M.Sc. IV Semester
Sub - Chemistry
Paper - III (environmental chemistry)

NITROGEN CYCLE

Nitrogen cycle, one of the nature's **most vital dynamic cycle**, operates through ontinuous exchange of N_2 within the ecosystem. The atmospheric nitrogen is converted into ts compounds and the combined nitrogen again passes back to the atmosphere. Nitrogen nd its compounds (*e.g.*, proteins, amino acids, vitamins, nucleic acids, enzymes and lkaloids etc.) are essential for the maintenance of life processes in the biosphere. Today, N tom may be throbbing in the cells of meadow grass, tomarrow it may be pulsating through he tissues of a living animal.

The N atom may rise from decaying animal refuse and stream to the atmosphere where t may be yoked with oxygen in a flash of lightning and return as plant food (NO_3^-) to the oil in a torrent of rain or it may be directly absorbed from the atmosphere by the soil and here rendered available for plant food by the action of symbiotic bacteria. Thus, **each itrogen has undergone a never ceasing cycle of reactions through countless aeons of ime.**

Nitrogen Fixation.

Nitrogen is the main constituent (79%) of the atmosphere but it can not be absorbed lirectly by most forms of life. It must be fixed before it can be utilised by plants and animals. Nitrogen fixation is of two types.

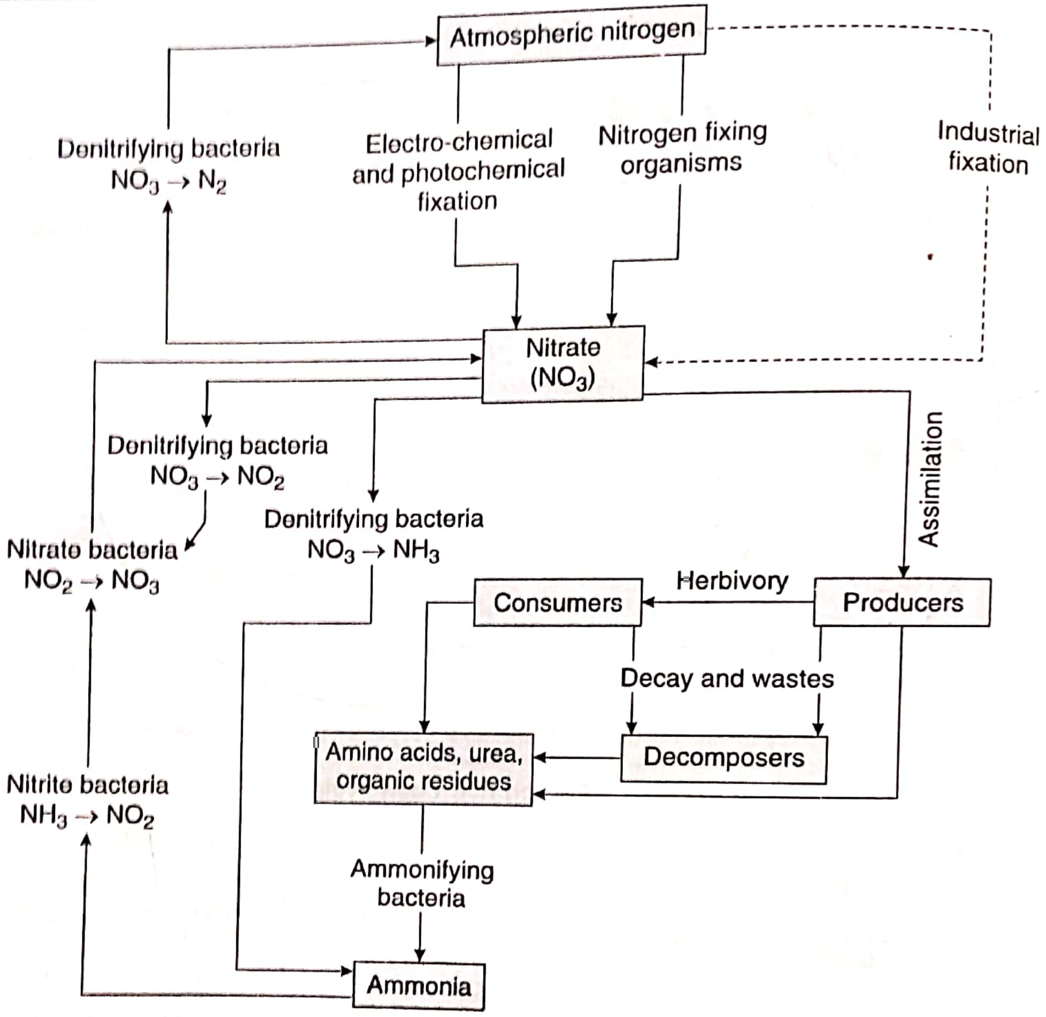


Fig. 7. Nitrogen cycle.

1. Nitrogen Fixation by Physico-chemical Reactions.

Due to thunder storm in rainy season, N_2 and O_2 of air combine with each other.

$$N_2 + O_2 \longrightarrow 2NO, \quad 2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Nitric acid (acid rain) comes to the earth and combine with basic components in soil to form nitrates which are the basic food of the plants in the soil.

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

2. Nitrogen Fixation or Nitrogen Transformations by Bacteria.

Nitrogen cycle, the micro-organisms mediated cycle, is based on four major chemical transformations.

(i) **Nitrogen fixation** where molecular N_2 is fixed as organic nitrogen by Rhizobium bacteria.

$$3\,[CH_2O] + 2N_2 + 3H_2O + 4H^+ \longrightarrow 3CO_2 + 4NH_4^+$$

(ii) **Nitrification** which is the process of oxidising NH_3 to NO_3^- by Nitrosomonas and Nitrobacter.

$$NH_3 + \frac{3}{2}O_2 \longrightarrow H^+ + NO_2^- + H_2O$$

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^-$$

(iii) **Nitrate reduction to nitrite ion.**

$$\frac{1}{2}NO_3^- + \frac{1}{4}[CH_2O] \longrightarrow \frac{1}{2}NO_2^- + \frac{1}{4}H_2O + \frac{1}{4}CO_2$$

(iv) **Denitrification**, which involves reduction of NO_3 and NO_3^- to NO_2^-, followed by recycling of N_2 to the atmosphere.

$$4NO_3^- + 5\,[CH_2O] + 4H^+ \longrightarrow 2N_2\uparrow + 5CO_2\uparrow + 7H_2O$$

Some soil micro-organisms transform nitrogen into soluble nitrogen compounds at a rate of 0·1 tonne per hectare per year. In the total cycle about 4–7 tonnes of nitrogen is added to the soil each year.

