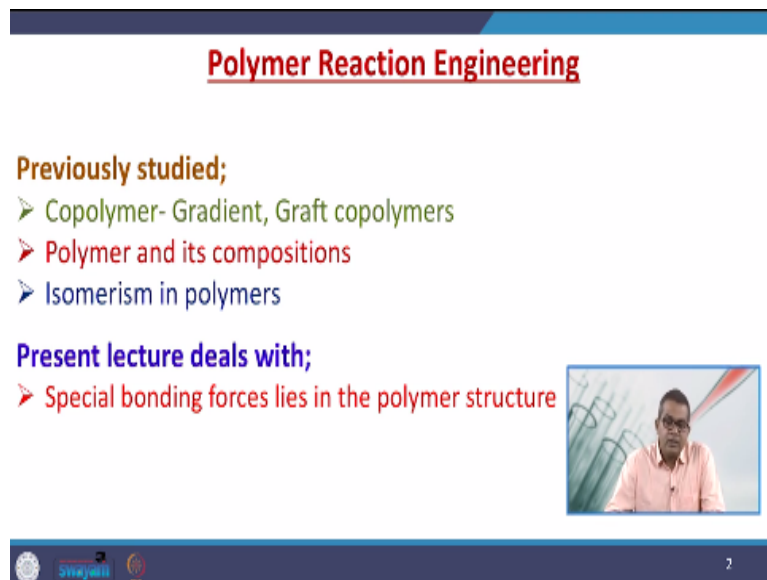


**Polymer Reaction Engineering**  
**Prof. Shishir Sinha**  
**Department of Chemical Engineering**  
**Indian Institute of Technology – Roorkee**

**Lecture – 06**  
**Bonding Forces in Polymers**

So, welcome to this lecture of Polymer Reaction Engineering. In this particular lecture, we will go to discuss about the bonding force in polymers, molecular weight and its distribution. Let us have a brief look about that what we studied previously. Previously, we have studied about the different type of a classification scheme of polymers, how we can carry out the different analysis of copolymer, gradient polymer and what are their definitions and what are their structural properties, etcetera.

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**Polymer Reaction Engineering**

**Previously studied;**

- Copolymer- Gradient, Graft copolymers
- Polymer and its compositions
- Isomerism in polymers

**Present lecture deals with;**

- Special bonding forces lies in the polymer structure



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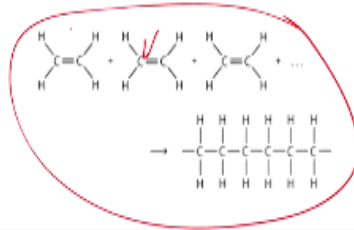
We had a discussion about the different type of isomerization schemes in the polymeric system discussed about the polymer and its composition. Now; in this particular lecture series, we will discuss about the special bonding force which are lies in the polymer structure.

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## Bonding forces in polymer structure

### ➤ Special bonding forces lies in the polymer structure

The polymer molecules are attached to each other with different bonding forces such as primary bonding (covalent bond, ionic bonds) and secondary bonding (hydrogen bonding, dipole interaction, van der Waal force and) in the structure.



So, let us have a look about the bonding forces. Before we go into detail, I would like to give you a brief introduction about the importance of a bonding. If you recall that in the previous lectures, we discussed about the different type of polymers, copolymer, graft polymer and different type of schemes.

And especially when we talk about the different type of amplification of the polymeric system, maybe from the flexible system to the high impact resistance system then sometimes, you may require to have a knowledge about the bonding because see in the previous lecture, we discussed that this polymeric system, they are composed of different type of a building blocks of monomeric unit.

Now, question arises that how these monomeric units are combined to each other and sometimes when especially perform the graft polymer or unique, you are looking for different kind of specialty polymer. In that case, you may require certain type of a bonding force among the polymeric molecules. So, based on this particular approach because this particular approach is extremely important when we design any kind of a polymeric reaction system or reactors, etcetera.

So, this type of thing is extremely important. Now, reason apart from this, the reason for handling such type of system is that every bond is having its own bond energy. So, whenever we perform any kind of a polymerization reaction within the reactor may be exothermic or endothermic in nature so, we knew we need to know about the bond energies by incorporation of this we can synthesize different kind of polymers, etcetera.

