# Introduction to Polymer Physics
## Prof. Dr. Prateek Kumar Jha
## Department for Chemical Engineering
## Indian Institute of Technology-Roorkee

## Lecture-01
## Introduction to the Course, Macromolecules and Life, Molecular Flexibility

I am Dr. Prateek Jha from IIT Roorkee from Department of Chemical engineering. I will be teaching this course on introduction to Polymer Physics. This course will be relevant to undergrad students in Physics, Material Science, Chemical Engineering and also beginning graduate students in the same departments.

This Course will not focus on the chemical aspects of the polymers (like how to synthesise polymers), rather we discuss the universal features of the polymers and try to understand the physical aspects of the polymeric systems. In this course, we will have weekly assignments and proctored exam in the end.

In the first couple of lectures we will cover basic topics like

- What is a polymer?
- How are polymers different from other molecules?
- How are polymers made?
- Types/ Classification of polymers
- Basic motivation of studying polymers.

So, a polymer is a large molecule, polymer is also called a macromolecule and as you know when we say something is macro, we are talking about scales which are like more than something like 1 micron. They are molecules, which we can really see through a simple microscope, unlike small molecules like methane or ethane that we cannot see through any kind of a simple microscope and we need very specific more highly resolved microscope to see that. In the case of polymers, we can really see the molecules through a simple microscope in most cases.

However, the difference between the macromolecules and polymers is that all macromolecules are not really polymers. So, the polymer is a subset of a macromolecules and what really make polymers different from other macromolecules is that you must have a repeating sequence of units. For example, if you know about polyethylene that is the most common polymer, the polyethylene has a repeating sequence of

$$(\text{--}CH_2\text{-}CH_2\text{---})_n$$

In this case, $(\text{--}CH_2\text{-}CH_2\text{---})$ = repeating units & n = number of repeating units.

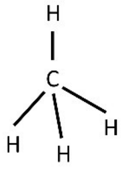
Now, as you probably know if the n is very small, let us say an n=1 or n=2 what you have is what we call alkanes, for example butane, pentane and so on, they are not polymers.

On the other hand if the n becomes slightly larger like 10 or 20, we refer to them as oligomers, we call it a polymer when n is really very high. So, typically and the terminology is not really very standard, if n is higher than 100 at least, then we actually we start calling them as like polymers and we will see like why exactly these kind of things which have higher value of n different from those which have like a smaller value of n. So, having said this, let me like briefly start telling about how are polymers different from other molecules.

Polymers are as said, is large than compare to other molecules but what is more important it is also flexible. So, think of like rubber band and you can really put your hands in there and you can stretch it. If you think of a rubber band, rubber band is a bit of the polymer and actually it is a cross linked polymer we will discuss about that later in the course. But this is the flexibility that we talk about. Okay. Now I will give you one more example that think of like the hands of a robot and compare that to hands of a human being.

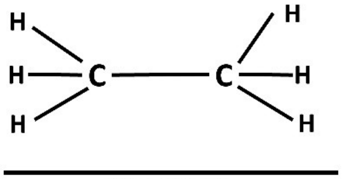
If you think of a robot and if you have seen like a robot or if you have seen in the movies it has hands which are like hinges together to some sort of a mechanical like fingers and the robot can really move along the hinges that is placed along the body. For example if there is a hinge the robot can rotate his hands along that particular hinge similarly for the fingers and so on. So, every hinge is giving it certain amount of flexibility, now you think of like a human hand and see like how it is very different. So, in the human hand then we have much more flexibility, for example we can do many kind of movements which for example is not possible in the case of a robot. So, the reason why we are different is because the flexibility we possess is because of presence of the macromolecules and the flexibility is really molecular in nature what it means it, it is happening at a much lower length scale than compare to the robot case where a length scales or the distances or which the hinge is placed is really very large. In our case we can start thinking about it and Ibuild on this description later our hinges inside the bodies are really placed much closed together and they are really at a molecular level and so, our flexibility has molecular origin and just like we are made up of macromolecules and polymers are also macromolecules. So, in their case too flexibility is built at a molecular level it is think start thinking about is as the hinges which are present at very small length scales. So, that is one more difference between there, so having said these things let me now try elaborate that why I am saying that n has to be large.

Let us consider a very small molecule which contains only one carbon and you know that is the methane molecule. If you remember from high school methane has a tetrahedral structure given three dimensional and now you start thinking like how this particular molecule can change its confirmation like what really can change about this molecule, of course this entire molecule can rotate as a whole, it can translate as a whole, but if I look in terms of an internal motion of these molecules that is very few. For example there is of course this carbon hydrogen bond and there are 4 such bonds. But their bond lengths are more or less fixed. If you really put a microscope there and try to measure the what the bond length is of course need very highly resolved microscopes you will not see much differences in the bond length that means that this molecules internal structure is rather fixed and you will not see any variation in this internal structured, I would say any variation that you can really differentiate easily.



