**Introduction to Polymer Science**
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**Lecture - 05**
**Molecular Weight, Big Picture of Polymer Science, Common Polymers**

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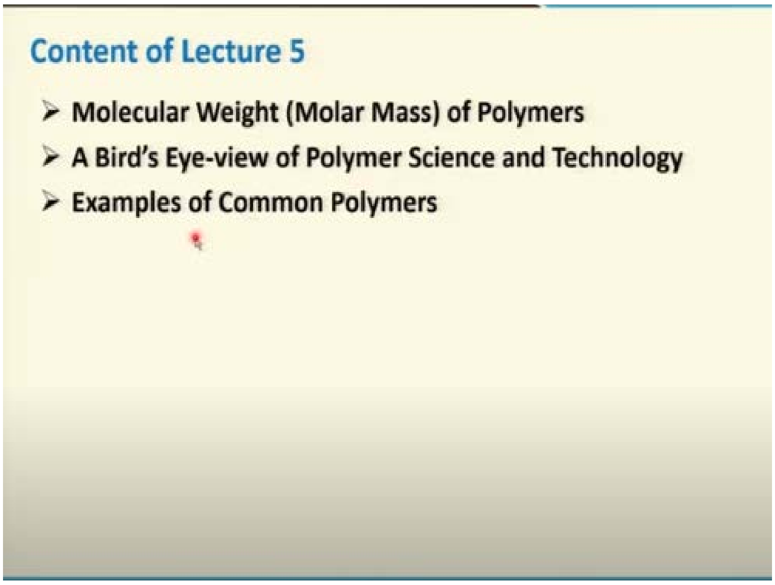


Welcome back. In this lecture 5, we will discuss polymer molecular weights and also give a bird's eye view of polymer science and technology give few examples of common polymers. Let us begin with the molecular weights of polymers.

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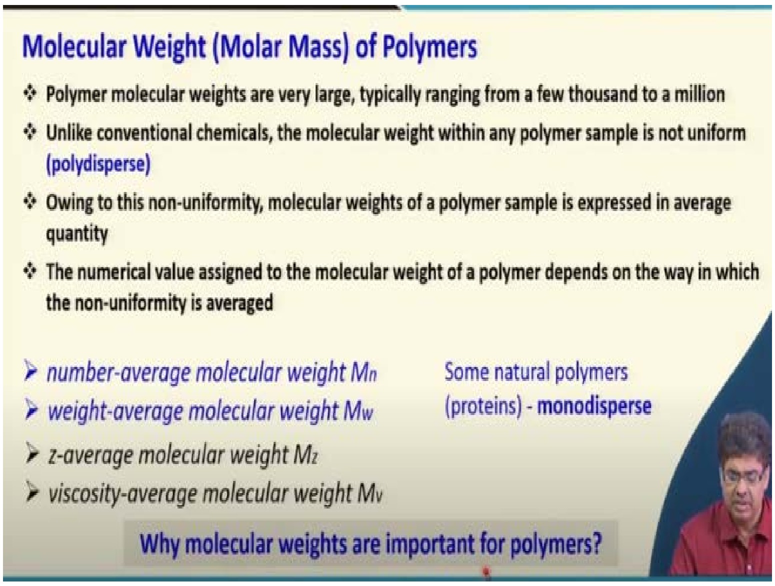

The molecular weight is used synonymously as molar mass. Generally, molecular weight has no unit, but the molar mass is generally expressed as g/mole. Molar mass is probably the more accurate way of expressing molecular weights of any compound including polymers. Polymers are expressed in molecular weight without any unit. The molecular weight of polymer molecules is very large, typically in the range of few thousand to a million. Now unlike conventional chemicals, the molecular weights of a polymer in a particular sample are different. For example, if we take a benzene, all the molecules of benzene in that particular sample are the same, but in the case of a polystyrene sample, the molecular weights of the chains of polystyrene molecules are not the same. They are not uniform and it is called a polydisperse sample. Now, because of this non-uniformity of molecular weights in a particular sample, the molecular weight of the polymer is generally expressed as average molecular weight. The average can be done in various ways and depending upon the way, the name changes. So the numerical value assigned to the molecular weight of polymer depends on how this non-uniformity is averaged. These are the typical four average molecular weights reported in the literature of which this number average molecular weight and weight average molecular weights are most important and most frequently reported.

Almost all synthetic polymers are polydisperse in nature, there is some exception in the case of natural polymers like in protein samples, all the polymer chains or macromolecules chains are having the same molecular weight.

Now, what is the importance of polymer molecular weight? Why should we bother about molecular weights of polymer?

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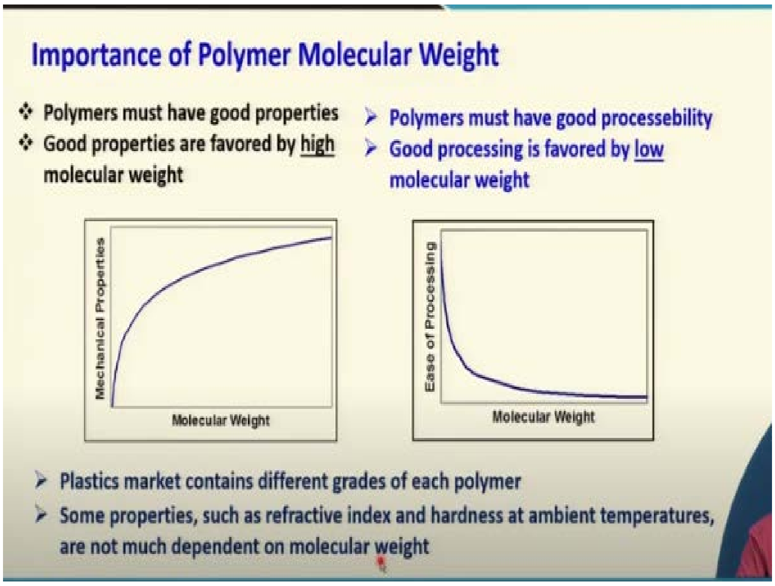


For any application, we always look for good properties and there is no exception for polymer-based products. So the polymer-based producsts must have good properties and good properties in most cases come from the high molecular weight of polymer molecules. For example, from the plot of mechanical properties versus polymer molecular weight, we can see that there is a sharp increase in the mechanical properties with molecular weight and it levels off at high molecular weight.