So, usually when we design the reactor especially when we need to carry out the temperature and pressure condition or we design any kind of a catalytic reaction for the development of any polymeric system maybe the isomerization, may be different type of a development of a polymeric system. The knowledge about the bonding force is extremely essential. So, we categorize all those things under the head of special bonding forces those lies in the polymeric structure.

So, usually if you see in the screen that these molecules are attached to each other with a different bonding forces; maybe these bonding forces are a primary bonding like covalent bond, ionic bonds, etcetera and it may be like secondary bonding like hydrogen bonding, sometimes dipole interaction, sometimes Van der Waals force, etcetera. Now, that is the purely based when you synthesize any kind of polymeric system.

So, based on the application sometimes may you require the strong bonding among the polymeric system, so that your molecules may not get dissociated over the period of application. Then you may require for the strong bonding structure and if you require that after the application they may get dissociated or if you are performing some type of intermediate thing where you require some weak bonds then you may have a special attention to those secondary bonding systems.

So, you can have a look about this particular bonding system. Here you can see that these are the source of attraction. Here you can perform the polymeric system and there are a weak bonds or strong bond depending upon the condition lies.

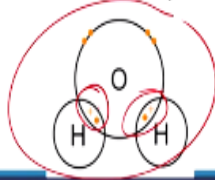
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## Bonding forces in polymer structure

### ❖ Covalent bond

Is formed when one or more pairs of valence electrons are shared between two atoms in the molecular structure, to form a stable electronic octet shell configuration. Sometimes they are also called as molecular bonds.

Valence electronic pairs are known as bonding pairs.



So, these kind of special bond as I discussed in this particular slide that they may be covalent bond, ionic bond, hydrogen bond, dipole interaction, van der Waal forces. So, there are so many forces. So, let us have a brief look because it is a partial domain to this particular lecture. So, let us have a brief look about those bonding system. Now, this covalent bond, this is formed when one or more pairs of valence electrons.

They are shared between the two atoms. So, there is a sharing and there may be an overlapping of the valence electron in the molecular structure. So, thus the structure whatever they form, they are having stable electronic octet and the shell configuration is very strong in this type of a structure. So, they are sometimes referred as a molecular bond. So, you can see that this particular figure here you can see that there is a sharing of valence electron structure.

These are the two atoms of oxygen and hydrogen and there is a sharing of these electronic valence electrons. So, such type of bonds are extremely, you can say this strong and dissociation of such type of a system is a bit difficult.

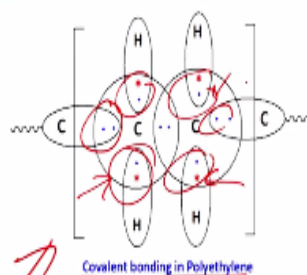
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## Bonding forces in polymer structure

A covalent bond forms when the difference between the electronegativities of two atoms is too small for an electron transfer to occur to form ions.

The dissociation energy of covalent bond is in the range of 50-200 kcal/mol.

