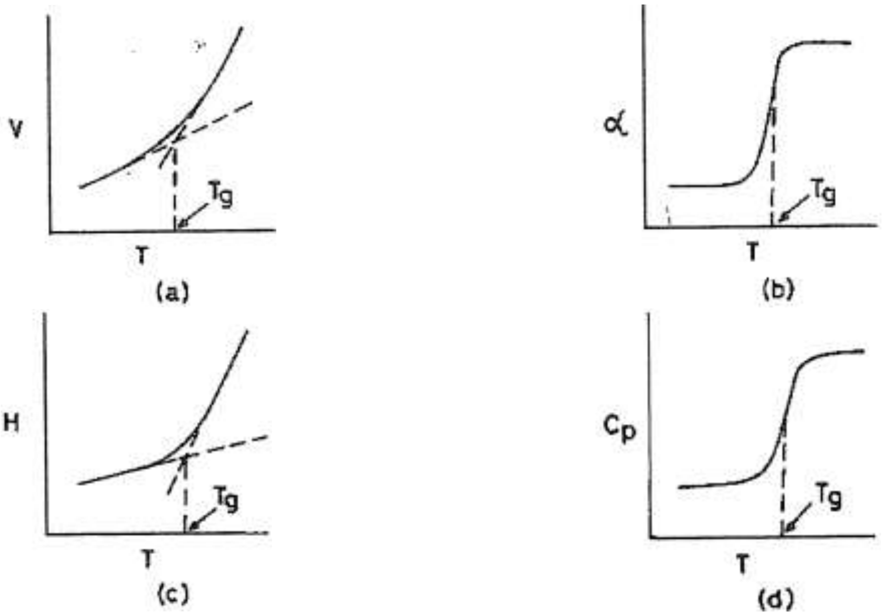
In second-order transitions, only a change in slope occurs and there is a marked change in the first derivatives (or the temperature coefficients), as is shown in the representative graphical representations below.

The glass transition is not a first-order transition, as no discontinuities are observed at T_g when the specific volume or enthalpy of the polymer is measured as a function of temperature. However, the first derivative of the property-temperature curve, that is, the temperature coefficient of the property (for example, C_p and α), exhibits a marked change in the vicinity of T_g; for this reason, it is sometimes called a second-order transition.



Idealized variations in (V) and enthalpy (H) with temperature. Also shown are $\alpha = V^{-1}(\partial V/\partial T)_p$, the volume coefficient of expansion and $C_p = (\partial H/\partial T)_p$, the heat capacity, which are slopes of the corresponding curves.

As T_g marks the onset of molecular motion, a number of factors that affect rotation about links (necessary for movement of polymer chains) will also influence the T_g of a polymer. These include (a) chain flexibility, (b) molecular structure (steric effects), (c) molecular weight, and (d) branching and crosslinking. The flexibility of the chain may be considered to be the most important factor that influences the T_g of a polymer. If the chain is highly flexible, T_g will generally be low and if the chain is rigid, the T_g value will be high. The chain flexibility depends on the rotation or torsion of skeletal bonds. Chains made up of bond sequences which are able to rotate easily are flexible, and hence polymers containing –(–CH_2–CH_2–)–, –(–CH_2–O–CH_2–)–, or –(–Si–O–Si–)– links will have correspondingly low values of T_g. For example, poly-(dimethyl siloxane), which has Si–O bonds in the backbone chain, has one of the lowest T_g values known (-123°C).

Useful generalizations of factors affecting T_m can be derived from the application of macroscopic thermodynamics. At T_m, the free energy change is zero, i.e., $\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$, whence $T_m = \Delta H_m / \Delta S_m$. Thus, a high melting point can be the result of a high value of the enthalpy change ΔH_m and/or a small value of the entropy change ΔS_m in melting. The former corresponds to stronger binding of adjacent but unbonded units in the polymer lattice and thus to higher degree of crystallinity. The factors that affect crystallinity and hence T_m can be classified as symmetry, intermolecular bonding, tacticity, branching, and molecular weight. Chain flexibility has a direct bearing on the melting point. Insertion of groups that stiffen the chain increases T_m, while introducing flexible groups into the chain lowers the value of T_m. Also, if the chain is substantially branched, reducing the packing efficiency, the crystalline content is lowered and hence the melting point. A good example is low-density polyethylene where extensive branching lowers the density and T_m of the polymer.

