

Polymer Process Engineering
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Lecture – 03
CHARACTERISTICS OF POLYMERS-I

Welcome to the next lecture on Polymer Process Engineering. Here, we are going to discuss the different characteristics of the polymers. We briefly discussed a lot of the classes of polymerization in the previous lecture. Apart from this, we discussed the various polymerization techniques and some of the commercial polymers. Now, the purpose of the discussion about this commercial polymerization, commercial polymers, is you have a brief idea of how important these polymers are and, in different segments, how these polymers are used. In this particular chapter, we are going to cover the different characteristics of the polymers, the molecular weight, and molecular weight distribution.

Topics to be covered

- Characteristics of polymers
- Molecular weight
- Molecular weight distribution

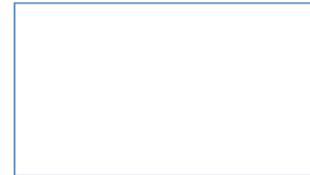
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You see, molecular weight plays a very vital role. We will discuss that to assess the different properties of the polymer, and because these are the chain components, then there is a distribution molecular distribution there is a range of this molecular weight, which we are going to discuss in this particular segment. Let us talk about the characteristics of the polymers. Now you see that these polymers are giant molecules.

CHARACTERISTICS OF POLYMERS

Polymers, as giant molecules, have a number of important structural characteristics that determine their end-use mechanical, electrical, thermal, chemical, and optical properties. These include:

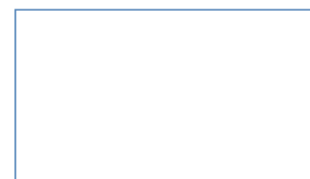
- Molecular weight
- Molecular weight distribution
- Degree of branching
- Degree of cross-linking
- Polarity of polymer chains
- Flexibility of polymer chains



They have a large number of important structural characteristics that usually determine or trigger effects on the end use of these polymers with respect to mechanical, electrical, thermal, chemical, and other optical properties. Now some of the properties are enlisted like molecular weight, molecular weight distribution, degree of branching, degree of cross-linking, polarity of these polymer chains, flexibility of the polymer chains, macro crystallinity of the structure, fine crystalline structures, different types of the orientation as we discussed that these polymers are composed of the different type of polymer chain. So, how these polymer chains are oriented? These are some of the main characteristics, and these characteristics basically depend on the intermolecular forces for a particular given polymer. These intermolecular forces are additive, and they give the polymer their peculiar end-use properties.

CHARACTERISTICS OF POLYMERS

- Macrocrystalline structure
- Fine crystalline structure
- Orientation of polymer chains
- The principal influence of these characteristics is on the intermolecular forces in a given polymer. Since such intermolecular forces are additive, they give polymers their peculiar end-use properties.



So, let us talk about the molecular weight. Now molecular weight of the polymer is extremely important in polymer synthesis and application. Now, usually, scientists use the term molecular weight to describe the size of a molecule. Now, the more accurate term is the molar mass, and usually, they are referred to as gram per mole. The term molecular weight is a ratio of the average mass per formula unit of a substance to one-twelfth of the mass of an atom because of the carbon atom, and it is dimensionless.

MOLECULAR WEIGHT

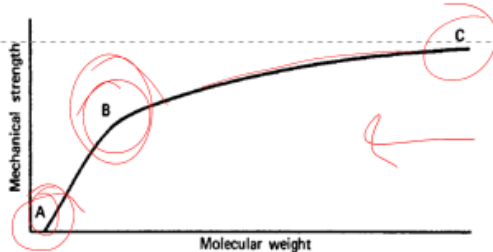
- The molecular weight of a polymer is of prime importance in the polymer's synthesis and application.
- Chemists usually use the term molecular weight to describe the size of a molecule.
- The more accurate term is molar mass, usually in units of g mol^{-1} .
- The term molecular weight is the ratio of the average mass per formula unit of a substance to 1/12th of the mass of an atom of ^{12}C and is dimensionless.

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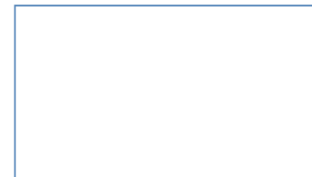
Now, the most important mechanical property depends on a very considerable molecular weight, which is seen in this particular figure. Now, there is a minimum polymer molecular weight that is referred to as A and usually 1000 to produce any significant mechanical strength at all. So, you see that the molecular weight and the mechanical strength these two things are interrelated. Now above A the strength increases rapidly with the molecular weight until it reaches a critical value. Now, that is referred to as a B in this particular figure.

MOLECULAR WEIGHT

- Most important mechanical properties depend on and vary considerably with molecular weight as seen in Figure. There is a minimum polymer molecular weight (A), usually a thousand or so, to produce any significant mechanical strength at all.



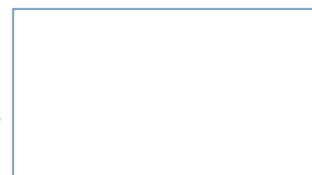
Dependence of mechanical strength on polymer molecular weight.



The mechanical strength increases more slowly above B and eventually reaches the limiting value at C. So, this is the triggering point where you need to assess whether further polymerization is essential or not. Now, the critical point generally corresponds to the minimum molecular weight for a polymer to begin and exhibit sufficient strength to be useful. The most practical application of polymer requires high molecular weight to obtain the high strength. The minimum useful molecular weight at B at this particular juncture is usually in the range of 5000 to 10000. This differs for different polymers.

MOLECULAR WEIGHT

- Above A, strength increases rapidly with molecular weight until a critical point (B) is reached. Mechanical strength increases more slowly above B and eventually reaches a limiting value (C).
- The critical point B generally corresponds to the minimum molecular weight for a polymer to begin to exhibit sufficient strength to be useful.
- Most practical applications of polymers require higher molecular weights to obtain higher strengths.
- The minimum useful molecular weight (B), usually in the range 5000–10,000, differs for different polymers.