**e.g.** In polyethylene each carbon atom are attached to same or different atoms with covalent bonds.

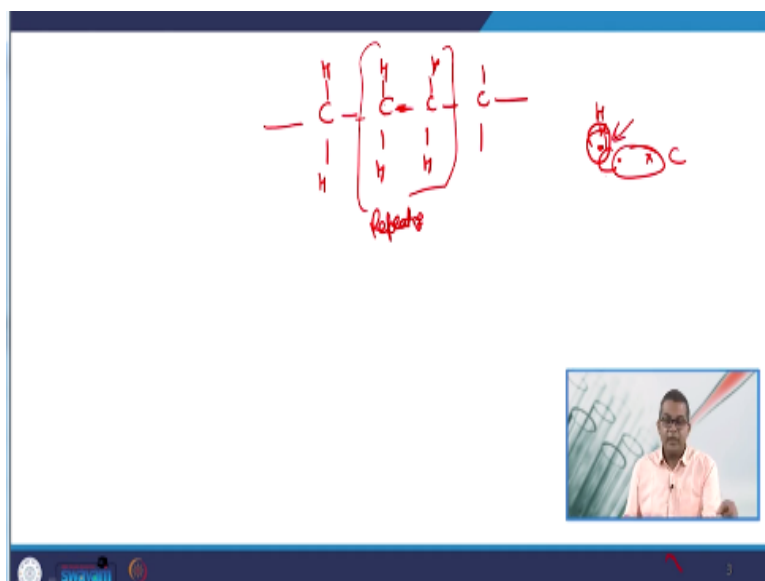


There are certain bonding forces in the polymeric structure when we talk about this particular aspect. The covalent bond forms when there is a difference between the electronegativities of two atoms. It may be too small for an electron transfer to occur to form an ion because ionic structure is a bit stronger than other type of structure. So, you see that here there are different type of bonding, like here you see that the covalent bond in the polyethylene structure.

So, as I talked about the bond energy among the different molecules so, in this case the dissociation energy of this covalent bond structure usually it is in the range of 50 to 200 kilocalorie per mole. Now; here you can see the polyethylene each carbon atom. They are attached to the same or different type of atom with covalent bonds. You can see over here like this.

So, as you recall that when we were talking about this formation of a polymerization or polyethylene with the help of ethylene molecule, there must be some motive. There must be some bonding, some joining force among all kind of a monomeric unit. So, you can explain this thing with the help of these valence sharing. Now; to be more precise, let us have a look about, now to explain this particular approach in more precise way.

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I have already discussed about the sharing of these valence electron in the previous slide. You can see that this is your polyethylene structure. Here, this is the repeating unit. Now, this repeating unit, see there are different type of bonds like here you are having the carbon-carbon bond. Here, you are having carbon hydrogen and this again carbon-carbon one. So, this is your repeating unit.

Now, as I described in the previous slide that you are having this C C structure. So, this is some sort of the valence electron sharing between the carbon-carbon atom and if you see that there is a hydrogen bond, now here this is again the sharing of this hydrogen, sharing of this carbon and hydrogen electron valence pair. So, by this way you can say that this particular structure having more and more strong character compared to the other ones.

So, that in due course of time the ethereal molecules they should, they do not get dissociate themselves and moreover their bonding energy is quite high. This is in the range of 50 to 200 kilo calorie per mole.

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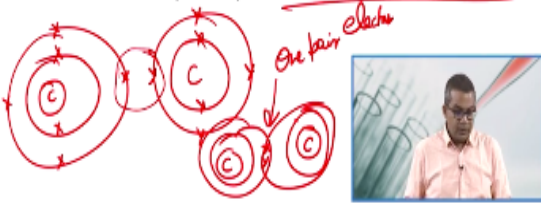
### Bonding forces in polymer structure

There are three types of Covalent bonds

- Single Covalent Bond.
- Double Covalent Bond.
- Triple Covalent Bond.

A **single covalent bond** is when only one pair of electrons is shared between atoms.

e.g



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Now; when we talk about the covalent bonds, these are characterized in 3 different aspects. One is the single covalent bond. Second one is the double covalent bond and third one is the triple covalent bond. So, single covalent bond is when only 1 pair of electron is shared between the atoms. Let us have a look about this particular structure. Here, we are having the carbon-carbon bonding.


Now; here you are having these, now this x, this valence electron is available over here. Now; here these are the y. These are the valence electron. Now, this y is may attach with this one. So, the structure would like this. Here x and y. So, this is here, you are having the single bond. This is only 1 pair of electron is shared. So, this is, this particular terminology is called as the single covalent bond.

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### Bonding forces in polymer structure

A double covalent bond is where two pairs of electrons are shared between the atoms rather than just one pair. Like  $O_2$