Simultaneously, to make the desired products, the polymer samples should undergo a processing step in which polymer flow is a very important property because polymers are generally melted and molded a particular shape to the final product. So good processability is generally favored by low molecular weight. So, ease of processing is inversely related to molecular weights. Higher is the molecular weight, lower is the ease of processing. So this is a dilemma for a polymer engineer, whether to synthesize a polymer of high molecular weight or low molecular weight. Depending upon the final application and property requirement, the plastics market contains different grades of each polymer and different grades in most cases have a different molecular weight of polymer chains. On the basis of final application, one can choose between these different grades and finally get the product from this polymer sample. Of course, there are few properties like refractive index and hardness. At ambient temperatures, they do not significantly depend on the molecular weights of polymers.

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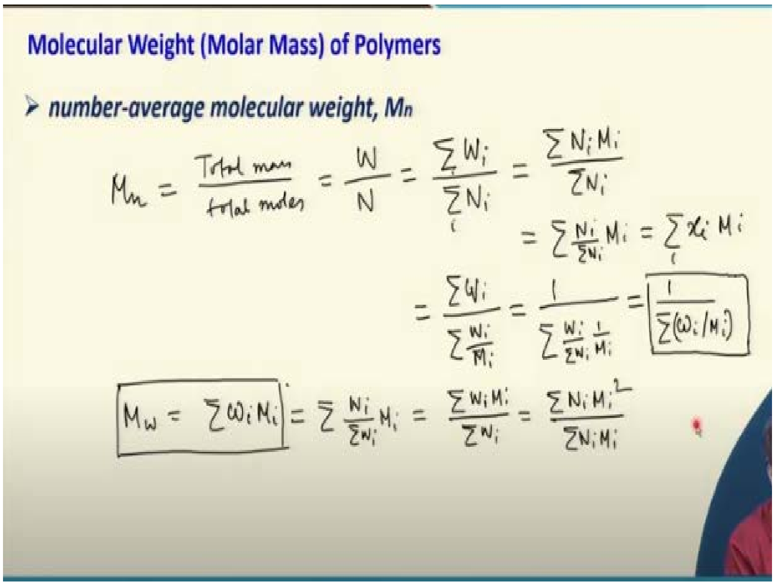


To quantify the different molecular weights, there are different expressions For example, number-average molecular weight is just arithmetic averaging. So $M_n$ is given by W/N. W is the total mass, divided by the total number of moles N. So we can write it as-

$$M_n = \frac{W}{N} = \frac{\sum_i W_i}{\sum_i N_i} = \frac{\sum_i N_i M_i}{\sum_i N_i} = \sum_i \frac{N_i}{\sum N_i} Mi = \sum_i x_i M_i$$

$w_i$ is the weight of the sample having a molecular weight of $M_i$ and similarly, $N_i$ is the number of moles of polymer molecules having a molecular weight of $M_i$. Where $x_i$ is the mole fraction of the polymer molecules having a molecular weight of $M_i$.

Now we can also rearrange the weight of the particular sample divided by total weight which will give us the weight fraction.

$$\sum_i x_i M_i = \frac{\sum_i w_i}{\sum_i \frac{w_i}{M_i}} = \frac{1}{\sum_i w_i / M_i}$$

So using this expression, we can calculate the number-average molecular weight.

Similarly, in the case of weight average molecular weight ($M_w$),

$$M_w = \sum w_i N_i = \sum \frac{w_i}{\sum w_i} M_i = \sum \frac{w_i M_i}{\sum w_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

So $w_i$, this is the weight of that particular sample having a molecular weight of $M_i$. So these are the expressions for $M_n$ and $M_w$. We always prefer to express molecular weight in terms of weight fraction because when we do a fractionation of a polymer sample, it is always better and easier to report the different fractions in terms of weight fraction rather than number fraction or mole fraction.

So that is why these expressions are useful and are typically used for determining polymer molecular weight.

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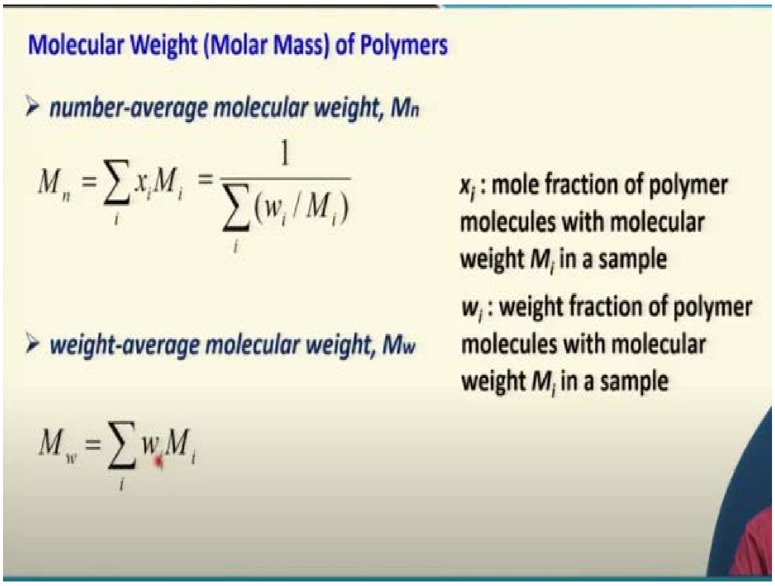


$M_n$ is given by $\sum_i x_i M_i$ where $x_i$ is the mole fraction of the polymer molecules with molecular weight $M_i$ in a sample. It can be rearranged to get where $w_i$ is the weight fraction of polymer molecule with a molecular weight of $M_i$ in a sample. And weight average molecular weight $M_w$ was expressed as $\sum_i w_i M_i$.