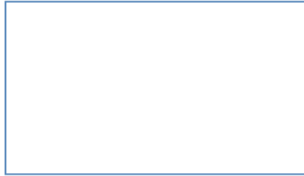





It depends on the different chains etc. Now this is generally this particular figure that we discussed in this slide generally shifts to the right as magnitude of the intermolecular forces decreases, and the polymer chains with stronger intermolecular forces like polyamide polyesters develop sufficient strength. This is to be useful at a lower molecular weight than polymer and having weaker

intermolecular forces like polyethylene. Properties other than strength also show a significant dependence on molecular weight. Most properties show the different qualitative or quantitative dependencies on molecular weight.

MOLECULAR WEIGHT

- The plot in figure generally shifts to the right as the magnitude of the intermolecular forces decreases. Polymer chains with stronger.
- Polymer chains with stronger intermolecular forces, for example, polyamides and polyesters, develop sufficient strength to be useful at lower molecular weights than polymers having weaker intermolecular forces, for example, polyethylene.
- Properties other than strength also show a significant dependence on molecular weight. However, most properties show different quantitative dependencies on molecular weight.

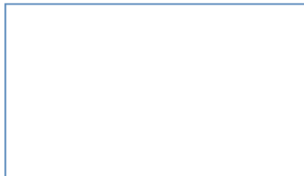





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A few properties may increase with the molecular weight to a maximum value and then decrease with a further increase in the molecular weight. Now that is why molecular weight is very important. Processibility usually begins to decrease past some molecular weight as the viscosity becomes too high and may flow too difficult. So, you need to have a proper or appropriate or optimum molecular weight to make the polymer processible. The practical aspect of polymerization this requires one to carry out the process to obtain the compromised molecular weight which is a molecular weight sufficiently high to obtain the required strength for a particular application without overly sacrificing other properties.

MOLECULAR WEIGHT

- Further, a few properties may increase with molecular weight to a maximum value and then decrease with further increase in molecular weight.
- An example is the ability to process polymers into useful articles and forms (e.g., film, sheet, pipe, fiber).
- Processability begins to decrease past some molecular weight as the viscosity becomes too high and melt flow too difficult.

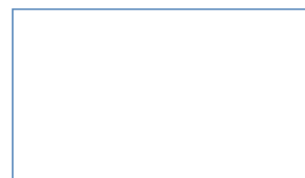


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Now, see, this is an art because the polymerization process is an art to make the monomer polymerizable. Now second thing is that you created a polymer, but to make that particular polymer a processible that is again art at what time you need to truncate the reaction is an art, so this particular polymer must possess the molecular weight that is required to have the proper strength and proper properties. So, this is an art. Now synthesizing the highest possible molecular weight is not necessarily the objective because if you go for a further higher molecular weight, it may not become processible, and other properties that are desired properties may get altered. The utility of the polymerization is mainly reduced unless the process can be carried out to yield the specified molecular weight.

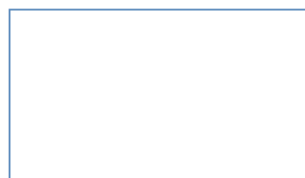
MOLECULAR WEIGHT

- Thus the practical aspect of a polymerization requires one to carry out the process to obtain a compromise molecular weight—a molecular weight sufficiently high to obtain the required strength for a particular application without overly sacrificing other properties.
- Synthesizing the highest possible molecular weight is not necessarily the objective of a typical polymerization. Instead, one often aims to obtain a high but specified, compromise molecular weight.



MOLECULAR WEIGHT

- The utility of a polymerization is greatly reduced unless the process can be carried out to yield the specified molecular weight.
- The control of molecular weight is essential for the practical application of a polymerization process.
- When one speaks of the molecular weight of a polymer, one means something quite different from that which applies to small-sized compounds.
- Polymers differ from the small-sized compounds in that they are polydisperse or heterogeneous in molecular weight.



The control of molecular weight is why it is essential for practical application. Now, if we say that the molecular weight of a polymer one means there is something quite different from what applies to the small-sized compound where you have the fixed molecular weight, but here you will have a range of

the molecular weight. So, the polymer differs from the small-size compounds in that they are polydispersed and heterogeneous in molecular weight. Now the polymers in their purest form are a mixture of molecules of different molecular weights. The reason for this polydispersity lies in the statistical variation presence of the polymerization process.

MOLECULAR WEIGHT

- Polymers differ from the small sized compounds in that they are polydisperse or heterogeneous in molecular weight.
- Polymers, in their purest form, are mixtures of molecules of different molecular weight. The reason for the polydispersity of polymers lies in the statistical variations present in the polymerization processes. When one discusses the molecular weight of a polymer, one is actually involved with its average molecular weight.
- Both the average molecular weight and the exact distribution of different molecular weights within a polymer are required in order to fully characterize it.

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Like in suppose we start like this is my monomer, and if it reacts with different monomers, it forms the, say P2 like P1 and P2, and this P2 may react with either P1 or it may react with P2. So, it may form either P3 or it may form P4. This contributes to the reaction mass. So, it may have molecular weight differences and this contributes to the entire polymer mass and that is why this is there is a range within the polymeric one because you cannot have a unique number of monomers in that particular chain. This contributes to the molecular weight.

MOLECULAR WEIGHT

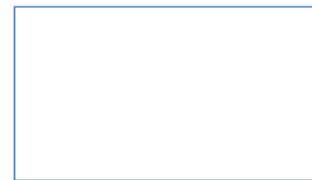
- The control of molecular weight and molecular weight distribution (MWD) is often used to obtain and improve certain desired physical properties in a polymer product.
- Various methods based on solution properties are used to determine the average molecular weight of a polymer sample.
- These include methods based on colligative properties, light scattering, and viscosity.
- The various methods do not yield the same average molecular weight.

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Now, the control of molecular weight and the molecular weight distribution is often used to improve the certain desired physical properties in the polymer product. So different methods based on the solution properties are used to determine the average molecular weight of a polymer sample. Now, we can use different molecular weights, number average weights, and average molecular weights. We will discuss all these things in due course of time. Now this includes the method based on the colligative properties, light scattering, and viscosity, and there are various methods that do not yield the same average molecular weight.