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While T_m is a first order transition, T_g is a second order transition and this precludes the possibility of a simple relation between them. There is, however, a crude relation between T_m and T_g. Analysis of the T_m and T_g data reveals that the ratio T_g/T_m ranges from 0.5 to 0.75 when the temperatures are expressed in degrees Kelvin. The ratio is closer to 0.5 for symmetrical polymers such as polyethylene and polybutadiene, but closer to 0.75 for unsymmetrical polymers, such as polystyrene and polyisoprene. The difference in these values may be related to the fact that in unsymmetrical chains with repeat units of the type $–(–CH_2–CHX–)–$ an additional restriction to rotation is imposed by steric effects causing T_g to increase, and conversely, an increase in symmetry lowers T_g.

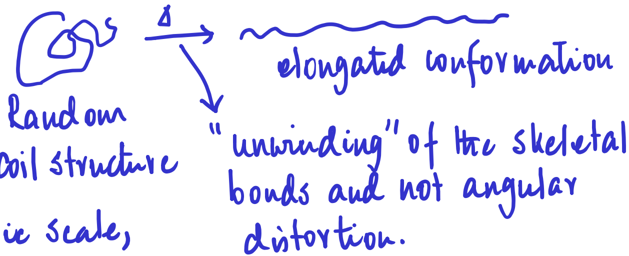
Factors affecting the glass transition temperature, T_g

T_g : a temp. at which molecular motions start.

Rotation about bonds is important: necessary for the movement of polymer

(a) Chain flexibility
(b) molecular structure (steric effect)
(c) molecular wt.
(d) branching and cross-linking

depends more on the rotation/torsion about single bonds and less on the bond angles.



∴ flexibility depends, on a macroscopic scale, on torsional mobility; higher the torsional mobility, lower is the T_g.

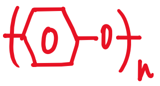
for symmetric polymers, the chemical nature of the backbone is important

$\left(CH_2-CH_2 \right)_n$ $\left(CH_2-O-CH_2 \right)_n$ $\left(Si-O-Si \right)_n$ low values of T_g.

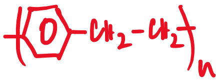
poly(dimethyl siloxane), $T_g = -123°C$ (Si–O bonds have high torsional mobility)

$T_g\uparrow$ when groups are inserted in the chain which stiffen the chain by hindering the rotation, so that more thermal energy is required for rotation

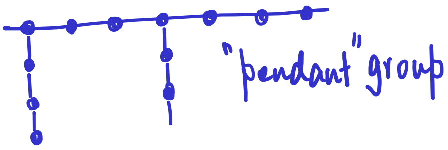
poly(p-phenylene) 

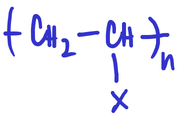

poly(p-phenylene oxide)
$T_g = 83°C$

vs. $\left(CH_2-CH_2-O \right)_n$
poly(ethylene oxide)
$T_g = -67°C$


poly(p-xylene)
$T_g = 280°C$

vs. $\left(CH_2-CH_2 \right)_n$
poly(ethylene)
$T_g = -93°C$



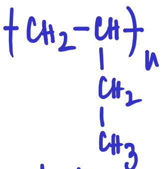


$$\left(CH_2-\underset{X}{CH} \right)_n$$

X = bulky pendant group
Sym → unsym.