Man has interfered with this natural cycle by industrially fixing nitrogen. Modern agricultural practices dump about 40 million tonnes of nitrogeneous fertilizers each year to world's cultivated land. Fresh water resources, *viz.*, rivers, lakes, streams get polluted by agricultural run-off, *i.e.*, leaching of excessive nitrate from agricultural lands. The increased run-off has also contributed to the process of eutrophication.

PHOSPHORUS CYCLE

The phosphorus cycle occurs naturally in environment as PO_4^{3-}, HPO_4^-, H_2PO_4 or soluble inorganic, organic phosphate, particulate phosphate or as mineral phosphate. Phosphorus differs from other elements of the biosphere in that it does not form gaseous compounds at normal temperatures and pressures. Phosphates are necessary for the growth and maintenance of animal bones and teeth while organo-phosphates are essential for cell division involving the production of DNA and RNA. Plants and animals derive their nutrition via energy metabolic pathways with chemical utilising **adenosine triphosphate, ATP.**

Phosphate minerals are located in rocks and soil, where phosphates exist in soluble and insoluble forms. Terrestrial plants absorb inorganic phosphate salts from the soil and convert them into adenosine diphosphate (ADP) and ATP. These are utilised by plants as energy carriers for their metabolic reactions. The organic phosphates are transferred to consumers and decomposers and subsequently are made available as inorganic phosphates for recycling via., bacterial decomposition.

Animals and plants after their death and decay return phosphates to the soil which are finally converted to humus by the action of soil micro-organisms. Bulk of the phosphate in the soil is fixed or absorbed on the soil particles but part of it is lost by leaching out (run-off) into water courses (Fig. 8).

In fresh water phytoplankton quickly absorbs soluble inorganic phosphates and convert them into organophosphates. Algae are the sources of food for 200 planktons which in turn are eaten by other aquatic animals. All these forms of life after their decay settle to the bottom of water. In due course the organic waste decomposes by the action of micro-organisms, releasing phosphates into the water body for recycling again.

Lack of phosphorus in the soil causes soil infertility and to replenish the lost phosphorus, superphosphate or triple superphosphate are now being used. Because of the accelerated use of fertilizers and detergents, the phosphorus cycle is substantially affected. Phosphorus pollution has contributed to eutrophication which reduces the dissolved oxygen in water and disrupts the natural food chains.

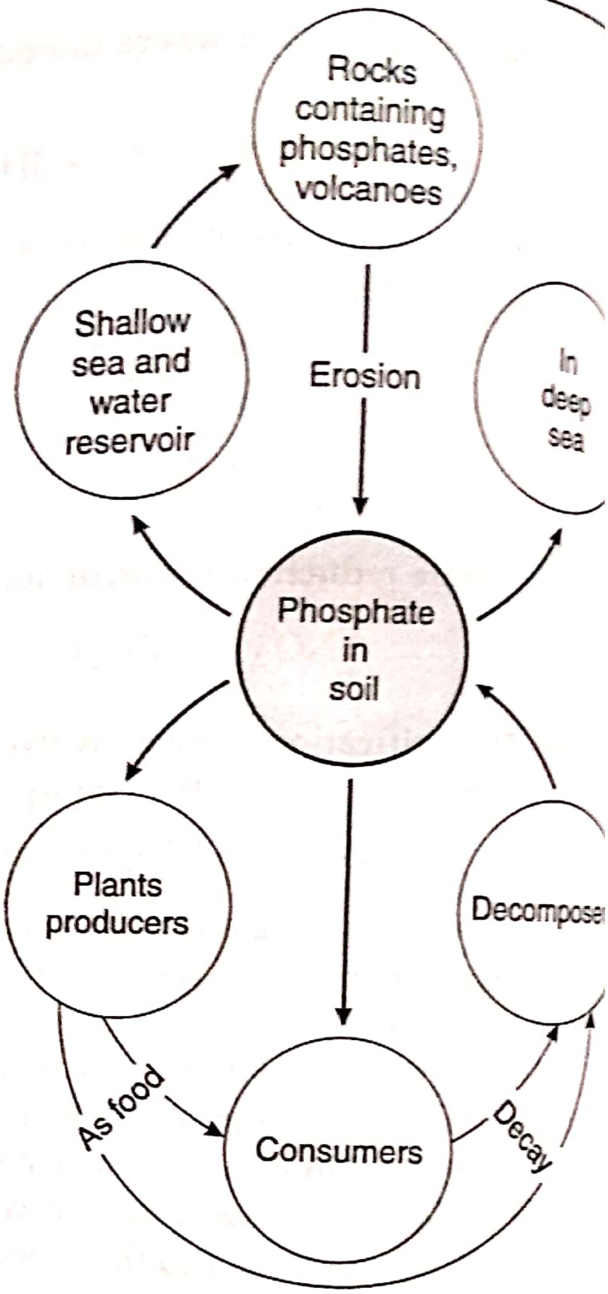


Fig. 8. **Phosphorus cycle.**

SULPHUR CYCLE

Sulphur is an essential constituent of proteins and amino acids. In nature, it mainly exists in the form of elemental sulphur, sulphides and sulphates. Sulphur cycle may be gaseous cycle or sedimentary cycle (**Fig. 9**).

Gaseous Sulphur Cycle. Sulphur enters the atmosphere through bacterial emission (H_2S), fossil fuel burning (SO_2), wind blown sea salts (SO_4^{2-}) and volcanic emissions (H_2S, SO_2, SO_4^{2-}). Most of the sulphur in the form of SO_2 or H_2S is converted to SO_3 which dissolves in water droplets to form H_2SO_4. The sulphur cycle is overloaded due to burning of fossil fuels. As a result, SO_2 emitted into the atmosphere constitutes a significant fraction of total global sulphur transport. This increased amount of sulphur is changed to sulphuric acid in rain water causing adverse ecological effects.