e.g

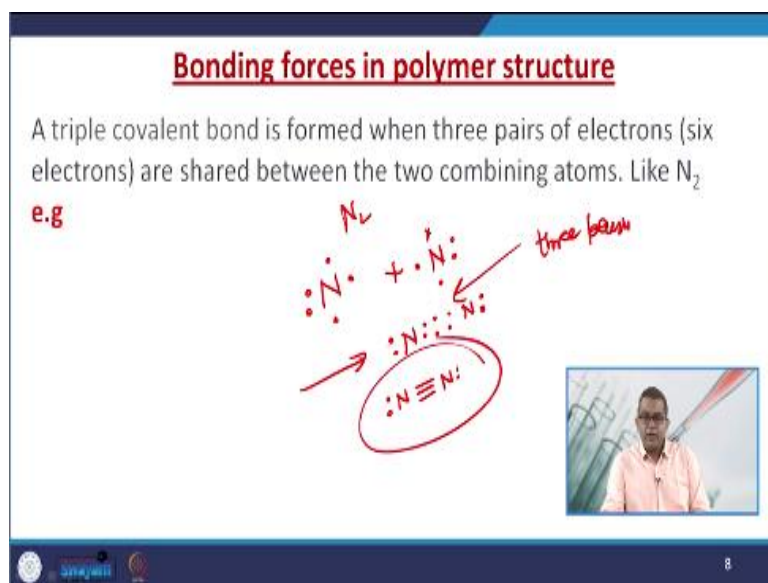


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Now, let us have a look about the other type of things. Like here, we are having the double covalent bond. Now, double covalent bond where 2 pairs of electrons are shared between the atoms rather than just one pair as against in the previous one. Now, here you can see again I am just depicting the example of say, this is the oxygen molecule and here these are 2 pairs.

You can see, there are 2 pairs of electrons are shared. So, this is again other type of covalent bonding system.

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Now, let us have a look about the triple covalent bond. Usually, they are formed when 3 pairs of electron that is 6 electrons in totality are shared between the 2 combining atoms. Let us have a look about the nitrogen, example of  $N_2$ . Now; here, you see now, when they formed or they join together with respect to the bonding, now; here there are 3 pairs or sometimes it is referred as.

Now, this is a very useful type of structure because this may invites several other opportunities for bonding. So, we have discussed about these 3 different types of covalent bonding system.

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### Bonding forces in polymer structure

❖ **Ionic bond**

When there is the transfer of an electron from one atom to another to obtain stable electronic configuration, the bond formation is called an ionic bond.

Sometimes they are referred as electrovalent bonds. It is attributed to the linkage formed from the electrostatic attraction between oppositely charged ions in a **chemical** compound.



Another brief look about the ionic bonds. Now, ionic bond when usually there is a transfer of an electron from one atom to another to obtain any kind of a stable structure configuration. So, the bond formation is called an ionic bond. Now, just before we go into detail about this ionic bond structure. This bonding structure we are discussing just to give you a broad spectrum of polymerization system to have a broad spectrum of a product profiling.

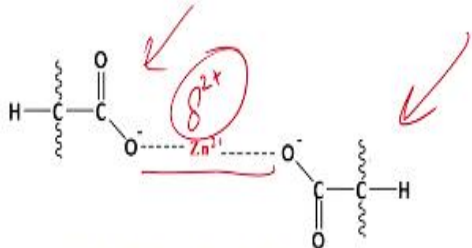
So, sometimes these ionic bonds they are referred as electrovalent bond and they are usually attributed to the linkage formed from electrostatic attraction between oppositely charged ion in the chemical components, a very common phenomena and we will discuss about like free radical polymerization or ionic polymerization. You will utilize this kind of a phenomena in those particular polymerization processes.

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### Bonding forces in polymer structure

It is the most stable electronic octet configuration. The dissociation energy of the ionic bond is in the range of 10-20 kcal/mol.

e.g.