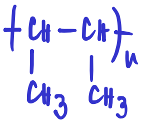
groups X hinder the rotation about the backbone
⇓
$T_g\uparrow$

poly(but-1-ene)
poly(but-2-ene)



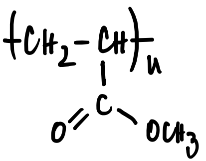
$$\left(CH_2-\underset{\underset{CH_3}{CH_2}}{CH} \right)_n$$

long, bulky side chain $T_g = -24°C$



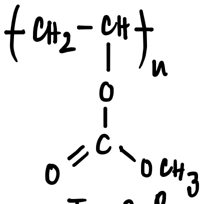
$$\left(\underset{CH_3}{CH}-\underset{CH_3}{CH} \right)_n$$

shorter side groups
$T_g = -73°C$



poly(methyl acrylate)

$T_g = 10^\circ C$



$T_g = 32^\circ C$

Factors affecting T_m

Solid ⇌ liq. T_m at a const. p

at T_m, $\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$

$\therefore\ T_m = \Delta H_m / \Delta S_m$

High T_m is possible

(a) high value of ΔH_m → Stronger binding of adjacent units; higher degree of crystallinity

(b) low value of ΔS_m → if melting does not change the conformational entropy substantially.

(c) both high ΔH_m and low ΔS_m

Factors affecting crystallinity

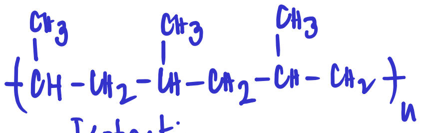
(a) Symmetry

(b) Intermolecular bonding

(c) Tacticity (geometric arrangement/orientation of the characteristic group of the monomer unit w.r.t to the main chain)

(d) Branching

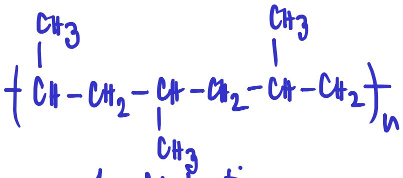
(e) Mol. wt.



$$-\!\!\left[\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\right]_n$$

Isotactic

ΔS_m is small, T_m is high.



$$-\!\!\left[\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2\right]_n$$

Syndiotactic

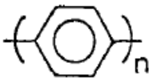
FACTORS AFFECTING T_g

As T_g marks the onset of molecular motion, a number of factors that affec rotation about links (necessary for movement of polymer chains) will als influence the T_g of a polymer. These include (a) chain flexibility, (b molecular structure (steric effects), (c) molecular weight, and (d) branchin and crosslinking.

The flexibility of the chain is undoubtedly the most important facto influencing the T_g of a polymer. The chain flexibility depends more on th rotation or torsion of skeletal bonds than on changes in bond angles. Whe a randomly coiled chain is pulled out into an elongated conformation, th skeletal bonds "unwind" rather than undergo angular distortion (see Fig 2.25). Thus, flexibility on a macroscopic scale depends on *torsional mobilit* at the molecular level. If a highly flexible chain is present, T_g will generall be low and if the chain is rigid, the T_g value will be high.

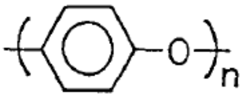
For symmetrical polymers, the chemical nature of the backbone chain i the important factor determining the chain flexibility and hence T_g. Chain made up of bond sequences which are able to rotate easily are flexible, an hence polymers containing –(–CH_2–CH_2–)–, –(–CH_2–O–CH_2–)–, or –(– Si–O–Si–)– links will have correspondingly low values of T_g. For example poly(dimethyl siloxane) has one of the lowest T_g values known (−123°C presumably because the Si–O bonds have considerable torsional mobility.

The value of T_g is raised markedly by the insertion of groups whic stiffen the chain by impeding rotation, so that more thermal energy i required to set the chain in motion. Particularly effective in this respec is the p-phenylene ring. Thus, a chain consisting entirely of p-phenylen rings, namely, poly(p-phenylene) (XVI)

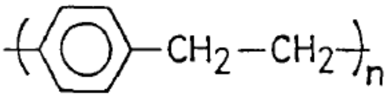


(XVI)