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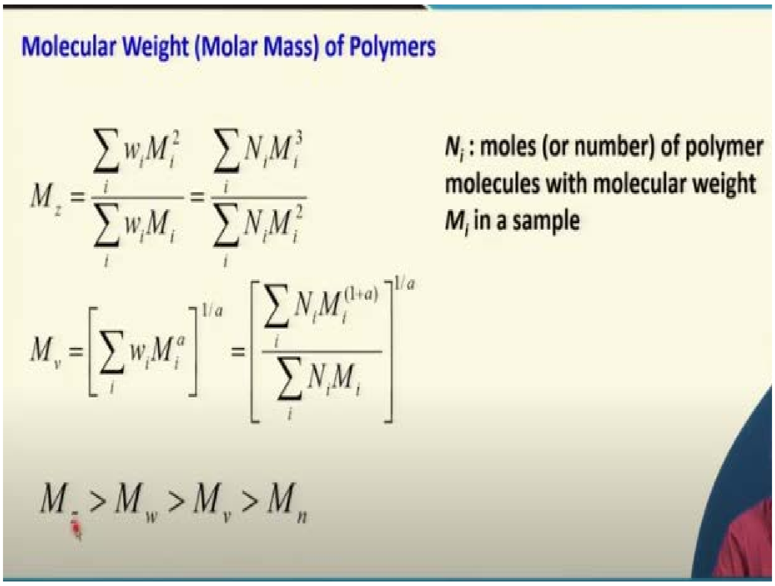

There are two more molecular weights one is Mz, and another one is Mv, the Mz can be expressed as,

$$M_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

$M_z$ is viscosity average molecular weight which is expressed by the expression-

$$M_Z = \left[\sum_i w_i M_i^a\right]^{1/a} = \left[\frac{\sum_i N_i M_i^{(1+a)}}{\sum_i N_i\, M_i}\right]^{1/a}$$

Again, these expressions are probably more useful because this is related to weight fraction rather than mole fraction. So, to determine the molecular weight of the polymer sample, these expressions are used.

In the expression, $N_i$ is the number of moles of polymer molecules with molecular weight $M_i$ in a particular sample and for any synthetic sample, $M_z > M_w > M_v > M_n$.

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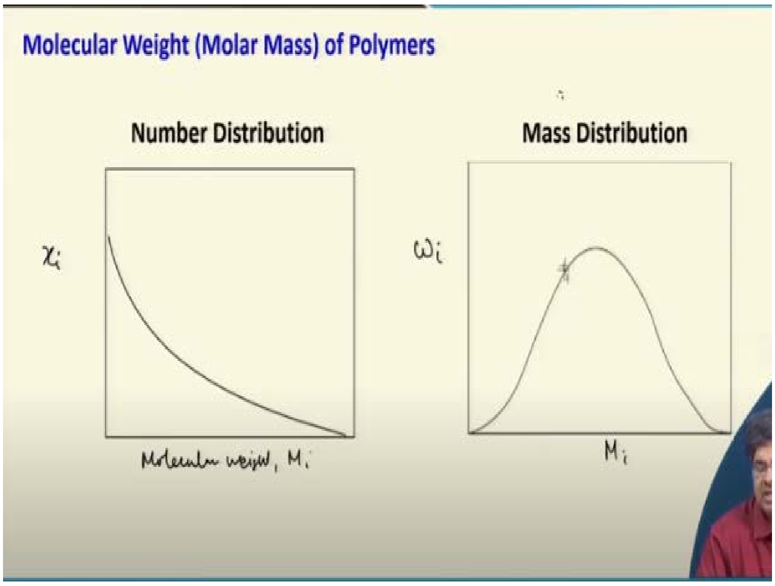


In a synthetic polymer or in any polymer sample, how the polymer chains are distributed in terms of their molecular weight? In number distribution, there is a number fraction or mole fraction ($x_i$) with a molecular weight of $M_i$. So, the plot between $x_i$ vs $M_i$ looks like that in a particular polymer sample, the lower molecular weights dominate by number. It is the lower molecular weights, which will have more numbers in that particular sample. If we talk about mass, then the plot of weight fraction ($w_i$) vs molecular weight of particular polymer ($M_i$) looks like the polymers having the lower molecular weight and the polymers having higher molecular weight are in low weight fraction in a particular sample. The polymers with intermediate molecular weight, dominate in terms of weight fraction.

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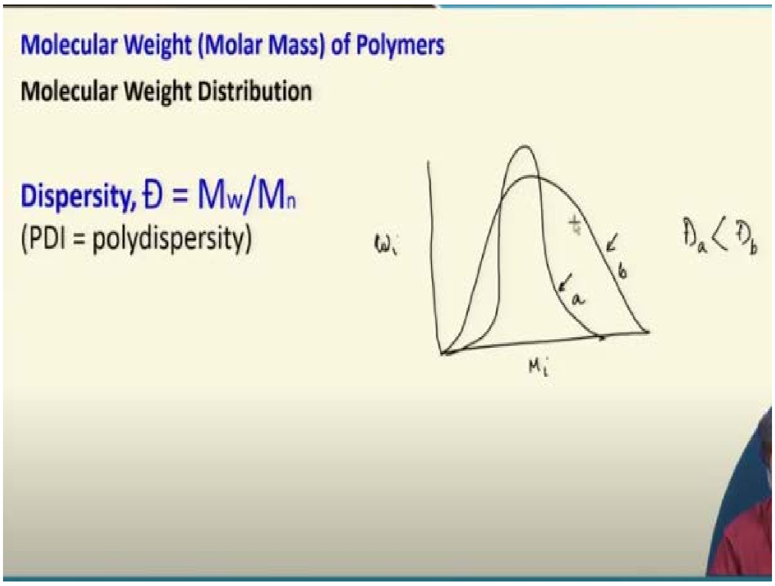


How to quantify these polymer distribution? It is very difficult to properly show the distribution but generally, it is shown as polydispersity index, expressd as Đ, which is equal to $M_w$ /$M_n$. The weight fraction vs molecular weight distribution of a polymer sample is a broader curve, then the dispersity Đ of this sample will be much higher compared to another sample. So if one is sample ‘a’ and another one is ‘b’, Đ of ‘a’ would be lower than Đ of sample ‘b’. This is a more standard way of expressing the breadth of polymer molecular weights present in a particular sample.