MOLECULAR WEIGHT

- Different average molecular weights are obtained because the properties being measured are biased differently toward the different-sized polymer molecules in a polymer sample.
- Some methods are biased toward the larger-sized polymer molecules, while other methods are biased toward the smaller-sized molecules.
- The result is that the average molecular weights obtained are correspondingly biased toward the larger or smaller-sized molecules.



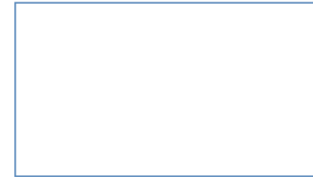
Now, different average molecular weights are obtained because the properties being measured are biased differently towards a different-sized polymer molecule on a different sample as we discussed in the previous slides. There are some methods biased towards the larger-sized polymer molecules while other methods are based towards the smaller-sized molecules. The result is that the average molecular weight obtained the correspondingly biased towards the larger or smaller-sized molecule, and that is why the term average molecular weight came into existence. Now, there are various ways through which you can find out the average molecular weight. One is the number average molecular weight sometimes represented as M_n .

MOLECULAR WEIGHT

- The following average molecular weights are determined:

Number-average molecular weight M_n

- It is determined by experimental methods that count the number of polymer molecules in a sample of the polymer.
- The methods for measuring M_n are those that measure the colligative properties of solutions—vapor pressure lowering (vapor pressure osmometry), freezing point depression (cryoscopy), boiling point elevation (ebulliometry), and osmotic pressure (membrane osmometry).



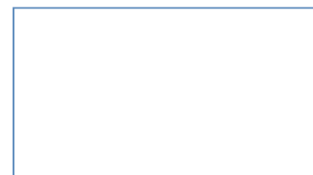
Now, this is determined by the experimental method that counts the number of polymer molecules in a sample of a polymer. This method of measuring M_n are those that measures the colligative properties like lowering of vapor pressure, vapor pressure osmometry, freezing point depression that is cryoscopy, boiling point elevation, ebulliently, and osmotic pressure is membrane osmometry. So, the number average molecular weight is mathematically represented by this formula where the summation of overall different sizes of polymer molecules ranges from x is equal to 1 to x is equal to infinity, and n_x is the number of moles whose weight is m_x . The most common methods of measuring the number average molecular weight are membrane osmometry and vapor pressure osmometry. Since reasonably reliable commercial instruments are available for those methods.

MOLECULAR WEIGHT

- The number-average molecular weight is

$$\bar{M}_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x}$$

where the summations are over all the different sizes of polymer molecules from $x = 1$ to $x = \text{infinity}$ and N_x is the number of moles whose weight is M_x .

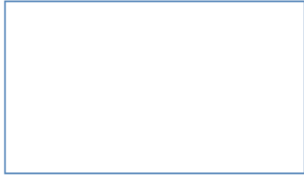





Now the vapor pressure osmometry measures the vapor pressure indirectly by measuring the change in the temperature of polymer solution and dilution by the solvent vapour and this is generally useful

for the polymers with the number average molecular weight below 10,000 or in the range of 10,000 to 15,000 range. Membrane osmometry is limited to polymers with the number average molecular weight above the range of 20000 to 30,000 or below five lakhs. The lower limit is the consequence of the partial permeability of available membranes to smaller-sized polymer molecules. Now above the molecular weight of, say, 5 lakhs the osmotic pressure of the polymer solution becomes too small to measure accurately. End-group analysis is also a very useful measurement for determining the number average molecular weight for a very limited number of polymers.

MOLECULAR WEIGHT

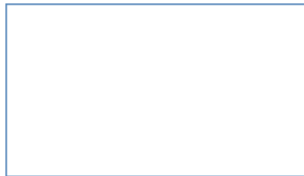
- The most common methods for measuring M_n are membrane osmometry and vapor pressure osmometry since reasonably reliable commercial instruments are available for those methods.
- Vapor pressure osmometry, which measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor, is generally useful for polymers with M_n below 10,000–15,000.






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MOLECULAR WEIGHT

- Membrane osmometry is limited to polymers with M_n above about 20,000–30,000 and below 500,000.
- The lower limit is a consequence of the partial permeability of available membranes to smaller-sized polymer molecules.
- Above molecular weights of 500,000, the osmotic pressure of a polymer solution becomes too small to measure accurately.




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Now, examples like the carboxylic end group of the polyester can be analyzed by the titration method, and carbon-carbon double bond end groups can be analyzed by NMR. Light scattering, light scattering by polymer solution, unlike the colligative properties, is greater for larger-sized molecules than for

smaller-sized molecule. The average molecular weight obtained from the light scattering measurement is the weight average molecular, which is referred to as M_w . Here, in this formula, you can determine the weight average molecular weight where w_x is the weight fraction of the molecules whose weight is M_x . Now, this weight average molecular weight can be determined by this mathematical formula.

MOLECULAR WEIGHT

- End-group analysis is also useful for measurements of M_n for certain polymers.
- For example, the carboxyl end groups of a polyester can be analyzed by titration with base and carbon-carbon double bond end groups can be analyzed by 1H NMR.
- Accurate end-group analysis becomes difficult for polymers with M_n values above 20,000–30,000.



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MOLECULAR WEIGHT

- **Light scattering** by polymer solutions, unlike coligative properties, is greater for larger-sized molecules than for smaller-sized molecules. The average molecular weight obtained from light-scattering measurements is the weight-average molecular weight M_w defined as

$$M_w = \sum w_x M_x$$

where w_x is the weight fraction of molecules whose weight is M_x .


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Here this C_x is the weight concentration of M_x molecule, which C is the total weight concentration of the all-polymer molecules and you can seek the help of this relationship w_x is equal to C_x over C and C_x is the $N_x M_x$. Now, since the amount of light scattered by a polymer solution increases with molecular weight this method becomes more accurate for higher molecular weights. Now, there is no upper limit for the molecular weight that can be accurately measured except the limit imposed by

the insolubility of the polymer. So, the lower limit of average molecular weight by the light scattering method is close to 5000 to 10000. Now, below this molecular weight range, the amount of scattered light is too small to measure accurately.