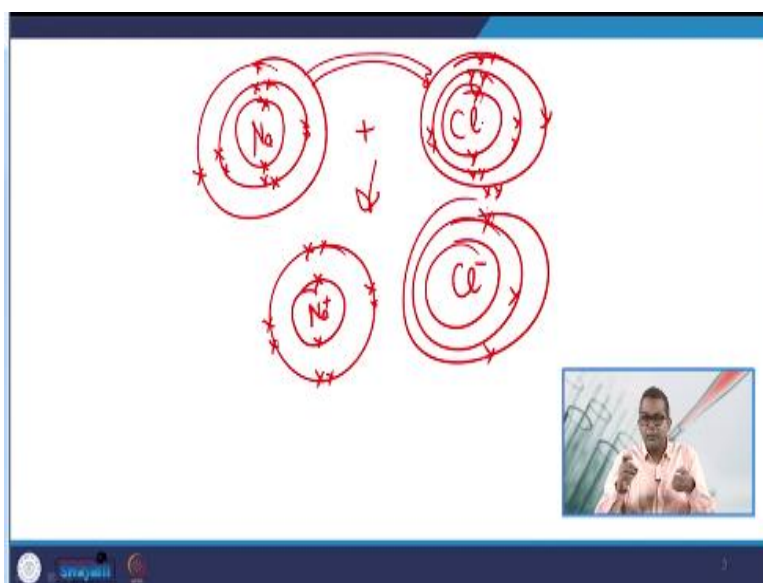
Ionic bond by transfer of electrons



Now, as I told you that it is the one of the most stable electronic octet configuration and dissociation energy of this ionic bond is usually in the range of 10 to 20 kilo calorie per mole. Now; here you see that this ionic bond by transfer of electron, these 2 are the system and here the electronic bond transfer sometimes referred as this one. So, they are transferred to each other to form the polymeric structure.

Another; you can say the best part of this particular approach. I will show you in the white board that let us see that the formation of NaCl.

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Now; here you see; now there are different ionic structure plus let us have Cl. Now, let us denote with y, like this. So, there is a transfer of the system from here to here and by this way there is a formation of unstable ionic bond which represents like  $\text{Na}^+$  and this is  $\text{Cl}^-$ . So, this is as I told you that this particular type of a structure is most stable one because of the affinity of 2 opposite charged system.

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## Bonding forces in polymer structure

### ❖ Dipole forces

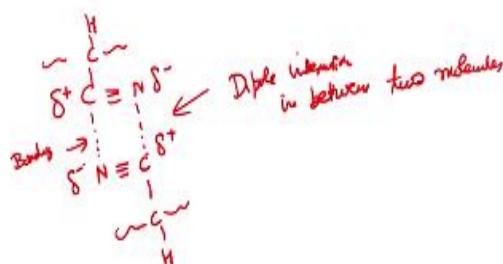
When there are opposite charges (such as positive and negative) on the electronegative atoms in the molecule, two poles are generated. The force of attraction exists in between the same or two different molecules.



Now, let us have a look about the dipole forces. So, when there are opposite charges like positive or negative on the electro negative atoms in the molecule, the two poles are usually generated. So, the force of attraction exist between these molecules; may be the same or 2 different molecules in character. So, the different forces are there. So, with the help of all these things the strong you can say the dipole moment exist between these molecules.

Let us have a look about this attraction. Here, we are discussing about this one. This is represented as now, you can see, there is an attraction between the two molecules. Now; to be more precise if you would like to give a practical example of these dipole interaction. Let us move to this blank sheet.

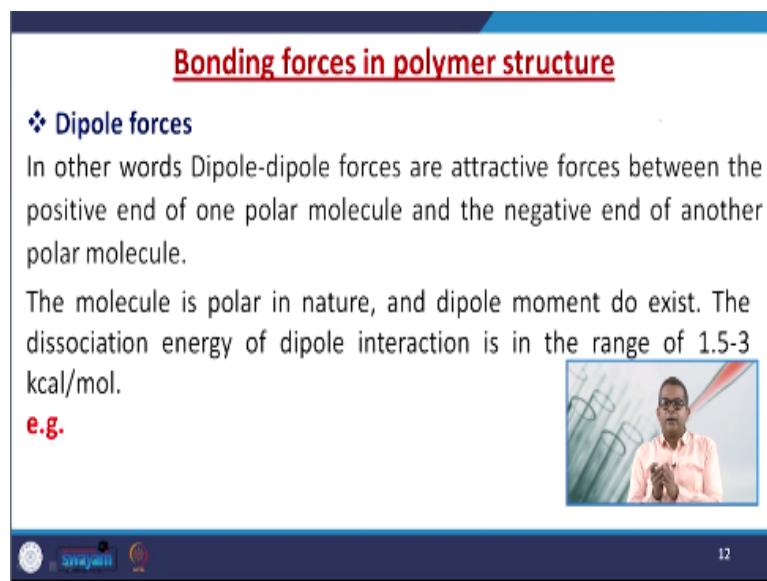
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Now; here, you see that. Now; here, this dipole force are represented as delta. Now, this represents the interaction or bonding. Now; here, you see that the dipole interaction in between 2 molecules. So, this particular approach is again very important and whenever we talk about the engineered polymer in that case this thing is extremely useful. So, that you can orient the polymer or you can develop a newer kind of thing.