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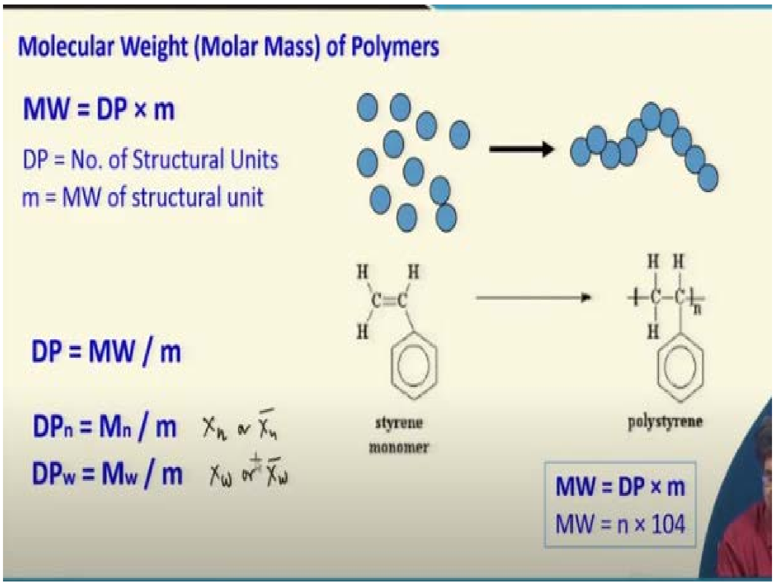


There is a relationship between the degree of polymerization and molecular weight. 'n' is the number of repeat units as well as the number of structural units. So 'n' is the degree of polymerization. So molecular weight is given by the degree of polymerization multiplied by the molecular weight of the structural unit or repeat unit,

$$MW = DP \times m$$

Where DP is the number of structural units and 'm' is the molecular weight of the structural unit. In the case of polystyrene, the molecular weight MW= (n×104) where 104 is the molecular weight of this particular unit.

Now, the degree of polymerization can be expressed as molecular weight divided by 'm' from this expression and because molecular weights are average molecular weights, so the degree of polymerization is also expressed as a different average degree of polymerization.

So if we use molecular weight as number-average molecular weight ($M_n$), then we call it number-average degrees of polymerization generally this is written as $X_n$ or $\bar{X}_n$. If we use $M_w$, weight-average molecular weight then we call this a weight-average degree of polymerization and represented it as $X_w$ or $\bar{X}_w$.

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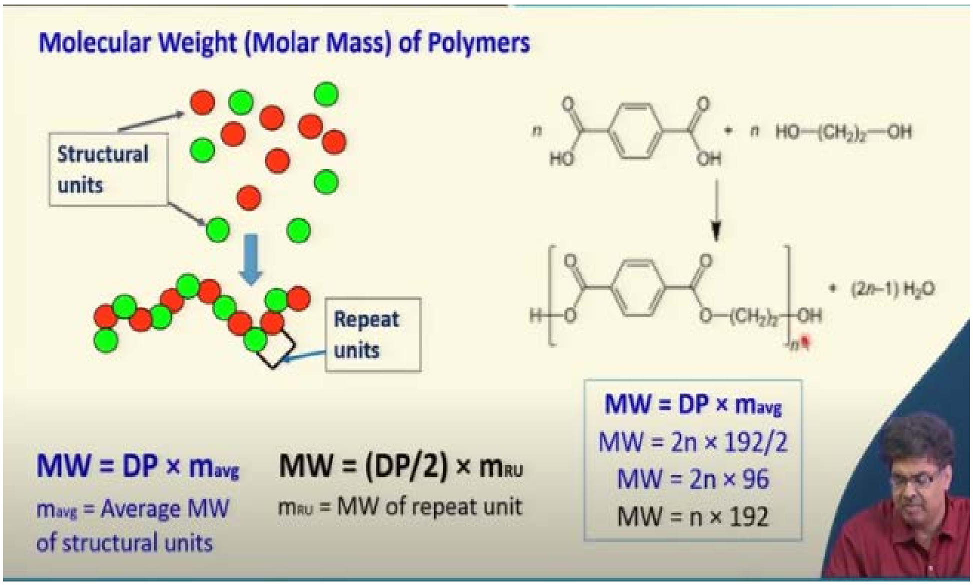


Now for a polymer, the molecular weight is given by

$$MW = DP \times m_{avg}$$

Where $m_{avg}$ is the average molecular weight of the structural unit which constitutes the polymer or it is half of the degree of polymerization multiplied by the molecular weight of the repeat unit i. e.

$$MW = (DP/2) \times m_{RU}$$

$m_{RU}$ is the molecular weight of the repeat unit. Since in the particular example, the molecular weight of the repeat unit is 192, so the molecular weight is DP × $m_{avg}$. So the degree of polymerization DP is in this case is, 2n× (192/2) = 2n ×96 or n×192.