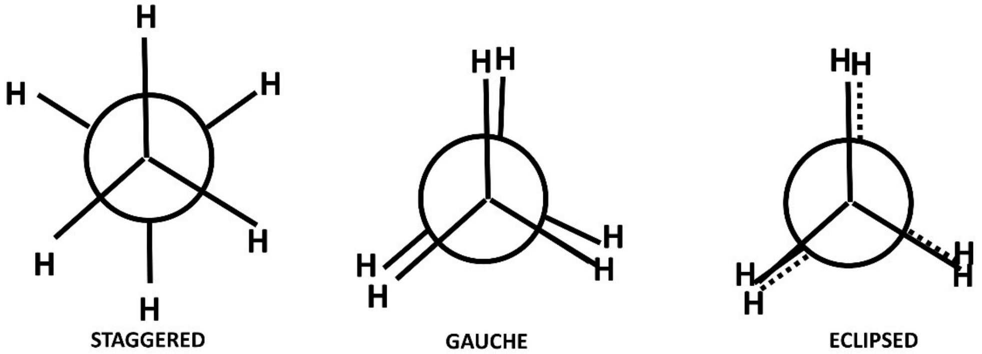
Methane Molecule

Now let us say what really happens, if we have more number of carbons. So, think of the next molecule that is my Ethane. So, ethane now has a $CH_3$ along with a $CH_3$ again it is a 3 dimensional structure, but now there are 2 carbons and 2 carbons has 3 hydrogens each. And now if you know about from chemistry classes, you can also easily see in this particular case is there is a possibility of rotation around this particular carbon-carbon bond and the way to see that is I will try to do representations of these molecules looking from this particular end and put my eye here and I am looking at the carbon-carbon bond okay. So, in that case what I will do, I will put my first carbon that I see from the right side and I put its 3 hydrogens like these and then if I am looking from here, then the carbon behind is at the centre of the circle that I have just drawn and this also will have 3 hydrogens. So, now there is 1 carbon on top, 1 carbon just beneath it you cannot see it in the graph but that is given by this circle. And then we have 3 hydrogens of the front carbon and 3 hydrogens of the carbon behind it okay, now the 3 hydrogens in the front can be rotate it with respect to 3 carbon hydrogens behind it, for example this can be in this particular configuration. But this can also be for example something like that ok where the 3 hydrogens are located for the front and back which are rather close to each other in what we see but basically it means they are roughly in the same plane okay, it can be like even closer where you will start to see that both of them are pretty much aligned with respect to each other. So, 3 hydrogens behind and 3 hydrogens front are pretty much in line in the same plane. This particular configuration I will refer to as an eclipsed confirmation this is what I will refer as staggered confirmation. And this is what I will refer to as gauche conformations, there are 3 possible conformations of ethane molecule.



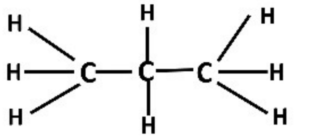
Ethane Molecule

Let us look at the energies of these particular conformations, then staggered happens to be the most stable one and very rarely I would say it never occurs that these conformations are observed. Because they are very less stable. But having said that there are there is a possibility of 3 conformations 2 of them has much lower energy compared much higher energy compared to third one and that's the reason why we see always staggered confirmation right.

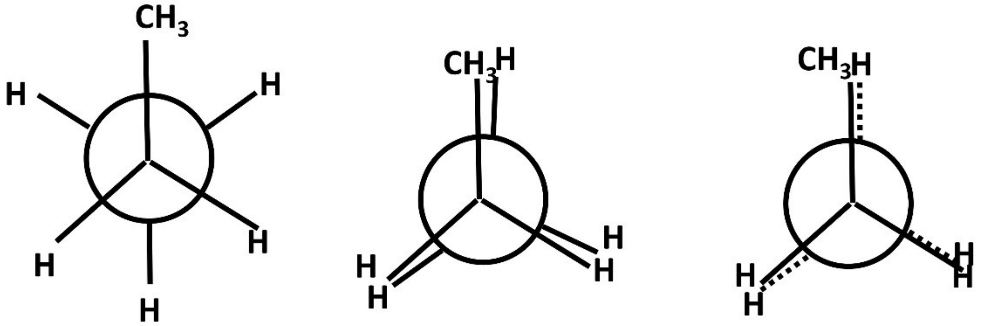


DIFFERENT TYPES OF CONFIGURATION

In the case of propane there are 3 carbons, the middle one has 2 hydrogens and then in the 2 ends we have 3 hydrogens each. So, there are 2 carbon-carbon bonds and thus many rotation is possible. So from looking at one carbon the projection is like this that the front carbon it attach to a $CH_3$ and 2 hydrogens and the behind one has only 3 hydrogens. So, in the propane molecule we have possibility of 3 conformations- eclipsed, gauche and staggered. It turns out just like the case of ethane, even in that case they staggered one is the most stable or has the least energy and these conformations are again very less stable and so they are not really observed. But again there is a possibility of 3 possible conformations.