And you may generate suppose if you are talking about say the polymeric beads. They can be used as a good support for the catalytic system. Then sometimes you require this type of approach in totality.

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**Bonding forces in polymer structure**

❖ **Dipole forces**

In other words Dipole-dipole forces are attractive forces between the positive end of one polar molecule and the negative end of another polar molecule.

The molecule is polar in nature, and dipole moment do exist. The dissociation energy of dipole interaction is in the range of 1.5-3 kcal/mol.

**e.g.**

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Now, the dipole forces usually they are attractive force between the positive and 1 polar molecule and negative end of other polar molecule as we discussed in this particular slide. Now, the molecule is usually polar in nature and dipole moment do exist. So, the dissociation energy of dipole interaction usually in the range of 1.5 to 3 kilo calorie per mole. So, this is you can say the characteristics of the dipole.


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### Bonding forces in polymer structure

❖ **Hydrogen bond**

It is the attractive force (partially intermolecular bonding interaction) in between the electronegative atoms such as **F, O and N** (the atoms have lone pair on electron donor atom) and **H** atom.

Hydrogen bonding can occur in the same or different molecules.



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Another interesting bonding force is the hydrogen bond. Hydrogen bond is very common. Now, it is the attractive force partially that is sometimes referred as the intermolecular bonding interaction in between the electronegative atoms like F, O and N. These atoms have lone pair on electron on the donor side. The hydrogen bonding can occur in same or different kind of a molecule that all depends on the affinity between these 2 systems.

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### Bonding forces in polymer structure

- Hydrogen bond can be an either intermolecular (in which the donor and acceptor units are found in two different molecules) or intramolecular phenomenon (in the same molecule).
- The dissociation energy of hydrogen bond is in the range of 3-7 kcal/mol.

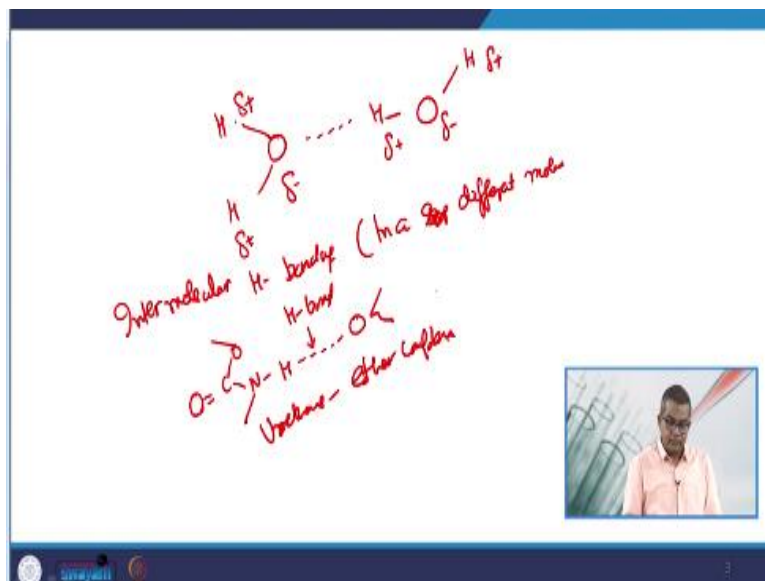
e.g.

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So, they can be either intermolecular in which the donor and acceptor units are found in 2 different molecules, may be the donor is available at here and the acceptor unit is available here. This may be formed in the two different molecules or intramolecular phenomena in the same molecule, sometimes maybe like this. So, the dissociation energy of hydrogen bond is usually in the range of 3 to 7 kilo calorie per mole.