Sedimentary Sulphur Cycle. In sedimentary phase (long termed) sulphur tied up in organic and inorganic deposits is released by weathering and decomposition. Sulphur so released as SO_4^{2-} ion is carried to terrestrial and aquatic ecosystems in a salt solution. Thus apart from S, H_2S and organic sulphur, the sulphate may come from soil and sediments, also from minerals present naturally or from fertilizers added to the soil. Sulphate ion is reduced after being absorbed from the soil by plants and bacteria and ultimately incorporated as the sulphydryl group (—SH) in proteins.

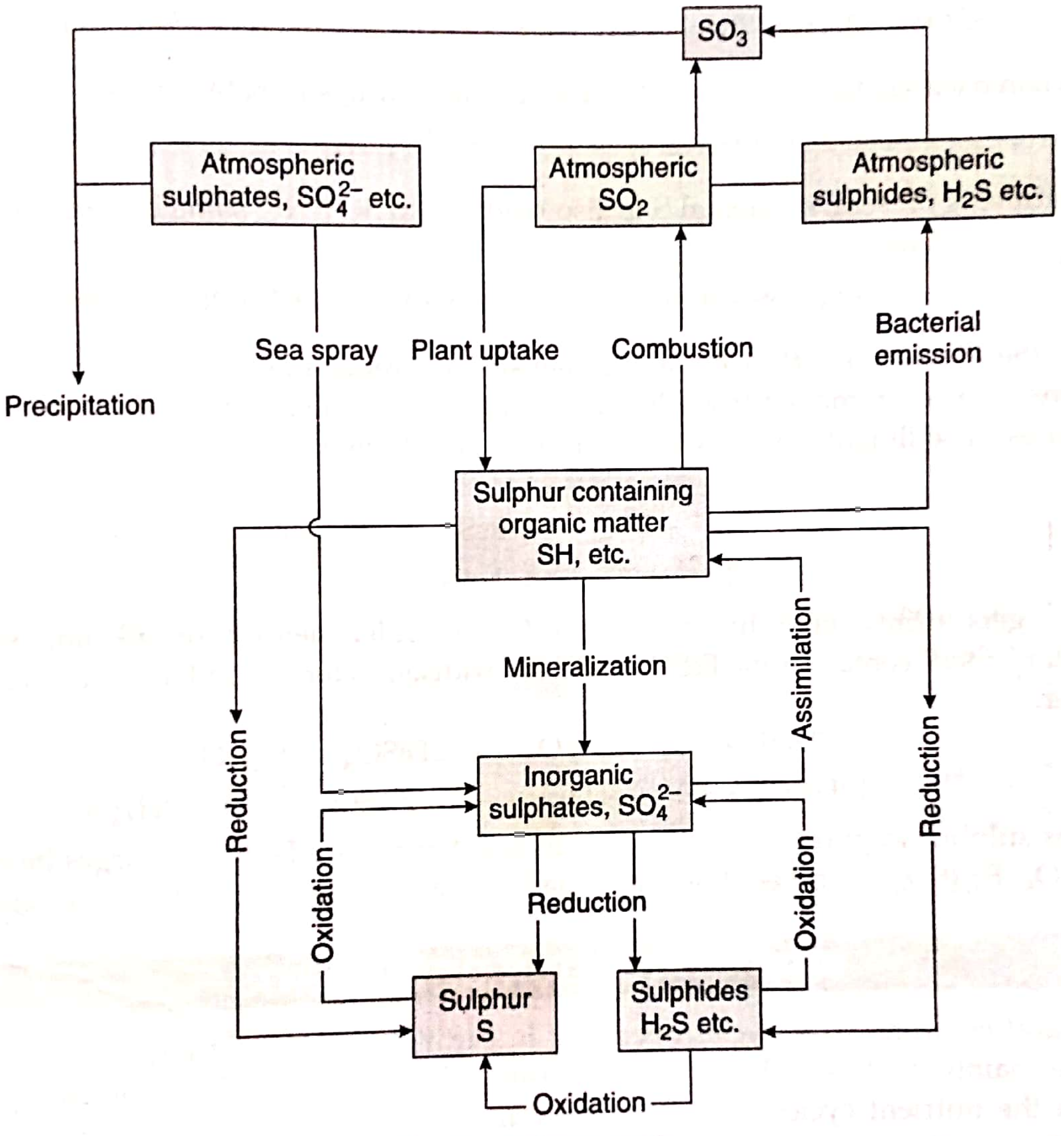


Fig. 9. Sulphur cycle.

From the producers, the S in proteins or amino acids is transferred to consumers. Excretion of excess sulphur is carried back to the soil and bottom of the water bodies. Some sulphates are reduced under anaerobic conditions directly to sulphides, H_2S or elemental S by **Desulfovibrio** bacteria found at the bottom of oceans. H_2S thus produced escapes into the air and replenishes the sulphur lost by precipitation. H_2S is also oxidised in an aerobic environment to SO_4^{2-} by bacteria of genus Thiobacillus.

$$H_2S + 2O_2 \longrightarrow SO_4^{2-} + 2H^+$$

The sulphate so formed can then be used by autotrophs again. In the bottom of certain lakes and ponds, where there exists an anaerobic environment, it is difficult to oxidise sulphide by the above process. But if UV radiation is present, photosynthetic bacteria such as **Chlorobacteriaceae and Thiorhodaceae** are capable of using sulphide (H_2S) in the manufacture of carbohydrates and oxidise H_2S to S or SO_4^{2-}.

$$6CO_2 + 12H_2S + h\nu \longrightarrow C_6H_{12}O_6 + 6H_2O + 12S$$

$$6CO_2 + 12H_2O + 3H_2S + h\nu \longrightarrow C_6H_{12}O_6 + 6H_2O + 3SO_4^{2-} + 6H^+$$

Certain bacteria may also convert elemental sulphur to sulphate in presence of oxygen.

$$2S + 3O_2 + 2H_2O \longrightarrow 2SO_4^{2-} + 4H^+$$

If nitrate is present, elemental S is also oxidised to SO_4^{2-} by some bacteria even under anaerobic conditions.