MOLECULAR WEIGHT

- M_w can also be defined as


$$\bar{M}_w = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

where c_x is the weight concentration of M_x molecules, c is the total weight concentration of all the polymer molecules, and the following relationships hold:

$$w_x = \frac{c_x}{c}$$


$$c_x = N_x M_x$$

$$c = \sum c_x = \sum N_x M_x$$


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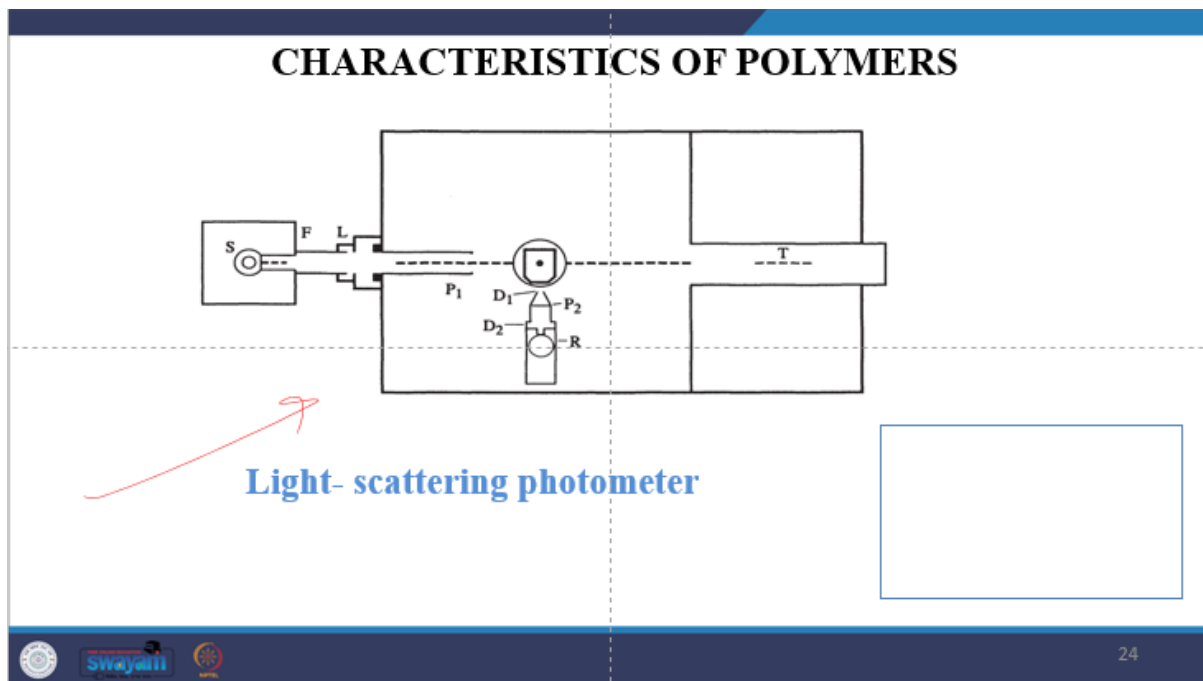
MOLECULAR WEIGHT

- Since the amount of light scattered by a polymer solution increases with molecular weight, this method becomes more accurate for higher polymer molecular weights.
- There is no upper limit to the molecular weight that can be accurately measured except the limit imposed by insolubility of the polymer.
- The lower limit of M_w by the light scattering method is close to 5000–10,000.
- Below this molecular weight, the amount of scattered light is too small to measure accurately.


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This is the typical diagram of a light scattering photometer which is very common. Now solution viscosity is also useful for molecular weight measurement. Now, viscosity like light scattering is greater for the large-size polymer molecules than for smaller ones. Now the solution viscosity does not measure the weight average molecular weight since the exact dependence on the solution viscosity on molecular weight is not exactly the same as light scattering. Now solution viscosity measures the viscosity of average molecular weight and is referred to as mV .

So, you can determine the viscosity average molecular weight through this mathematical formula. Here, this A is constant, and the viscosity and average molecular weight are equal when A is unity. Now this viscosity's average molecular weight is less than weight average molecular weight of most polymers. Since this is A, is usually ranges from 0.



5 to 0.9. Now viscosity of the average molecular weight is much closer to weight average molecular weight than the number average molecular weight and usually within 20% of weight average molecular weight. The value of "a" is dependent on the hydrodynamic volume of the polymer and the effective volume of the solvated polymer molecules in solution and varies with polymer solvent and temperature. So, these three are the essential parameters. More than one average molecular weight is usually required to reasonably characterize a polymer sample. So, there is no such need for a mono dispersed product like one composed of the molecules whose molecular weight weights are all the same for which all three average molecular weights are the same.

MOLECULAR WEIGHT

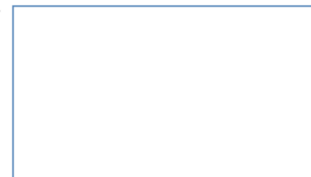
- Solution viscosity is also useful for molecular-weight measurements. Viscosity, like light scattering, is greater for the larger-sized polymer molecules than for smaller ones.
- However, solution viscosity does not measure M_w since the exact dependence of solution viscosity on molecular weight is not exactly the same as light scattering.
- Solution viscosity measures the viscosity-average molecular weight M_v defined by

$$\bar{M}_v = \left[\sum w_x M_x^a \right]^{1/a} = \left[\frac{\sum N_x M_x^{a+1}}{\sum N_x M_x} \right]^{1/a}$$



MOLECULAR WEIGHT

- where a is a constant. The viscosity- and weight-average molecular weights are equal when a is unity.
- M_v is less than M_w for most polymers, since a is usually in the range 0.5–0.9.
- However, M_v is much closer to M_w than M_n , usually within 20% of M_w .
- The value of a is dependent on the hydrodynamic volume of the polymer, the effective volume of the solvated polymer molecule in solution, and varies with polymer, solvent, and temperature.



So, this situation is quite different for a poly-disperse polymer where all three molecular weights are different. Now, for polydispersed polymers the differences between the average molecular weight increasing as the molecular weight distribution broadens. So, weight average molecular weight is greater than the viscosity average molecular weight which is also greater than the number average molecular weight. Now, this is the typical polymer sample that will have a molecular weight distribution, which is shown in the figure, and the approximate positions for the different average molecular weights are indicative in the distribution curve. You see, this is the weight fraction and a molecular weight.