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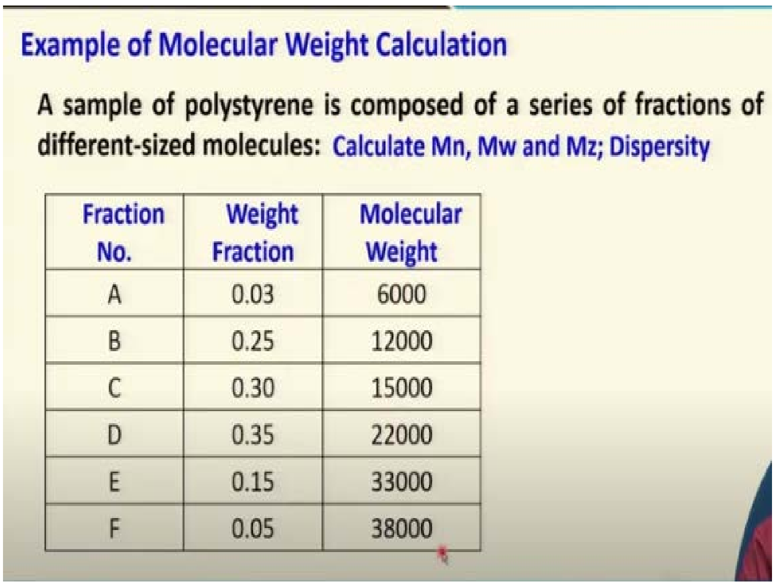


| Fraction No. | Weight Fraction | Molecular Weight |
|---|---|---|
| A | 0.03 | 6000 |
| B | 0.25 | 12000 |
| C | 0.30 | 15000 |
| D | 0.35 | 22000 |
| E | 0.15 | 33000 |
| F | 0.05 | 38000 |

This is the example where a polystyrene sample is composed of a series of fractions of different-sized molecules. So in this case, we get a continuous value of molecular weights and corresponding weight fractions. In a hypothetical situation, if we fractionate the sample and get these fractions which has these corresponding molecular weights then we need to know how to calculate the molecular weight for this particular sample.

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Example of Molecular Weight Calculation

| Weight Fraction | Molecular Weight | $\sum_i (w_i/M_i)$ | $\sum_i w_i M_i$ | $\sum_i w_i M_i^2$ |
|---|---|---|---|---|
| 0.03 | 6000 | $0.5 \times 10^{-5}$ | 180 | |
| 0.25 | 12000 | $2.08 \times 10^{-5}$ | 3000 | |
| 0.30 | 15000 | $2.00 \times 10^{-5}$ | 4500 | |
| 0.35 | 22000 | $1.59 \times 10^{-5}$ | 7700 | |
| 0.15 | 33000 | $0.45 \times 10^{-5}$ | 4950 | |
| 0.05 | 38000 | $0.13 \times 10^{-5}$ | 1900 | |
| | | $= 6.75 \times 10^{-5}$ | = 22,230 | |

So there is a table of data for weight fraction and corresponding molecular weights. So to find out $M_n$, we need to find out this particular value, weight fraction divided by the molecular weight of that particular sample or this particular fraction. So,

$$M_n = \frac{1}{\sum_i \left({}^{w_i}/_{M_i}\right)}$$

Similarly, for $M_w$,

$$M_w = \sum_i w_i M_i$$

Similarly for $M_z$,

$$M_z = \sum_i w_i M_i^2$$

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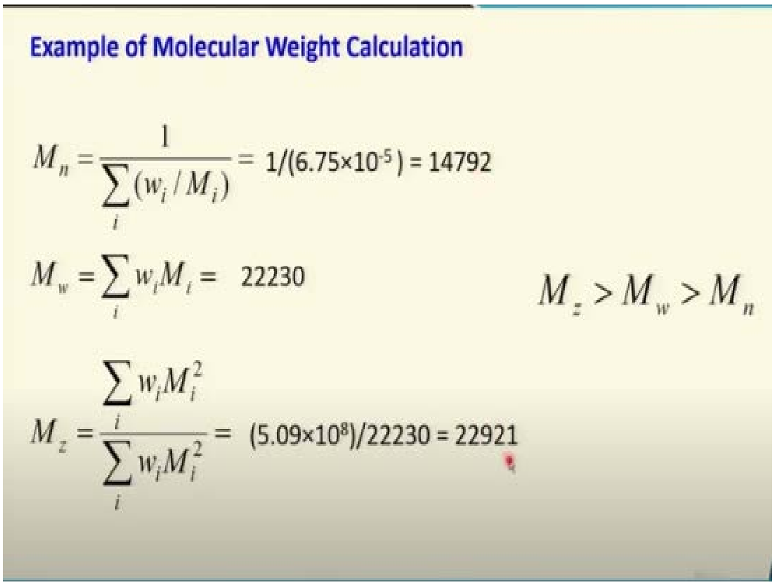


$M_n$, $M_w$ and $M_z$ can be calculated by these equations. The order of the molecular weight is, $M_z > M_w > M_n$. In practice when we report polymer molecular weight, we do not give very accurate numbers, but rather we round it off, since we cannot determine the molecule weights to such levels of accuracy.

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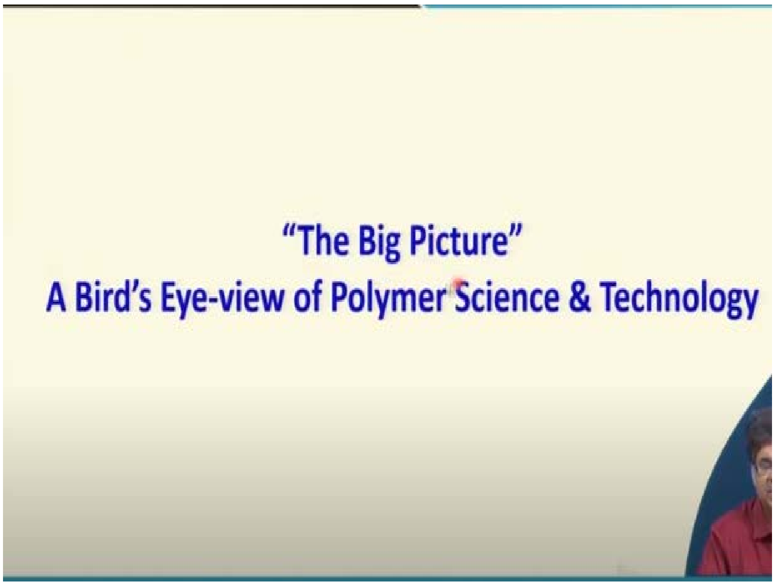


A Bird's eye view of polymer science and technology is how the polymer chain looks like in different life stages when we look at it from the top.