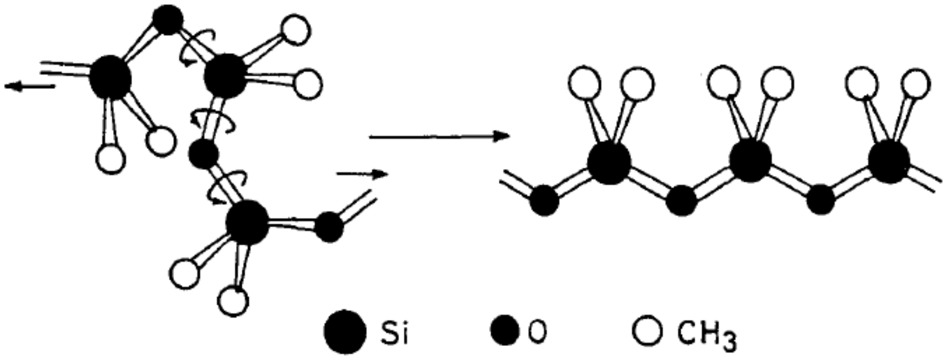
has a highly intractable, rigid structure with no softening point. This structure can be modified by introducing flexible groups in the chain to produce tractable polymers with high values of T_g. Some examples are poly(phenylene oxide) (XVII), T_g = 83°C and poly(p-xylylene) (XVIII), $T_g \simeq$ 280°C as compared to polyethylene, T_g = −93°C and poly(ethylene oxide), T_g = −67°C.



(XVII)



(XVIII)



Problem 2.21 Presence of flexible pendant groups reduces the glass transition of the polymer, whereas bulky or stiff side groups increase it. Why?

Answer:

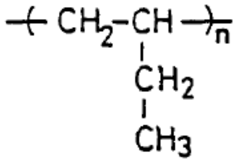
In general, factors that increase the energy required for the onset of molecular motion increase T_g and those that decrease the energy requirement lower T_g. Flexible pendant groups act as "inherent diluents" and lower the frictional interaction between chains reducing the T_g thereby. Bulky or stiff side groups, on the other hand, increase interchain friction and energy requirement for molecular motion, thereby increasing T_g.

Problem 2.22 Account for the differences in glass transition temperatures for the following pairs of isomeric polymers having similar chemical structures:

(a) Poly(but-1-ene) (–24°C) and poly(but-2-ene) (–73°C).
(b) Poly(ethylene oxide) (–41°C) and poly(vinyl alcohol) (85°C).
(c) Poly(methyl acrylate) (10°C) and poly(vinyl acetate) (32°C)
(d) Poly(ethyl acrylate) (–24°C) and poly(methyl methacrylate) (105°C)

Answer:

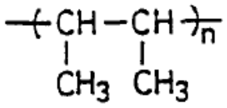
(a)



$-\!\!\left(CH_2-CH(CH_2CH_3)\right)\!\!-_n$

$T_g = -24°C$

The side group is long and bulky; therefore, rotation is difficult.



$-\!\!\left(CH(CH_3)-CH(CH_3)\right)\!\!-_n$

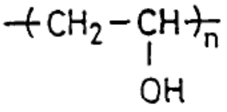
$T_g = -73°C$

The side groups are shorter; therefore rotation is easier.

(b) $-\!\!\left(CH_2-CH_2-O\right)\!\!-_n$

$T_g = -41°C$

The backbone chain is flexible; so rotation is easy.

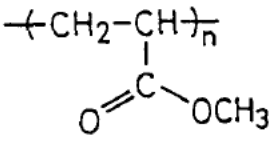


$-\!\!\left(CH_2-CH(OH)\right)\!\!-_n$

$T_g = 85°C$

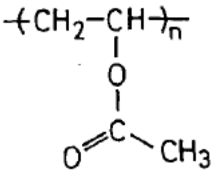
The steric effect of the –OH group restricts rotation. Superimposed on this is the effect of polarity which increases the lateral forces in the bulk state and leads to higher T_g.

(c)



$T_g = 10°C$

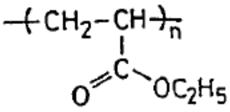
The bulky group hinders rotation causing T_g to increase.



$T_g = 32°C$

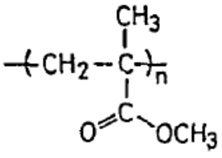
The bulky part of the side group is farther from the chain, making rotation more difficult.