$$6NO_3 + 5S + 2CaCO_3 \longrightarrow 2CaSO_4 + 3SO_4^{2-} + 2CO_2 + 3N_2$$

All these reactions provide a mechanism for regulating the availability of S to autotrophs. The S is removed from the organic phase as elemental S which is insoluble and accumulates in sediments. In presence of iron, sulphide may combine with it to form iron sulphide.

$$Fe^{2+} + S^{2-} \longrightarrow FeS$$

$$Fe^{2+} + 2S \longrightarrow FeS_2$$

FeS_2 gets firmly held in mud or wet soil under neutral or alkaline solutions. Sedimentary rocks contain some $FeSO_4$ which is oxidised to ferric sulphate in presence of air and water.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$12FeSO_4 + 2O_2 + 4H_2O \longrightarrow 4Fe_2(SO_4)_3 + 4Fe(OH)_2 \downarrow$$

Thus sulphur in pyrite rocks, exposed to weathering suddenly discharges heavy slugs of S, H_2SO_4, $Fe_2(SO_4)_3$ and $Fe(OH)_2$ into aquatic ecosystem causing water to be acidic.

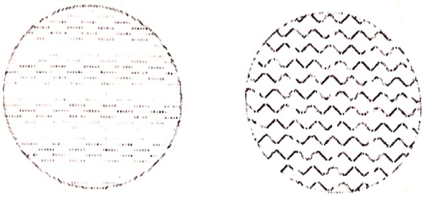
M.Sc. IV Semester

Chemistry

Paper-IV (Polymers)

2

POLYMER CHARACTERIZATION



PROLOGUE

- Average Molecular Weight Concept
- Measurement of Molecular Weights
- Chemical Analysis of Polymers
- Spectroscopic Methods
- Thermal Analysis
- Physical Testing

AVERAGE MOLECULAR WEIGHT CONCEPT

A polymer consists of molecules of different molecular weights, therefore, its molecular weight is expressed in terms of an 'average' value. For example, ethylene gas a simple compound which contains a low molecular weight. Its molecules have the same chemical structure, *i.e.*, $CH_2{=}CH_2$ and hence, the molecular weight is fixed, viz., 28.

But when ethylene is taken for polymerization, it gives a polymer named polyethylene and then we have its indefinite chemical structure as $[CH_2{-}CH_2]_n$ where, *n* is the number of monomer molecules, which can change its value from one polyethylene molecule to another in the same polyethylene sample. This is so because when ethylene is polymerised to give polyethylene, a number of polymer chains start growing at any instant, but all of them do not get terminated after growing to the same size. The termination of chain is a random process, and therefore, each polymer molecule formed can have a different number of monomer units and possesses different molecular weights.

For example, three structures of polyethylene molecules are shown below which have different molecular weight :

$R \left[CH_2 - CH_2 \right]_{200} R$ (molecular weight ≈ 5600)

$R \left[CH_2 - CH_2 \right]_{300} R$ (molecular weight ≈ 8400)

$R \left[CH_2 - CH_2 \right]_{400} R$ (molecular weight ≈ 11200)

In the above cases, it is clear that the three molecules of different sizes and different molecular weight, and yet, they are all polyethylene.

A polymer sample can, therefore, be assumed of as a mixture of molecules of the same chemical structure, but of different molecular weights. In this case, the molecular weight of polymer is expressed only statistically and shown as some average of the molecular weight contributed by the individual molecules that make the sample.

◆ NUMBER-AVERAGE CONCEPT

The number-average molecular weight of a polymer can be calculated by the following ways :

Suppose, a bag containing four different types of fruits : apples, papayas, pine apples and watermelons. To clarify and just for understanding, let each apple of the apple lot weight the same, and similarly also each of the other fruits. Suppose that the number of each fruit and its weight are as given below :

Fruits	Number (n)	Weight M (g)	Total weight of each fruit $W = nM$ (g)
Apples	6	10	60
Papayas	4	50	200
Pine apples	3	100	300
Watermelons	2	200	400
	15		960

Now, we have to find out the average weight of the fruits present in the bag. It is assumed that the individual fruit contributes to the average weight in the ratio of its numbers. Then we get the number-average weight as follows :

Total number of fruits in the bag = 15

Total number of the apples in the bag = 6

Therefore, number fraction of fruits (to the total number of fruits) = 6/15

In the same manner,

Number fraction of papayas = 4/15

Number fraction of pine apples = 3/15

Number fraction of watermelons = 2/15

Contribution made by 6 apples towards average weight of fruits in the bag ;

Number fraction of apples × weight of each apple

$$= 6/15 \times 10$$

$$= 4.0 \text{ g}$$

Similarly, contribution made by 4 papayas to the average weight of fruits in the bag

$$= \frac{4}{15} \times 50 = 13.30 \text{ g}$$

Similarly, contribution made by 3 pine apples to the average weight of fruits in the bag

$$= \frac{3}{15} \times 100 = 20.0 \text{ g}$$

Similarly, contribution made by 2 watermelons to the average weight of fruits in the bag

$$= \frac{2}{15} \times 200 = 26.60 \text{ g}$$

By summing up the contributions made by each fruits variety, we get the number-average weight of the total fruits as the :

$$4.0 + 13.30 + 20.0 + 26.60 = 63.90 \text{ g}$$

Weight-Average Concept

The weight-average can be calculated by the other method which is based on the assumption that the individual fruit variety contribute to the total weight in the proportion not of its number but its weight. The weight-average can be get as :

Total weight of all the fruits present in the bag = 960 g

Weight of apples present in the bag = 60 g

Therefore,

$$\text{Weight fraction of apples} = \frac{60}{960}$$

Similarly, weight fractions of papayas, pine apples, and watermelons are 200/960, 300/960 and 400/960 respectively.