MOLECULAR WEIGHT

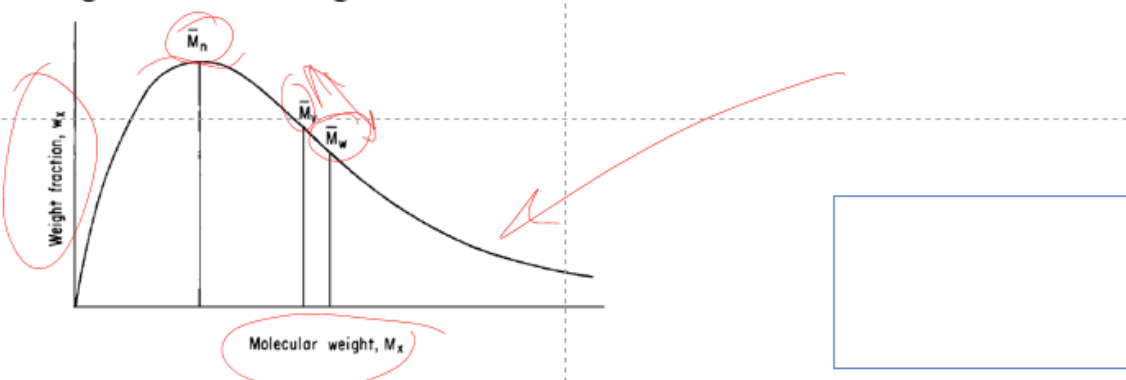
- For a polydisperse polymer with the differences between the various average molecular weights increasing as the molecular-weight distribution broadens.

$$\bar{M}_w > \bar{M}_v > \bar{M}_n$$

So, the maxima are approach with the number average molecular weight and viscosity average and weight average molecular weight are a bit closer. So, for most practical purposes, one usually characterizes the molecular weight for a polymer sample by measuring the number of average molecular weight and either weight average molecular weight or viscosity average molecular weight. Now, viscosity average molecular weight is commonly used as a close approximation of weight average molecular weight, which here you can see. In most instances, one is concerned with the number average molecular weight and weight average molecular weight of a polymer sample. Now this one, the number average molecular weight, is biased towards the lower molecular weight fraction while the latter is based on the high molecular weight fraction.

MOLECULAR WEIGHT

A typical polymer sample will have the molecular-weight distribution shown in figure. the approximate positions of the different average molecular weights are indicated on this distribution curve.



So the value of weight average molecular weight and number average molecular weight would be unity for a perfectly mono-dispersed polymer, and the ratio is greater than unity for all actual polymers

and increases with the increase, increasing polydispersity. The characterization of the polymer by number average molecular weights alone without regard to the polydispersities can be extremely misleading because it will not give complete information. Most polymer properties, such as strength, and melt viscosity are determined primarily by the size of the molecule that makes up the bulk of the sample by weight. Now the polymer properties are much more dependent on the larger-sized molecule in a sample than on the smaller ones. So, let us take an example: the hypothetical mixture containing 95% by weight of molecules of molecular weight, say 10,00, and 5% of molecules of molecular weight of, say, 100.

MOLECULAR WEIGHT

- For most practical purposes, one usually characterizes the molecular weight of a polymer sample by measuring M_n and either M_w or M_v .
- M_v is commonly used as a close approximation of M_w , since the two are usually quite close (within 10–20%).
- Thus in most instances, one is concerned with the M_n and M_w of a polymer sample.
- The former is biased toward the lower-molecular-weight fractions, while the latter is biased toward the higher-molecular-weight fractions.

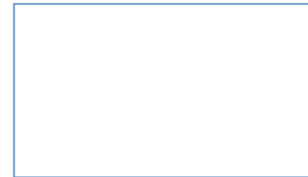
MOLECULAR WEIGHT

- The value of M_w/M_n would be unity for a perfectly monodisperse polymer.
- The ratio is greater than unity for all actual polymers and increases with increasing polydispersity.
- The characterization of a polymer by M_n alone, without regard to the polydispersity, can be extremely misleading, since most polymer properties such as strength and melt viscosity are determined primarily by the size of the molecules that make up the bulk of the sample by weight.

MOLECULAR WEIGHT

$P_2 - - P_n$

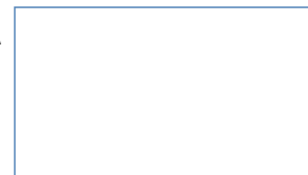
- Polymer properties are much more dependent on the larger-sized molecules in a sample than on the smaller ones.
- Thus, for example, consider a hypothetical mixture containing 95% by weight of molecules of molecular weight 10,000, and 5% of molecules of molecular weight 100. (The low-molecular-weight fraction might be monomer, a low-molecular-weight polymer, or simply some impurity.)
- In addition to the different average molecular weights of a polymer sample, it is frequently desirable and necessary to know the exact distribution of molecular weights.



The lower molecular weight fraction might be a monomer, a low molecular weight polymer, or simply some impurities like we discussed that P_2, P_3 like this up to P_n . In addition to the different average molecular weights of a polymer sample, it is frequently desirable and necessary to know the exact distribution of molecular weight. We have already discussed that there is a usual molecular weight range for which any given polymer property will be optimum for a particular application. So, you cannot go on increasing the molecular weight because some of the properties may get reduced, or sometimes the processability may be very difficult. So, the polymer sample containing the greatest percentage of polymer molecules of the size is the one that has the optimum value of the desired properties, and these desired properties attribute the processability aspect to the other aspect which can be which can make that particular polymer useful.