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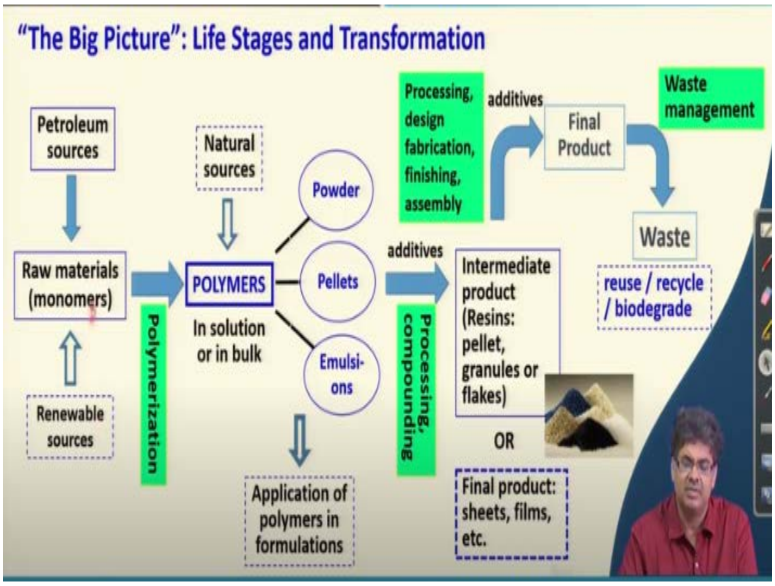


In the scheme, we observe that the sources of polymers can be natural resource or they can be synthesized from raw materials which are nothing but monomers. Now, from where do we get monomers? In few cases, we get it from renewable resources but in the majority of cases, we get from petroleum resources. The process of converting the monomers to polymers is called polymerization and we get the polymers in solution if we are doing the polymerization in a solution and if you are doing the polymerization without any solvent, then we get polymers in bulk.

Then, we isolate the polymers in the form of powder or pellets or sometimes in a heterogeneous form like emulsion. Now in some applications, these polymers are used in the formulation and are added with other ingredients to get the final products like paint or some medical applications like eye drops.

There are many other such examples where a polymer is one of the ingredients, along with other ingredients. So in this case, we use the polymers as an application of polymers in formulations but in most cases, after the isolation of the polymers, we go through another step, where we add additives like pigments or stabilizers. This process is called the processing step or compounding step where we get the intermediate products. Many companies which make polymers like DuPont or SABIC, actually sell polymers in this stage. Haldia Petrochemicals also makes this type of polymers and they sell these in the market.

So some small companies take these pellets and use them for further processing. Now in this particular processing or compounding step, we can also get the final product as sheets or films. However, in most cases, the intermediate products are sold like this in terms of granules or powder and then further additives are added and processing, fabrication, and finishing are done to get the final product. Now generally, these are done not in a typical polymer company but by original equipment manufacturer. After using, the polymeric part is discarded as waste, and where the waste management is required to be done properly. Ideally, we should be able to reuse or recycle the polymer products and if not, then it should be biodegradable. In the current scenario, the growing concern with polymers or plastics is because of the pollution created by them. So the main challenge of current polymer research is to find a proper way of handling the polymer waste either by recycling or by using a biodegradation procedure. There is another challenge also which is probably to a lesser extent than earlier, that is about the source of the monomers. Most of the monomers are sourced from raw materials, petroleum sources and these petroleum sources are getting depleted with time, so we should also look for finding monomers from renewable resources. Also currently, there are a lot of applications where petroleum resources are used. Petroleum sources are probably not depleting at that faster rate as it was thought to be earlier due to shifted focus to renewable energy resources. So at present, managing the waste is probably more challenging and more important than generating alternative renewable resources for monomers.

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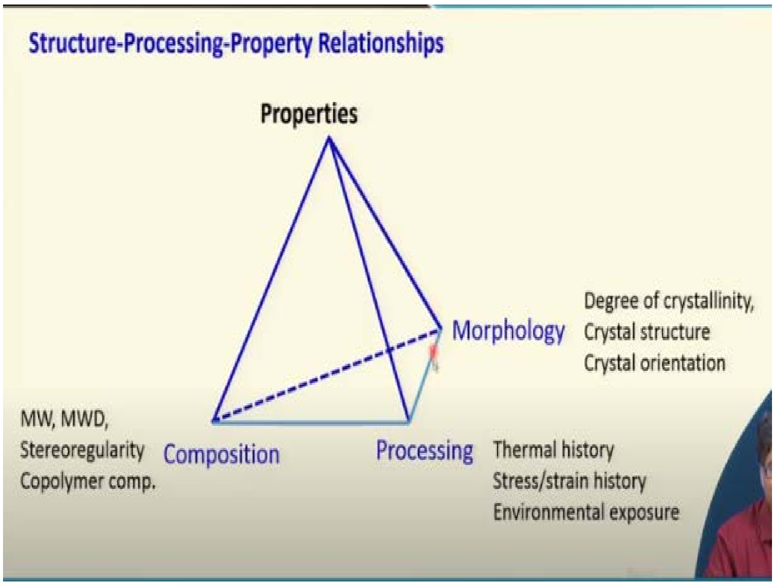


The final property of the products depends on three factors, one is the polymer composition i.e. the actual chemical structure, the molecular weight, molecular distributions, stereoregularity etc. Secondly, it depends on processing because processing involves a lot of thermal treatment. This is also a very important aspect of polymer properties. The last factor is the morphology of the polymer sample, which is determined by both composition and processing. These three properties can determine the final property of polymers.