Next, contribution made by apples towards average-weight of fruits in the bag = Weight fraction of apples × Average weight of apples

$$= \frac{60}{960} \times 10 = 0.62 \text{ g}$$

Similarly,

$$\text{Corresponding contribution by papayas} = \frac{200}{960} \times 50 = 1.41 \text{ g}$$

$$\text{Corresponding contribution by pine apples} = \frac{300}{960} \times 100 = 31.2 \text{ g}$$

$$\text{Corresponding contribution by watermelons} = \frac{400}{960} \times 200 = 83.3 \text{ g}$$

Summing up the contributions made by each fruit variety, we get the weight-average weight of the total fruits as :

$$0.62 + 1.41 + 31.2 + 83.3 = 116.53 \text{ g}$$

Generalisation of the Foregoing Concepts

The number-average molecular weight is designated as $\overline{M}_n$ and the weight-average molecular weight is designated as $\overline{M}_w$.

To calculate the molecular weight of a polymer one can also use either the number-fraction or the weight-fraction of the molecules present in the polymer.

With the help of ordinary mathematics, one can be easily generalised the method of working out $\overline{M}_n$ and $\overline{M}_w$. Suppose that there are n number of molecules are present in a polymer sample and n_1 of them have M_1 molecular weight, and n_2 have M_2 molecular weight and so on till one get n_i having M_i molecular weight;

Now, the total number of molecules (n) given by :

$$n = n_1 + n_2 + n_3 \ldots + n_i = \Sigma n_i$$

Number of molecules in fraction $1 = n_1$

Number-fraction of fraction $1 = \dfrac{n_1}{n} = \dfrac{n_1}{\Sigma n_i}$

Molecular weight contribution by fraction $1 = \dfrac{n_1 M_1}{\Sigma n_i}$

Similarly, molecular weight by contribution by other fractions will be as follows :

$$\frac{n_2 M_2}{\Sigma n_i}, \frac{n_3 M_3}{\Sigma n_i}, \ldots \frac{n_i M_i}{\Sigma n_i}$$

Number-average molecular weight of the whole polymer will then be given by,

$$\frac{n_1 M_1}{\Sigma n_i} + \frac{n_2 M_2}{\Sigma n_i} + \ldots + \frac{n_i M_i}{\Sigma n_i} = \frac{\Sigma n_i M_i}{\Sigma n_i} = \overline{M}_n$$

Similarly, total weight of the polymer $= W = \Sigma n_i M_i$

Weight of fraction $1 = W_1 = n_1 M_1$

Weight-fraction of fraction $1 = \dfrac{n_1 M_1}{W} = \dfrac{n_1 M_1}{\Sigma n_i M_i}$

Molecular weight contribution by fraction 1 is given by

$$= \frac{n_1 M_1 M_1}{\Sigma n_i M_i} = \frac{n_1 M_1^2}{\Sigma n_i M_i}$$

Similarly, the molecular weight contribution by the other fractions will be

$$\frac{n_2 M_2^2}{\Sigma n_i M_i}, \frac{n_3 M_3^2}{\Sigma n_i M_i}, \ldots, \frac{n_i M_i^2}{\Sigma n_i M_i}$$

The weight-average molecular weight of the whole polymer will then be

$$\frac{n_1 M_1^2}{\Sigma n_i M_i}, \frac{n_2 M_2^2}{\Sigma n_i M_i} + \ldots + \frac{n_i M_i^2}{\Sigma n_i M_i} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} = \overline{M}_w$$

For all synthetic polymers, $\overline{M}_w$ is greater than $\overline{M}_n$. If they were to be equal, the polymer sample may be considered as perfectly homogeneous (*i.e.*, each molecule has the same molecular weight), but this does not happen.

Viscosity-Average Molecular Weight

Besides of $\overline{M}_n$ and $\overline{M}_w$, there are two other ways of expressing the molecular weight. Such type of expression is based on the sedimentation and flow behaviour of the polymer in solution. They are $\overline{M}_z$, *i.e.*, Z-average molecular weight and $\overline{M}_v$, *i.e.*, viscosity average molecular weight, given as

$$\overline{M}_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2}$$

$$\overline{M}_v = \left(\frac{\Sigma n_i M_i^{1+a}}{\Sigma n_i M_i} \right)^{1/a}$$

and

Here, n_i = The number of molecules having the molecular weight of M_i present in the sample.

a = It is a variable (and its value ranging from 0.5 to 1) in the Mark-Houwink equation.

POLYDISPERSITY AND MOLECULAR WEIGHT DISTRIBUTION

To know a polymer property, we must have a knowledge of both, the average molecular weight as well as its dispersion pattern.

In monodispersed system, a simple chemical compound contains molecules, each of which has the same molecular weight. But in polydispersed system, a polymer consists of molecules, each of which have different molecular weights. The conceptual representation of monodispersed and polydispersed system is given in fig. 1.

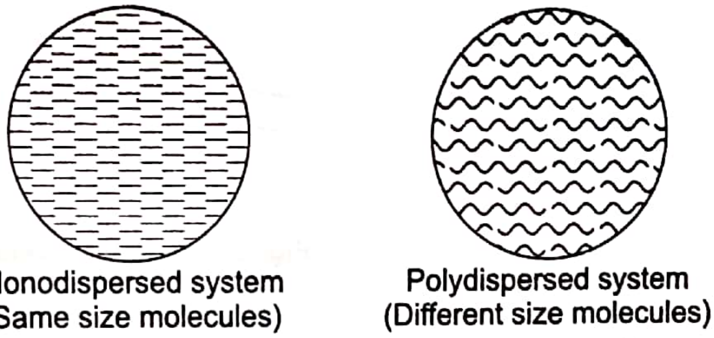


Fig. 1.

Simple chemical compounds like water, alcohol, are monodispersed systems, while polymers are polydispersed systems. Two polymer samples of the same 50,000 $\overline{M}_n$ can show similar properties in some respects but not in so others. Suppose, a polymer sample contains its average molecular weight, say, 50,000. This may mean that the molecules have molecular weight ranging from 10,000 to 70,000 or 500 to 100,000, this number is uncertain.

The polydispersity is a very important parameter. It tells about the lowest and the highest molecular weight sample as well as the distribution pattern of the intermediate molecular weight samples. The polydispersity is expressed by a simple molecular weight distribution curve. For a polymer sample, this curve is computed by plotting the number fraction (n_i) of molecules of having a particular molecular weight (M_i) against the corresponding molecular weight.