(d)



$T_g = -24\,°\mathrm{C}$

The side group is long but flexible, so rotation is easier.



$T_g = 105\,°\mathrm{C}$

The 1,1-disubstituted side groups make rotation more difficult leading to higher T_g.

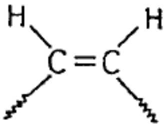
FACTORS AFFECTING T_m

The application of macroscopic thermodynamics leads to some useful generalizations of factors affecting T_m. At T_m, the free energy change is zero, i.e.,

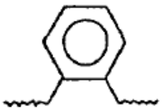
$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0$$

whence $T_m = \Delta H_m / \Delta S_m$. This expression for T_m predicts that a high melting point can be the result of a high value of the enthalpy change ΔH_m and/or a small value of the entropy change ΔS_m in melting. The former corresponds to stronger binding of adjacent but unbonded units in the polymer lattice and thus to higher degree of crystallinity. The factors that affect crystallinity and T_m can be classified as symmetry, intermolecular bonding, tacticity, branching, and molecular weight. These are discussed below. If ΔS_m is small, melting does not result in a large gain of conformational entropy and, to some degree, the structure of the solid must persist in the melt. For example, molecules of isotactic polypropylene crystallize in the form of helices and these are thought to occur in the melt also, thus making ΔS_m small and T_m high.

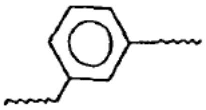
Linear symmetrical molecules such as polyethylene, polytetrafluoroethylene, and other linear molecules with more complex backbones containing -(-O-)-, -(-COO-)-, and -(-CONH-)- groups, such as polyethers, polyesters and polyamides, all possess a suitable symmetry for crystallite formation and usually assume extended zig-zag conformations when aligned in the lattice. On the other hand, chains containing irregular units, which impair the symmetry, reduce the ability of the polymer to crystallize. Thus *cis*-double bonds (**XIX**), *o*-phenylene groups (**XX**) and *m*-phenylene groups (**XXI**) all encourage bending and twisting in the chains and make close-packing very difficult.



(XIX)



(XX)



(XXI)

If, however, the phenylene rings are *para*-oriented, the chains retain their axial symmetry and can crystallize more readily. Similarly, double bonds in *trans* configuration maintain the chain symmetry thus allowing for crystallite formation. This is highlighted by a comparison of the amorphous elastomeric *cis*-polyisoprene ($T_m = 28°\mathrm{C}$) with highly crystalline *trans*-polyisoprene ($T_m = 74°\mathrm{C}$) which is a non-elastomeric rigid polymer, or *cis*-1,4-polybutadiene ($T_m = -11°\mathrm{C}$) with *trans*-1,4-polybutadiene ($T_m = 148°\mathrm{C}$).

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Any interaction between polymer chains in the crystal lattice serves to hold the structure more firmly and raise the melting temperature. In polyethylene, the close packing in crystallites achieved due to high chain symmetry and lack of substituents on the chains allows the van der Waals forces to act cooperatively and provide additional stability to the lattice. In polymers containing polar substituents, e.g., Cl, CN, or OH, the chains can be aligned and held rigidly by the strong dipole-dipole interactions between the substituents. This effect is more obvious in the symmetrical polyamides.

Chain flexibility has a direct bearing on the melting point. Insertion of groups that stiffen the chain increases T_m, while introducing flexible groups into the chain lowers the value of T_m (cf. **Factors Affecting** T_g). Branching in the side group tends to stiffen the chain and raise T_m, as shown in the series poly(but-1-ene) ($T_m = 126°C$), poly(3-methyl but-1-ene) ($T_m = 145°C$), poly(3,3′-dimethyl but-1-ene) ($T_m > 320°C$). However, if the side group is flexible and nonpolar, T_m is lowered. Also, if the chain is substantially branched to reduce the packing efficiency, the crystalline content is lowered and hence the melting point. A good example is low-density polyethylene where extensive branching lowers the density and T_m of the polymer.