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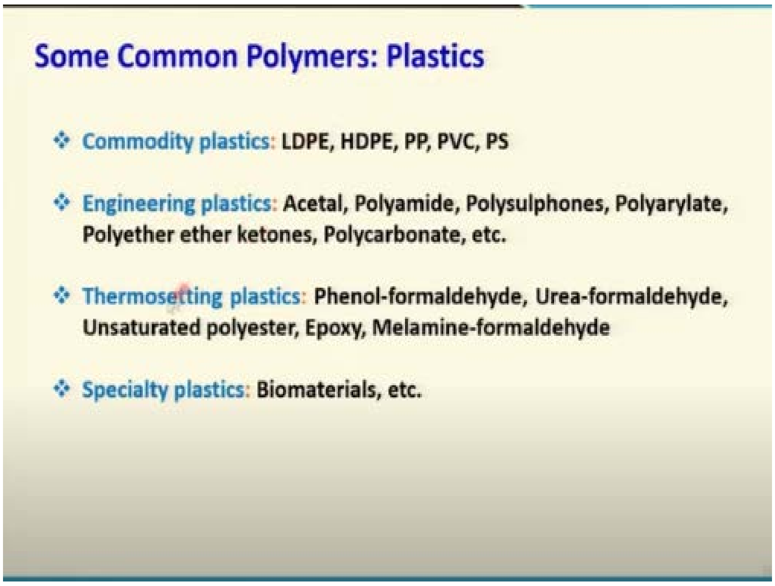


Now, there are some names and examples of commonly used plastics. For example, the most common plastics are commodity plastics, engineering plastics, thermosetting plastics, and some specialty plastics.

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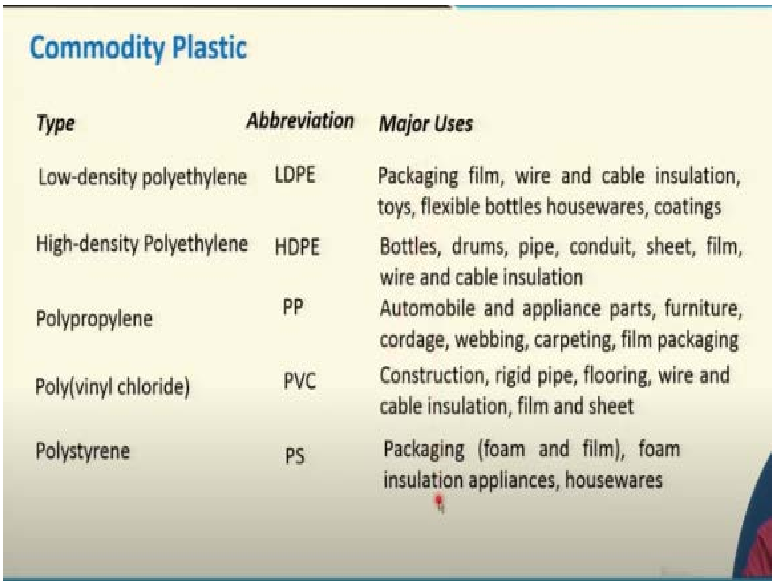
Commodity Plastic

| *Type* | *Abbreviation* | *Major Uses* |
|---|---|---|
| Low-density polyethylene | LDPE | Packaging film, wire and cable insulation, toys, flexible bottles housewares, coatings |
| High-density Polyethylene | HDPE | Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation |
| Polypropylene | PP | Automobile and appliance parts, furniture, cordage, webbing, carpeting, film packaging |
| Poly(vinyl chloride) | PVC | Construction, rigid pipe, flooring, wire and cable insulation, film and sheet |
| Polystyrene | PS | Packaging (foam and film), foam insulation appliances, housewares |

Commodity plastics are those which are used in a very bulk amount. For example, low-density polyethylene, high-density polyethylene, polypropylene, polyvinyl chloride, polystyrene, and some of the examples are listed here.

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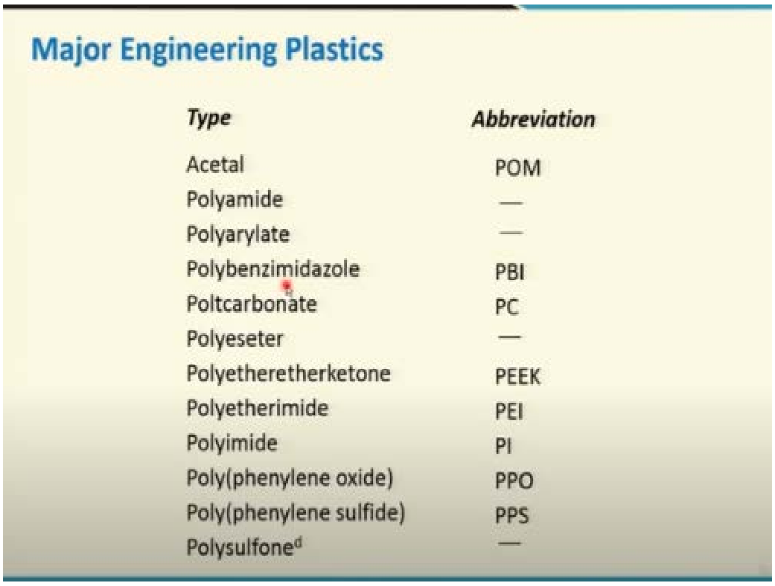

## Major Engineering Plastics

| Type | Abbreviation |
|---|---|
| Acetal | POM |
| Polyamide | — |
| Polyarylate | — |
| Polybenzimidazole | PBI |
| Poltcarbonate | PC |
| Polyeseter | — |
| Polyetheretherketone | PEEK |
| Polyetherimide | PEI |
| Polyimide | PI |
| Poly(phenylene oxide) | PPO |
| Poly(phenylene sulfide) | PPS |
| Polysulfone[d] | — |

The name of the major engineering plastics and their corresponding abbreviations are listed here. Engineering plastics means their applications in engineering and structural applications, not in a commodity items like household common applications. They are used in some engineering applications or structural applications.