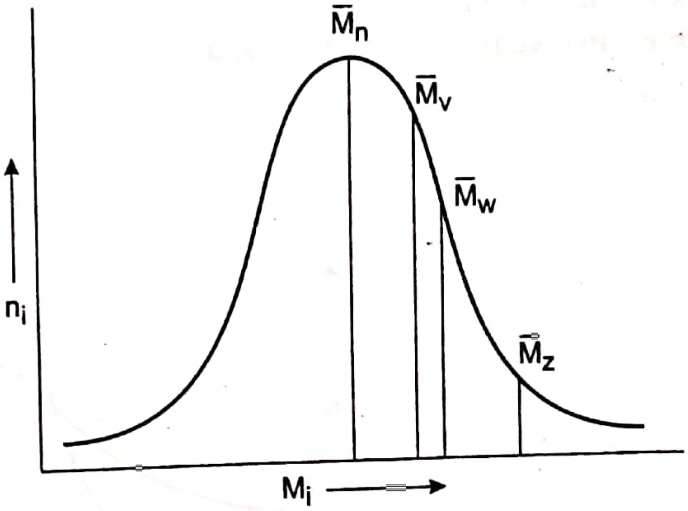


Fig. 2. Distribution curve for a polydispersed polymer sample

The above molecular weight distribution curve brings out the relative positions of various average molecular weights in a polydispersed polymer sample. In this case, $\overline{M}_w$ is greater than $\overline{M}_n$ and $\overline{M}_v$ is closer to $\overline{M}_w$ than to $\overline{M}_n$.

In another curve, the molecular weight distribution in two polymer samples having th same number-average molecular weight but different polydispersities. The polymer sampl 1 consists of a narrower dispersion pattern and, hence, have a lower polydispersity tha polymer sample 2.

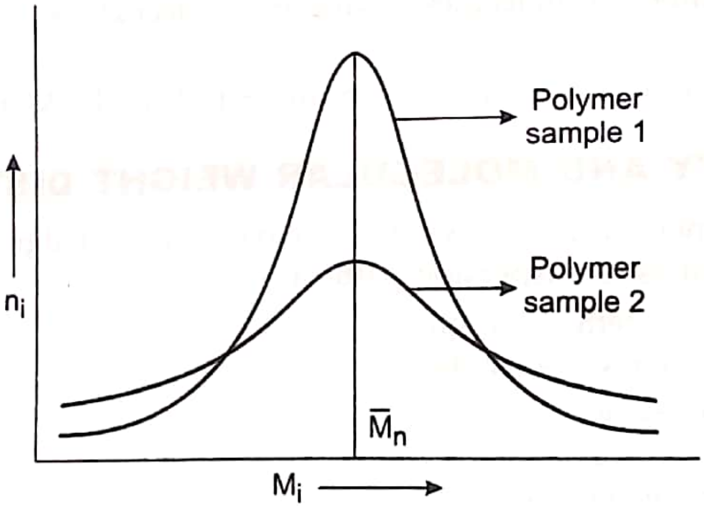


Fig. 3. Molecular weight distribution curve

The $\frac{\overline{M}_w}{\overline{M}_n}$ ratio is the indicative extent of polydispersity. The value of $\overline{M}_w$ and $\overline{M}_n$ can b calculated by two different experimental methods. For all synthetic polymers, $\overline{M}_w / \overline{M}$ value is more than 1. As the molecular weight distribution becomes larger, the value c $\overline{M}_w / \overline{M}_n$ increases. The molecular weight distribution curve for the three polymer sample with different polydispersities is shown here. It expresses the dispersity ratio increasing fo the three samples with the same $\overline{M}_n$, but a different molecular weight distribution.

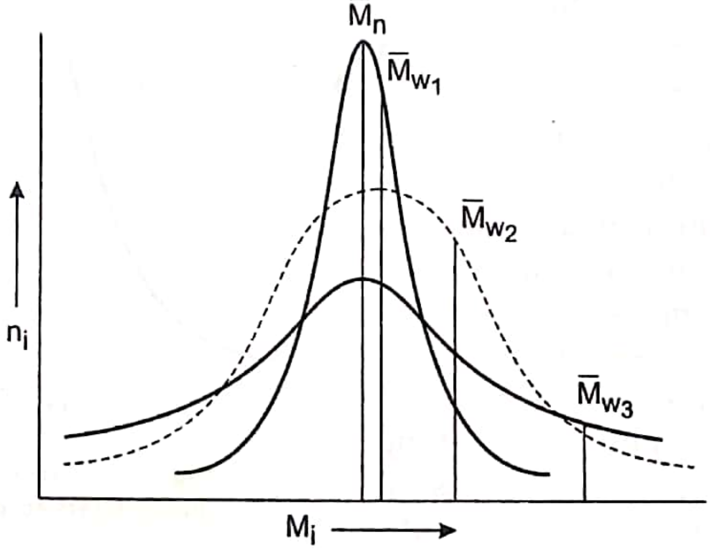


Fig. 4. Molecular weight distribution curve

The Practical Significance of Molecular Weight

The practical use of the knowledge of molecular weight of a polymer is very importan The polymers are used for commercial purposes. They are selected on the basis of thei properties, *e.g.*, tensile strength, impact strength or melt viscosity. Such properties are directly dependent on the molecular weight of the polymer or its degree of polymerisation.

The tensile and impact strength increases with molecular weight. The trend shows that it increases upto a point and then decreases as given in fig. 5.

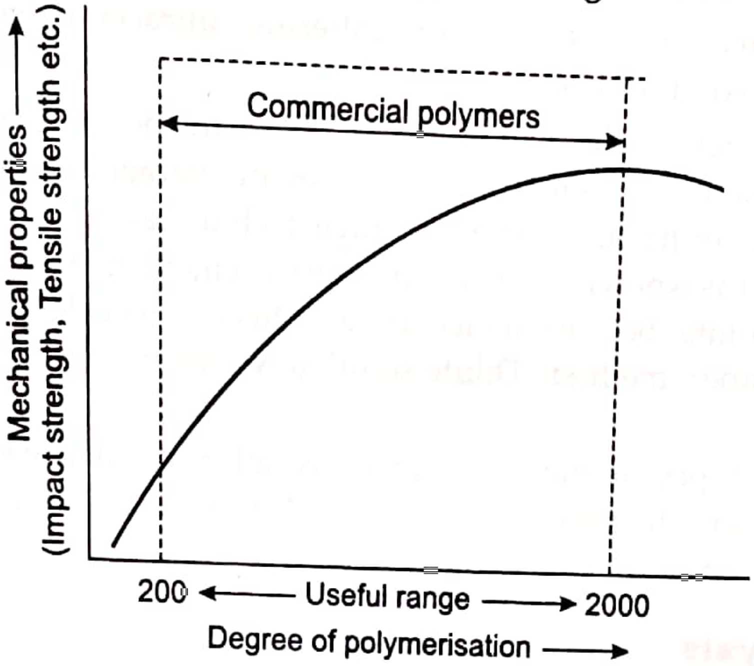


Fig. 5. Curve between mechanical properties of a Polymer vs. Degree of Polymerization

Another polymer property, melt viscosity possesses different type of characteristic. It increases more steeply at very high molecular weights, while decreases at low molecular weights as shown in fig. 6.