MOLECULAR WEIGHT

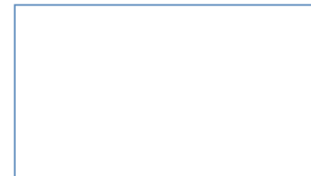
- As indicated previously, there is usually a molecular weight range for which any given polymer property will be optimum for a particular application.
- The polymer sample containing the greatest percentage of polymer molecules of that size is the one that will have the optimum value of the desired property.
- Since samples with the same average molecular weight may possess different molecular weight distributions, information regarding the distribution allows the proper choice of a polymer for optimum performance



Since the sample with the same average molecular weight may possess different molecular weight distributions information regarding the distribution allows the proper choice of a polymer for optimum performance. Various methods have been used in the past to determine the molecular weight distribution of a polymer sample. This includes fractional extraction and fractional precipitation. These methods which we discussed are laborious and determination of the molecular weight distribution and not routinely performed. So once the size exclusion chromatography or gel permeation chromatography these techniques developed, and apart from this, the availability of various automated commercial instruments has changed the entire situation, and now we can precisely predict the different range of molecular weight for a particular polymer sample.

MOLECULAR WEIGHT

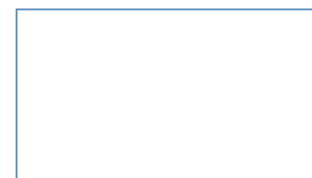
- Various methods have been used in the past to determine the molecular weight distribution of a polymer sample, including fractional extraction and fractional precipitation.
- These methods are laborious and determinations of molecular weight distributions were not routinely performed.
- However, the development of **size exclusion chromatography (SEC)**, also referred to as **gel permeation chromatography (GPC)** and the availability of automated commercial instruments have changed the situation.



MOLECULAR WEIGHT

- Size exclusion chromatography involves the permeation of a polymer solution through a column packed with microporous beads of crosslinked polystyrene.
- The packing contains beads of different-sized pore diameters.
- Molecules pass through the column by a combination of transport into and through the bead and through the interstitial volume (the volume between beads).

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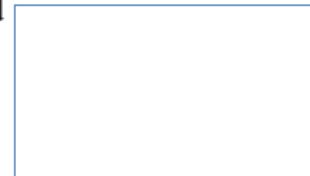


Now, the size exclusion chromatography involves the permeation of a polymer solution through a column packed with microporous beads of cross-linked polystyrene. The packing contains beads of

different sizes of pore diameters like small beads. The molecules pass through the column by the combination of the transport into or through beads and through the interstitial volume this volume between the beads is the closely packed beads, and this is called the interstitial volume, this space between beads. Now molecules that penetrate or penetrate the beads are slowed down more in moving through the column than the molecules that do not penetrate the beads in other words transport through the interstitial volume is faster than through the pores. Now the distribution of molecular weight in a typical polymer sample is sometimes referred to as a small-size polymer molecule they penetrate all the beads in the column since the molecular size that their hydrodynamic volume is smaller than the pore size of the beads with a smaller size in that case these beads occur these acts as a mesh to screen out that smaller molecular weight polymers.

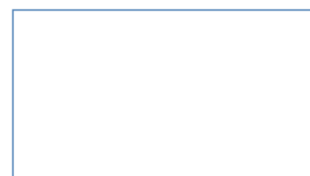
MOLECULAR WEIGHT

- Molecules that penetrate the beads are slowed down more in moving through the column than molecules that do not penetrate the beads; in other words, transport through the interstitial volume is faster than through the pores.
- Distribution of molecular weights in a typical polymer sample.
- The smaller-sized polymer molecules penetrate all the beads in the column since their molecular size (actually their hydrodynamic volume) is smaller than the pore size of the beads with the smallest-sized pores.



MOLECULAR WEIGHT

- A larger-sized polymer molecule does not penetrate all the beads since its molecular size is larger than the pore size of some of the beads.
- The larger the polymer molecular weight, the fewer beads that are penetrated and the greater is the extent of transport through the interstitial volume.
- The time for passage of polymer molecules through the column decreases with increasing molecular weight.



A larger size molecule does not penetrate all the beads since the molecular size is larger than the pore size of some of the beads. The larger the polymer molecule weight, the fewer beads that are penetrated and the greater the extent of transport through the interstitial volume. So, the time of passage of the molecules through the column decreases with the increasing molecular weight because of the heavy character that is screened out. The use of an appropriate detector is very important in detecting things, and the reflective index viscosity light scattering these are measures the amount of polymer passing through the column as a function of time. So not only does the SCC yield the molecular weight distribution but the number average and weight average also the viscosity average are also calculated in situ.

MOLECULAR WEIGHT

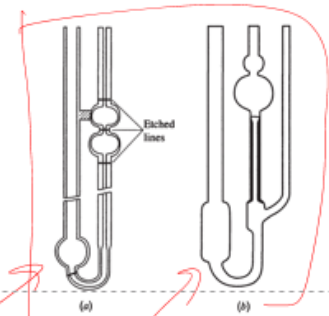
- The use of an appropriate detector (refractive index, viscosity, light scattering) measures the amount of polymer passing through the column as a function of time.
- Not only does SEC yield the molecular weight distribution, but M_n and M_w (and also M_v if α is known) are also calculated automatically.
- SEC is now the method of choice for measurement of M_n and M_w since the SEC instrument is far easier to use compared to methods such as osmometry and light scattering.

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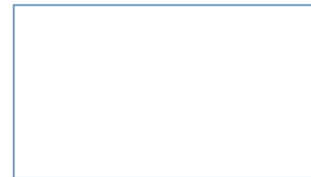
Size exclusion chromatography is now the method of choice for the measurement of number average and a weight average molecular weight. Now, this size exclusion chromatography instrument is far easier to use compared to the methods that were used, like osmometry and light scattering. Another method that is being widely used for the measurement of molecular weight is the measurement of viscosity. There are different types of viscometers available. This is done by measuring the viscosity behavior of a polymer in a dilute solution, and these measurements are usually made at constant temperature in a capillary viscometer. These are the capillary viscometers listed. This one is the Oswald viscometer, and this is the Abell-Houdt viscometer.