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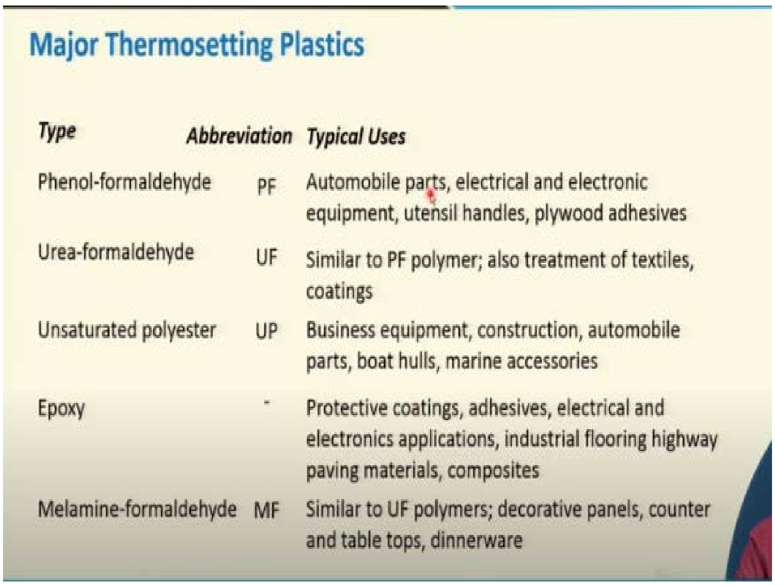

## Major Thermosetting Plastics

| Type | Abbreviation | Typical Uses |
|---|---|---|
| Phenol-formaldehyde | PF | Automobile parts, electrical and electronic equipment, utensil handles, plywood adhesives |
| Urea-formaldehyde | UF | Similar to PF polymer; also treatment of textiles, coatings |
| Unsaturated polyester | UP | Business equipment, construction, automobile parts, boat hulls, marine accessories |
| Epoxy | - | Protective coatings, adhesives, electrical and electronics applications, industrial flooring highway paving materials, composites |
| Melamine-formaldehyde | MF | Similar to UF polymers; decorative panels, counter and table tops, dinnerware |

Major thermosetting plastics are like phenol-formaldehyde urea-formaldehyde, unsaturated polyesters, epoxy, melamine-formaldehyde, and their typical uses are listed here.

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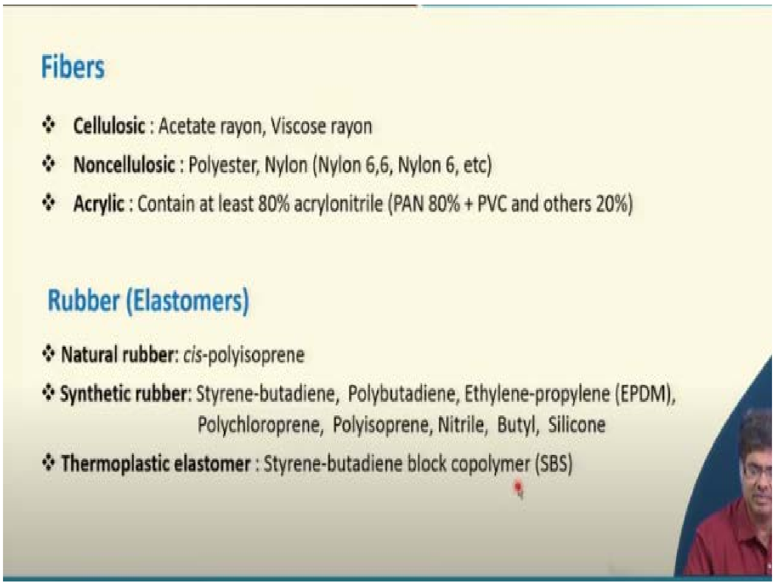


Other polymers are useful as fibers and rubbers or elastomers and some of the examples are given as cellulosic, noncellulosic like acetate rayon, polyesters, nylon as fibers. Acrylics fiber is also there. And rubber, natural rubber, cis-isoprene synthetic rubbers are also available. And thermoplastic elastomers are also there which are based on styrene-butadiene block copolymer.

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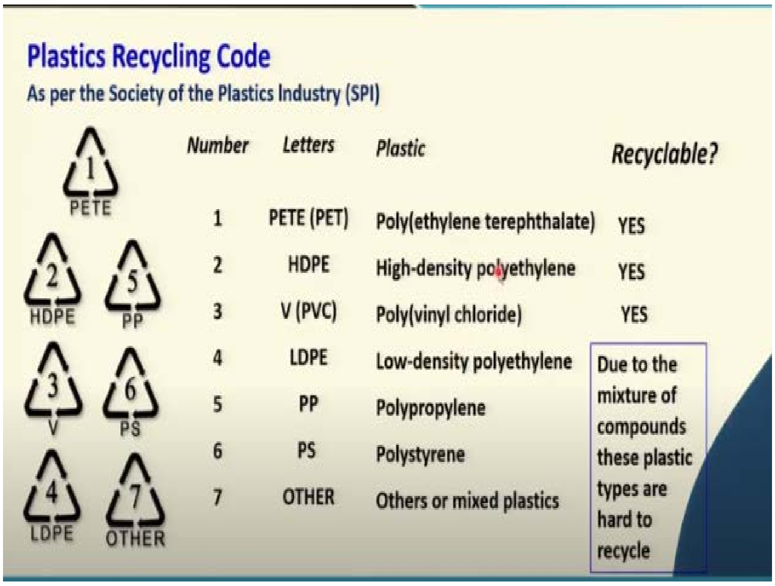

Now typically you may also come across polymer bags having this label. These labels are related to different polymers and related to the recycling code for the polymers as per the Society of Plastic industry. And this number corresponds to a particular polymer as 1 corresponds to recyclable PET, 2 corresponds to HDPE high-density polyethylene which is also recyclable, 3 corresponds to polyvinyl chloride which is also recyclable. Others are not, they are recycled but practically it is very difficult to do because they generally also have other ingredients. So basically it is very hard to recycle these 4 to 7 like LDPE, polypropylene, polystyrene, and other polymers.

So with this, we come to the end of this lecture 5. And the next lecture we will move to step-growth polymers, synthesis of step polymers by step-growth polymerization.