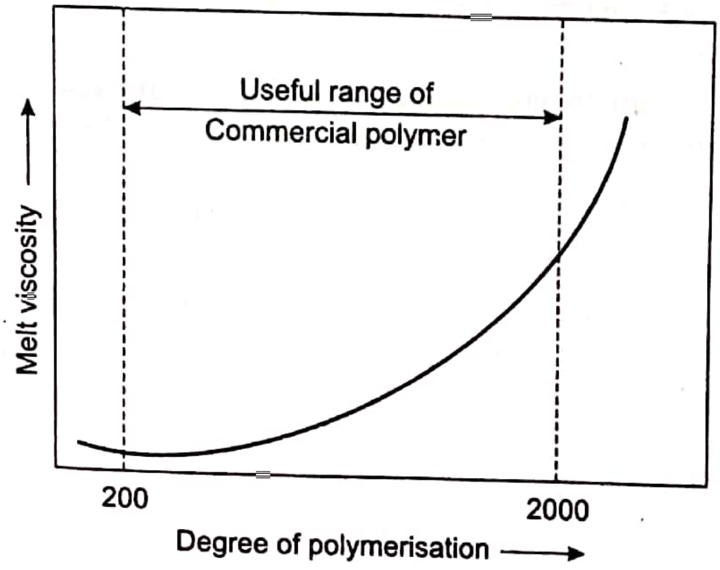


Fig. 6. Melt viscosity of a polymer vs degree of polymerization

A commercially useful polymer should consists of good strength as well as low melt viscosity. Both the above curves give an idea about to choose the useful range of molecular weights for polymers.

Measurement of Molecular Weights

There are various types of molecular weights, such as number-average molecula weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), viscosity-average molecular weigh ($\overline{M}_v$), etc. These are measured by different chemical and physical methods, viz., cryoscopy ebulliometry, osmometry, viscometry, light scattering, ultracentrifugation techniques an measurement of dilute solution viscosity.

The number-average molecular weight ($\overline{M}_n$) can be determined by cryoscopy ebulliometry, and osmometry-methods. While weight-average molecular weight ($\overline{M}_w$) i measured by light scattering and ultracentrifuge techniques. Similarly, viscosity-averag molecular weight ($\overline{M}_v$) is known by viscosity measurement method. The above method except the last are absolute. Because molecular weights can be calculated without referenc to calibration by another method. Dilute-solution viscosity is not a direct measure o molecular weight.

Besides of some types of end-group analysis, all molecular-weight methods requir solubility of the polymer. The polymer sample is taken in the solution form which contain very low concentration, say less than 1.0 g/dl.

End Group Analysis

For the determination of number-average molecular weight of polymers, end grou analysis is performed. In this method, the sample should contain reactive functional group at one or both the ends of molecule. The end group analysis method can be used reliabl only for samples consisting of linear molecules with determinable end groups and for thos obtained by a known polymerisation mechanism without giving any side reactions. Sinc during polymerisation, side reaction may introduce errors in the assumed functionality an causes erroneous results.

While going into detail in end group analysis, we are considering the example o polymer, carboxyl-terminated polybutadiene and hydroxyl-terminated polybutadien These molecules possess carboxyl and hydroxyl functional groups at their respective ends. I shows two functional groups in each polymer sample. Thus, their functionality (number o reactive functional groups) is two.

The total number of functional groups in a given weight of sample can be determine by various chemical methods. The total number of functional groups in a given sampl weight is known as *functional group equivalent*. By knowing it and functionality value, th molecular weight can be determined by using following formula :

$$\overline{M}_n = \frac{\text{Functionality}}{\text{Functional group equivalent}}$$

where, $\overline{M}_n$ = number average molecular weight

Experimental Method

To determine the end group the polymer sample (carbonyl-terminated polybutadiene of known quantity is dissolved in a mixture of toluene and ethanol) (in 1 : 3 ratio). For this purpose, ethanol is distilled first, and neutralised with a dilute solution of alcoholic potassium hydroxide. Then it is mixed with toluene in 1 : 3 ratio. A precisely weighed amount (> 1g) polymer sample is dissolved into this mixture. A solution of 0.1 N alcoholic potassium hydroxide is also prepared. The polymer solution is titrated against 0.1 N potassium hydroxide solution using phenolphthalein as an indicator. It gives slightly pink colour at the end point. By using the above readings, the molecular weight of the polymer sample can be calculated as :

Normality of KOH solution $= N$

Weight of the polymer sample $= W$ g

Volume of KOH consumed $= V$ mL

Value of carboxyl group $= \dfrac{VN(56.1)}{W}$ mg of KOH/g

Carboxyl equivalent/100 g $= \dfrac{VN(56.1)}{W \times (1000)} \times \dfrac{100}{56.1} = \dfrac{VN}{10W}$

If the functionality of the sample = 2

then, $\overline{M}_n = \dfrac{2 \times 100}{VN/10W}$

Viscometry

Viscometer is used to determine the viscosity-average molecular weight ($\overline{M}_v$) of polymers. The polymer solution consists of high viscosity than a pure solvent. The relationship between the viscosity of a polymer solution and the molecular weight is as follows :

$$[\eta] = K\overline{M}a$$

where, $[\eta]$ = intrinsic viscosity

$\overline{M}$ = molecular weight

K and a= constants for a polymer, solvent or temperature system.