MOLECULAR WEIGHT

- One of the most widely used and popular of these techniques is the measurement of **viscosity**.
- This is done by measuring the viscosity behavior of a polymer in a dilute solution. These measurements are usually made (at constant temperature) in capillary viscometers.
- (a) Ostwald-Fenske, (b) Ubbelohde



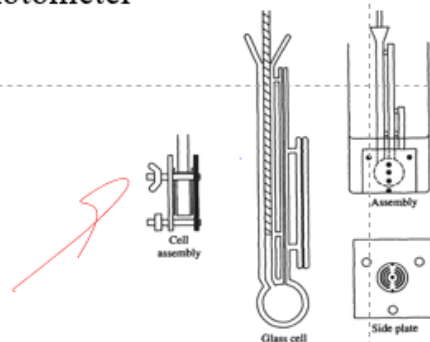
Capillary viscometers



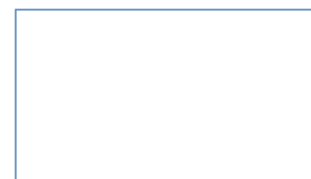
Other widely used technique for measuring molecular weight is the osmotic and light scattering method. Now this osmotic method they are carried out in the units which is shown here. The next is the light scattering method used in the light scattering photometer. Now this is the Zimm-Myerson osmometer.

MOLECULAR WEIGHT

Other widely used techniques for measuring molecular weight are **osmotic** and **light-scattering** methods. The former are carried out in units of the type shown in below figure, whereas the latter are measured in a light-scattering photometer



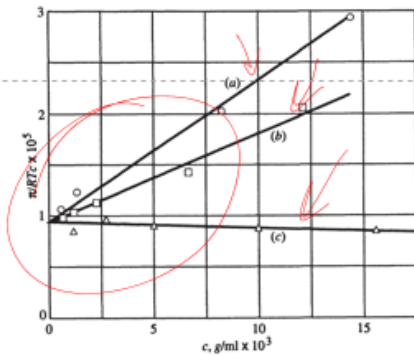
Zimm-Myerson Osmometer



Now, the procedure is quite simple. It is used to determine the molecular weight to carry out the test at various concentration levels and then extrapolate the data to the zero concentration like here. So, in this way, you can calculate how this is the plot for the molecular weight determination of the osmotic pressure for nitrocellulose in acetone, methanol, and nitrobenzene. This is the plot for the molecular weight determination of the cellulose acetate fraction by light scattering. Here, you see the concentration, and this is this one. Now, the intercept of osmotic pressure here you see data.

MOLECULAR WEIGHT

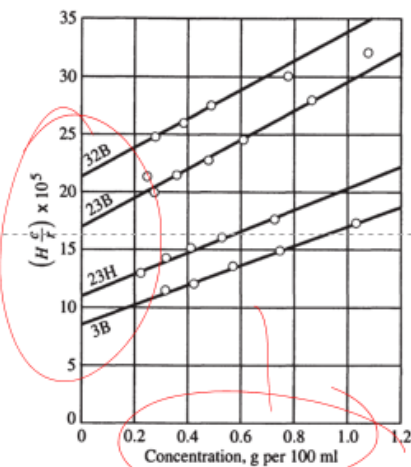
The procedure used to determine molecular weight is to carry out tests at various concentration levels and then to extrapolate the data to zero concentration, shown in plots given below:



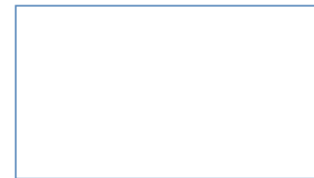
- Plot for molecular weight determination by osmotic pressure for nitrocellulose in (a) acetone, (b) methanol, and (c) nitrobenzene



MOLECULAR WEIGHT



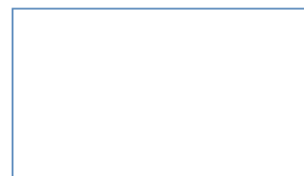
Plot for molecular weight determination of cellulose acetate fractions by light scattering



The osmotic pressure divided by the concentration gives the RT over M_n is the number where M_n is quite obvious. This is the number average molecular weight. Likewise, the HC or R intercepts, where H is the constant, C is the concentration, and T is the turbidity and this gives the value of 1 over weight average molecular weight. Now, let us talk about the molecular weight distribution. In brief, we discussed why we are more worried about this particular thing because, in a particular mass, you will find the monomer, you may find dimer, you may find trimer, and you may find different types of a polymer.

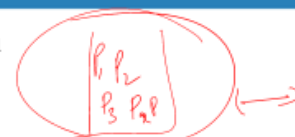
MOLECULAR WEIGHT

- The intercept for the osmotic pressure data (osmotic pressure π divided by concentration c) gives RT/M_n , where M_n is the number average molecular weight.
- Likewise, the H_c/r intercept, where H is a constant, c the concentration, and T the turbidity, gives a value of $1/M_w$, where M_w is weight average molecular weight.

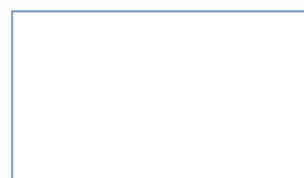


So that is why it represents the molecular weight distribution. So, the average molecular weights which we discussed a couple of slides ago, characterize the average degree of polymerization for the mass. It is also important in many instances to know the distribution of the molecular weights in the sample. Now, such distribution this gives the frequency of occurrence of a certain degree of polymerization. Now, such distribution of the frequency of occurrence of a certain degree of polymerization.

Molecular weight distribution

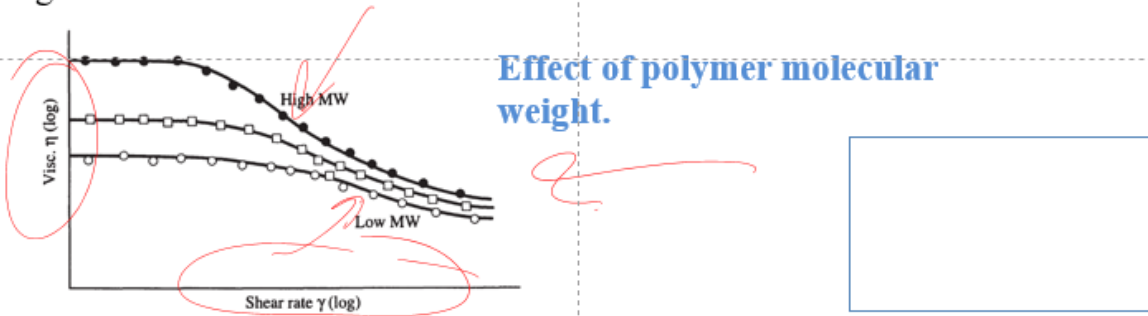


- Polymers are materials that have a variety of molecular weights present in any given mass.
- The average molecular weights, previously discussed, characterize the average degree of polymerization for that mass.
- It is also important in many instances to know the distribution of the molecular weights in the sample.
- Such distributions give the frequency of the occurrence of a certain degree of polymerization.