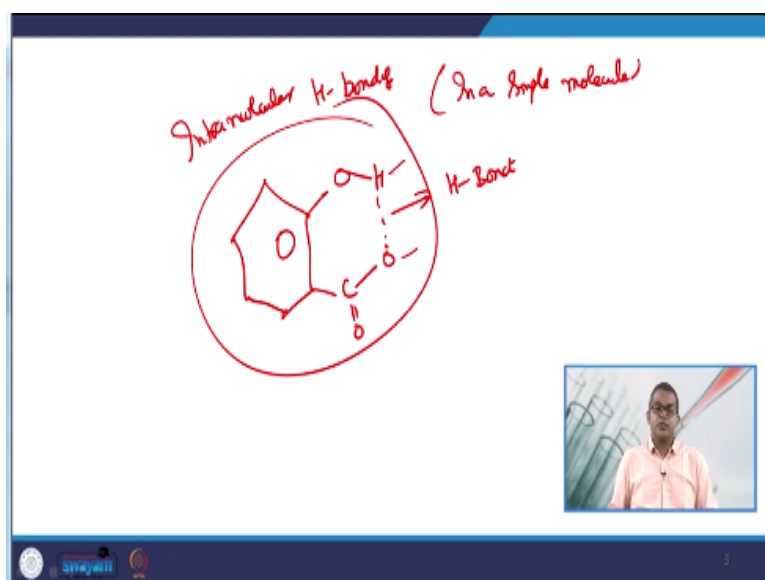
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Now, let us have a look about some examples of hydrogen bonding both the intermolecular and intramolecular. So, let us have about a brief. Before we go, let me give you a practical example of the hydrogen bonding. Now; here, this is the famous or well known molecule of water. Now, this is the hydrogen bonding. Now, let us have a look about the intermolecular hydrogen bonding.

As I told you that in a different molecule system. So, this is your example of a Urethane. So, this is Urethane-Ether complex.

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Now, another one is the intramolecular H bonding. Now, this is in a single molecule. Now, it is just like. Now, this is H bond. So, you can see this is within the single molecule. They are performing the hydrogen bonding. Now; here these 2 things are different hydrogen and

oxygen. So, there are intra-molecular within the system and 2 dissimilar type of molecules. So, these 2 are the characterization of classification of hydrogen bonding.

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**Bonding forces in polymer structure**

❖ **van der Waal forces**

- This is distance dependence forces (attractive, repulsive) between the nearby atoms or molecules and surfaces. It is not the result of electronic bond formation like as ionic or covalent bonds.
- It is weak force and sometimes called intermolecular forces and does not exist in the atoms or molecules at a longer distance, i.e. short-range force. It is independent of temperature (**except for dipole-dipole interaction**).

[Note]

- The dissociation energy of the van der Waal forces is in the range of 0.5 -2 kcal/mol.



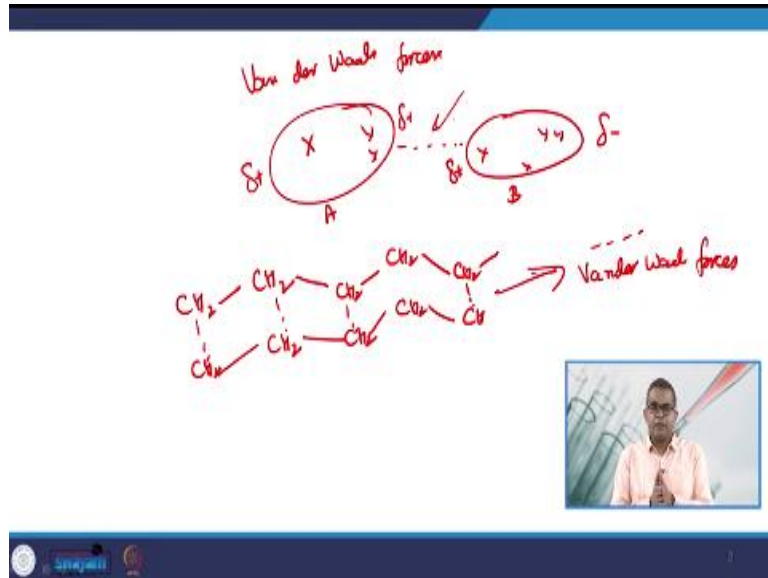
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Now, apart from this, another very significant type of force in picture and it is very well known force that is called the van der Waal force. Now, this is a distance dependence force and sometimes, they are in thermodynamic system. They are referred as a weak van der Waal force. So, they may be attractive; they may be repulsive between the nearby molecules or hydrogen surfaces.