For a polymer, the K and a values have to be measured. For such measurements, the polymer sample has to be fractionated into several fractions, and for each fraction, the molecular weight is determined by osmometer or by light-scattering technique. Intrinsic viscosity is also determined for this purpose. By plotting a graph between $[\eta]$ and $\overline{M}$ a straight line is obtained. The ordinate intercept and slope of this line will give the value of K and a, respectively.

For the determination of intrinsic viscosity the polymer solution, has to be passed through the capillary tube of viscometer.

Assume that the time required for the solution of volume V to pass through the capillary tube of radius r and length l is related to its absolute viscosity η by the Poiseuille equation as :

$$\eta = \frac{3.14\,\mathrm{P}r^4 t}{8Vl} \quad \text{...(1)}$$

where, P = Pressure head where the liquid flow occurs.

$$t = \frac{8Vl\eta}{3.14\ Pr^4} \qquad \ldots(2)$$

If η and η_0 are the absolute viscosities of a solution and the pure solvent, respectively, and t and t_0 are their corresponding flow times, the following relationships can be obtained :

$$t = \left(\frac{8Vl}{3.14\ Pr^4}\right)\eta \qquad \ldots(3)$$

$$t_0 = \left(\frac{8Vl}{3.14\ Pr^4}\right)\eta_0 \qquad \ldots(4)$$

For the same capillary tube, the quantities within parenthesis have the same value. Hence, dividing equation (3) by (4) :

$$\frac{t}{t_0} = \frac{\eta}{\eta_0} \qquad \ldots(5)$$

$\frac{\eta}{\eta_0}$ is known as the relative viscosity. Other terms related to viscosity measurements are as follows :

Relative viscosity $= \eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$

Specific viscosity $= \frac{(\eta - \eta_0)}{\eta_0} = \frac{(t - t_0)}{t_0} = \eta_r - 1 = \eta_{sp}$

Reduced viscosity $= \eta_{sp}/c = \eta_{\text{red}}$, dl/g

Inherent viscosity $= \ln \eta_r / c = \eta_{\text{inh}}$, dl/g

Intrinsic viscosity $= (\eta_{sp}/c)_{c\to 0} = (l_n\eta_r/c)_{c\to 0} = [\eta]$, dl/g

The intrinsic viscosity is also known as the Staudinger index or limiting viscosity number and it is the reciprocal of concentration as its dimension. For calculating the intrinsic viscosity of a polymer sample in solution, the flow time of a constant volume of solvent and the solutions through a particular capillary tube is required. For the determination of molecular weight by viscometer, this principle is used.

In an actual experiment, the solution of known concentrations of the polymer sample are prepared the solvent flow time (t_0) and the solution flow time (t) for different concentrations are measured by using the viscometer. For each concentration, the corresponding reduced viscosity and the inherent-viscosity are calculated the plots between reduced viscosity against concentration and inherent viscosity against concentration are made. The common ordinate intercept of these plots gives the intrinsic viscosity. The data for a typical measurements of viscosity are as follows :

Viscosity data for a polymer (Polymethyl acrylate) sample in benzene solution at 30°C

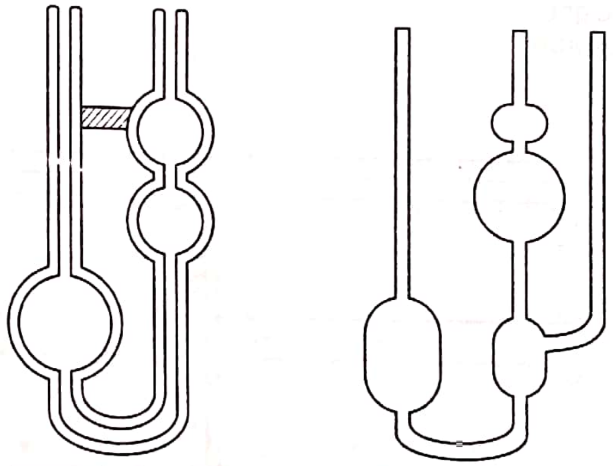
Concentration c (g/dl)	Flow time t (sec)	$t/t_0 = \eta_0$	$\eta_r - 1 = \eta_{sp}$	η_{sp}/c (dl/g)	$\ln \eta_r$	$\ln \eta_r / c$ (dl/g)
0.2716	459.8	2.1287	1.1287	4.156	0.7556	2.782
0.1940	378.2	1.7509	0.7509	3.870	0.5601	2.887
0.1509	337.9	1.5644	0.5644	3.740	0.4475	2.966
0.1235	312.8	1.4481	0.4481	3.629	0.3702	2.998
0.1045	296.4	1.3722	0.3722	3.562	0.3164	3.028

Measurement of Molecular Weight by Viscosity : Determination of molecular weight of polymers by viscosity measurement method is the most convenient and least complex method. The viscosity of the polymer solution is measured by viscometer. For the determination of viscosity two viscometers are generally used :

(a) Ostwald viscometer

(b) Ubbelohde suspended level viscometer

The viscometers are simple glass capillary instruments. In Ostwald viscometer all measurements should be taken using a constant volume of the solution; while in ubbelohde suspended level viscometer, a single solution of known concentration is required and it is unaffected by the volume of the solution taken.



(a) Ostwald viscometer

(b) Ubbelohde suspended level viscometer

Fig. 7.

Experimental Technique : A known volume of the solution is taken in the viscometer and the time of flow is measured. In Ubbelohde suspended level viscometer, known volumes of pure solvent is taken and mixed inside the viscometer itself. Thus subsequent concentrations can be achieved. This provides sufficient data of flow times at different concentrations. In Ostwald viscometer one has to empty, clean and refill the viscometer at each time with fresh solution before measuring the flow time.

Precautions :

1. Viscosity is a temperature dependant property, therefore, all the measurements must be taken at constant temperature.
2. Viscometer should be hold in vertical and straight direction in all the time, otherwise the pressure head will change in each measurements.
3. All solutions should be free from impurities, otherwise the capillary tube may choked and the flow of the solution may be obstructed.
4. The flow time of a solution or solvent must be sufficiently long. The difference in flow time between two successive concentrations should be atleast of 3 to 5 seconds.