Molecular weight distribution

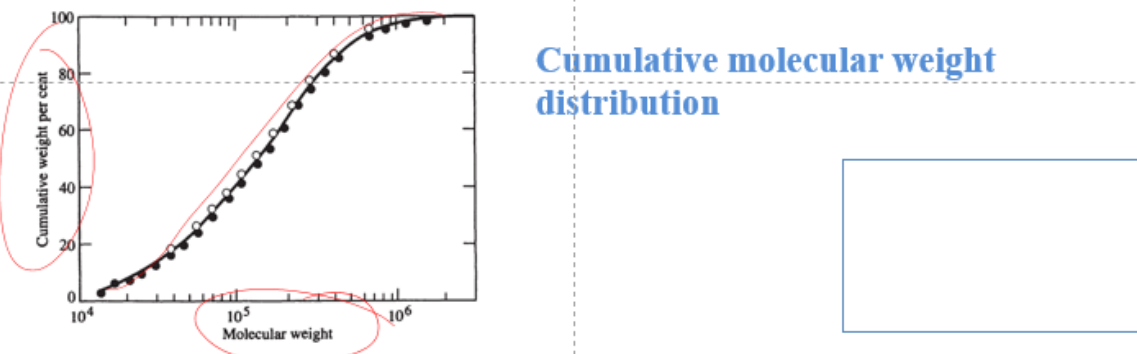
Such distributions give the frequency of the occurrence of a certain degree of polymerization. Typical distribution curves for two polymers are shown in fig. below.



Now, here you see the typical distribution curve for two polymers. This is the high molecular weight, and this is the low molecular weight, and this is the viscosity and the shear rate. You can see the effect of molecular weight on different molecules. Another method of presenting molecular weight distribution is by the cumulative curve. Here, you see that this is the molecular weight and the cumulative weight percent, and you can draw the curve like this, and you can predict the behavior of the polymer.

Molecular weight distribution

Another method of presenting molecular weight distributions is by a cumulative curve.



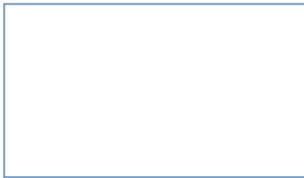
There are a number of methods for determining the distribution of molecular weights. The principal methods they are fractionation, sedimentation, GPC or gel permeation chromatography, or rapid estimates. The fractionation consists of separating a polymer solution into separate groups by


fractional precipitation and then measuring the mass and average molecular weight of the fraction. The sedimentation uses the ultra-centrifuge to determine the number of different molecular weights.

Molecular weight distribution

There are a number of methods for determining the distribution of molecular weights. The principal methods are:

- Fractionation
- Sedimentation
- Gel permeation chromatography
- Rapid estimates

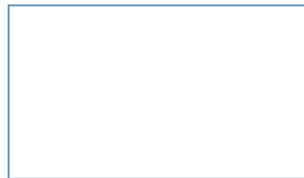



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Molecular weight distribution

Fractionation
It consists of separating a polymer solution into separate groups by fractional precipitation and then measuring the mass and average molecular weight of the fractions.

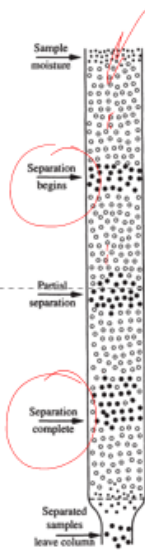
Sedimentation
The sedimentation use the ultracentrifuge to determine a number of different molecular weights



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GPC this is this we have already discussed. These polymer samples are separated by the size of the molecules. Here you see the different beads and you see that the separation begins, and here you find the separation completed. The separation is accomplished by using the beads of a rigid and obviously these are some sort of polymers and these are the porous gel. These pores are about the same size as the polymer molecule dimension. Now methods are also available for the rapid estimation of a polymer molecular weight distribution.

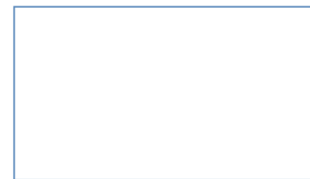
Molecular weight distribution



Gel permeation chromatography

The polymer samples are separated by size of molecule. The separation is accomplished by using beads of a rigid, porous gel whose pores are about the same size as polymer molecule dimensions.

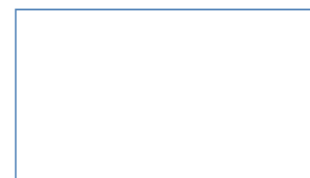
Schematic diagram of gel permeation chromatographic unit



Now these methods include the swelling in which the amount of polymer precipitated with respect to the non-solvent added gives this gives the cumulative distribution curve like higher molecular weight first precipitates out with the non-solvent addition. Then, turbidimetric titration uses the turbidity induced by the non-solvent addition as a measure of molecular weight distribution. So, in this particular segment, we discussed about because see molecular weight plays a very vital role in deciding the properties of polymer. So how we can determine the molecular weight, what is the role of molecular weight distribution and what are the different types of molecular weights? So, in this particular chapter, we have discussed all about this particular thing.

Molecular weight distribution

- Methods are also available for rapidly estimating polymer molecular weight distribution.
- These methods include swelling, in which the amount of polymer precipitated vs nonsolvent added gives a cumulative distribution curve (i.e., higher molecular weights first precipitate out with nonsolvent addition) .
- Turbidimetric titration, which uses turbidity induced by nonsolvent addition as a measure of molecular weight distribution.



References

- Richard G. Griskey Ph.D., P.E. (auth.) - Polymer Process Engineering- Springer Netherlands (1995)

For your convenience, we have enlisted a couple of references. You can use these references as per your need. Thank you very much. you