So, it is not the result of electronic bond formation like as ionic or covalent bond. So, as I told you that it is a weak force and sometimes, they are called intermolecular forces and they do not exist in the atom or molecules at a longer distance that is a short range and it is independent of a temperature except of the dipole-dipole interaction. So, I am just summing up this particular lecture.

Here, we have already discussed different type of a forces, different type of a bonds, etcetera. They are very much important in due course of polymerization process and especially in the reactor design and reaction engineering. Now, the dissociation energy of these van der Waal forces, you see that in the range of 0.5 to 2 kilo calorie per mole. So, as I told you that they are very weak type of forces and intermolecular forces but they are having very useful phenomena in this particular approach.

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So, let us have a look about the typical structure of van der Waal forces. Now, van der Waal forces like we are having 2 different segments. These are the molecule and this one is the B molecule. So, they may get attached like this. So, they are very weak type of system. Another practical example of this van der Waal force is now, you see here. These are the, these dotted lines are represented as van der Waal forces.

So, these forces are extremely important and because being the ability of a weak in nature. So, you may utilize this particular character in due course of other aspect of polymer synthesis.

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### Molecular weight and its distributions

**□ Molecular weight**  
It has prime importance in polymer synthesis and applications. As the **mechanical, chemical and thermal properties** of the polymer depend upon molecular weight.

- Some of the properties increase with molecular weight to a maximum value and then decrease on further an increase in the molecular weight.
- The problem with higher molecular weight polymer is the processibility as the viscosity become high and melt flow difficult.
- .

Now, let us have a look about the molecular weights and it is distribution. Now, see I told you in the previous lectures that the molecular weight of a polymer plays a very vital role.



We will give a detail into the subsequent lectures but usually polymer they do not possess a fixed molecular weight because of the availability of a different sized chain available within the polymeric mass.

So, the molecular weight, it has the prime importance in the polymer synthesis and application, maybe they are attributed to the mechanical, chemical, thermal properties. We will discuss about the glass transition temperature which reflects the thermal, chemical and mechanical property and this is purely attributed to the molecular weight. So, when we talk about the mechanical, chemical and thermal properties of a polymer, they usually depend upon the molecular weight.

Now, some of the properties they may change with the molecular weight and sometimes they may increase to a maximum value and sometimes they may decrease on further increase on the molecular weight. So, it is a very sensitive type of a thing. You have to maintain all those things and remember if you try to synchronize the things with the help of your knowledge and based on the previous slides that is the bonding or formation of a different forces, etcetera.

Then sometimes it may lead to have a very critical approach because sometimes unnecessary bonds may get form during the course of polymerization. So, you have to be very particular about this thing. Now, the problem of a higher molecular weight sometimes may create another problem with respect to the processability of because when you are having the bulky structure or a bulky molecular weight then the processing of that particular polymer would be extremely difficult.

So, either formation of a different shape or formation of other things, it may become difficult. It may create a problem attributed to the melt flow, etcetera.

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## References

- G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 | DOI:10.1002/047147875X
- J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1.
- M. Szwarc, Marcel Van Beylen (auth.) - Ionic Polymerization and Living Polymers, Springer Netherlands, (1993).
- Stephen L. Rosen. Fundamental principles of polymeric materials, An SPE textbook, John Wiley & Sons (1937), ISBN:0-471-08704-1.
- V. R. Gowariker, N. V. Viswanathan, J. Sreedhar. Polymer Science, New age international (P) limited, publishers (1986), ISBN-08-522-6307-4.
- Joel R. Fried. Polymer Science and Technology, Prentice-Hall, Inc., (1995), ISBN-81-203-1458-1.
- Shiao-Wei Kuo (2018), Hydrogen Bonding in Polymer Materials, First Edition. Wiley-VCH Verlag GmbH & Co. KGaA. Published 2018 by Wiley-VCH Verlag GmbH & Co. KGaA.



So, based on this particular approach we need to look into the importance of these molecular weight and how it is distributed, how we can define these molecular weights for different type of things in related to the polymer reaction engineering. We will discuss this thing into the next lecture. So, in this particular lecture, we have discussed about the bonding, importance of a bonding, different bond energies, different structures, etcetera.

Now, I have given you a brief overview about the molecular weight. We will carry on this molecular weight phenomena in the next lecture. Thank you very much.