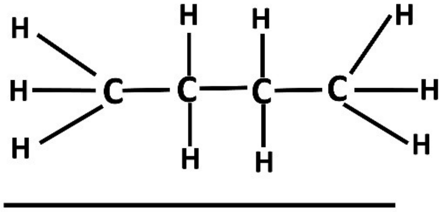
Propane Molecule



STAGGERED GAUCHE ECLIPSED

DIFFERENT TYPES OF CONFIGURATION OF PROPANE

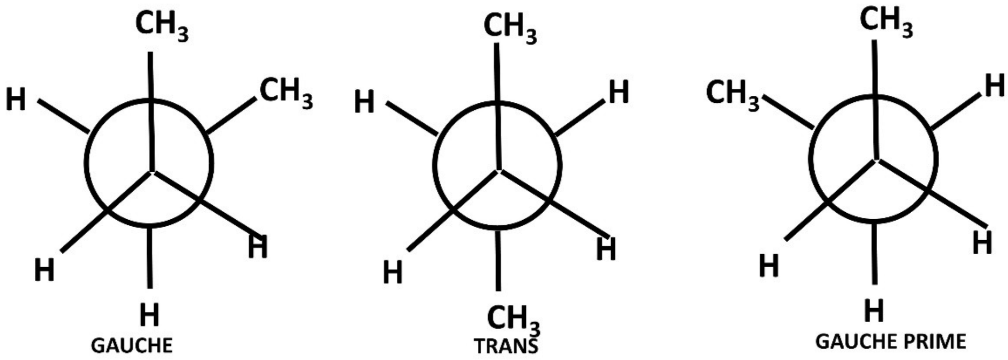
Let us consider butane molecule, in butane let us say look at this particular carbon to one to look at the rotation around this particular carbon. The front one has a $CH_3$ and 2 hydrogens, and back one also have a $CH_3$ and 2 hydrogens and thus we do not need gauche and eclipse confirmation which is anyway are less stable. In butane there are 3 staggered confirmation which are more or less equally stable. So, the front one is called gauche, the middle one is called trans and then this is referred to as a gauche plane. These conformations are difficult to obtain so it can be called intermediate confirmations. Thus in butane we have 3 are all staggered conformations and all are stable which means trans maybe slightly more stable compare to gauche and gauche prime but more or less all three states are observed as all of them have similar kind of energy labels.



Butane Molecule

So, from above discussion we understood that as we start from methane the internal structure is rather fixed and have only internal motion, and as we proceed to ethane and propane molecules there are possibility of 3 conformations but only one was the most stable, As we move to butane then we have possibility of 3 stable confirmation. It can have many other conformations as well but there are 3 stable conformations and which all can really happen in the system.

Now if we consider pentane hexane and so on then we will see that there is a possibility of many possible conformations. For example let us consider pentane molecule, we can look at rotations around 2 carbon bonds this will give you 3*3=9 staggered conformations, which means that along the first carbon-carbon bond it can be trans along the second it can be gauche that's one along the first it can be trans, along the next it can be trans and so on. So, along the first carbon, the first carbon-carbon bond, can be Tran's gauche or gauche prime rotation along the first C-C bond, irrespective of what it was along the first C-C bond. Now again the second bond can be again trans gauche or gauche prime. Similarly for other bonds you can have trans gauche and gauche prime rotations. Thus in a pentane molecule we have 9 conformations. If we extend this logic for the case of hexane we will have 27 conformations for the case of like heptane we will have like 81 and so on.



GAUCHE TRANS GAUCHE PRIME

DIFFERENT TYPES OF CONFIGURATION OF BUTANE

So, in general a polymer chain is composed of say around ‘m’ carbon atoms or repeating units, this will have something like $3^m$ stable conformations. Now we consider only m why not m-1 because for the case of m=1, we have only one confirmation considering m is in this case is very large so in the formula even if we put like m-1 or m-2 that will not make much difference.

The key point is that as the number of carbons increases in the chain, the number of possible conformations increases which give rise to molecular flexibility, thus the polymers can really adopt many possible conformations and that is why we refer to them as highly flexible.

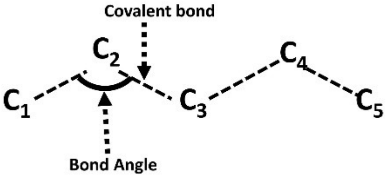
In polymers we elaborate on the rotation around carbon-carbon bond not on the rotation around for example carbon-hydrogen bond in the system. Let us try to understand this phenomena in detail.

Let us consider an example of 5 naming C1, C2, C3, C4 and C5. The bonds between the carbons say C1-C2 and so on are covalent bonds. A covalent bond is formed by the overlap of electron clouds, so if we really have to change this particular bond length then we have to mesh up with the electron clouds that is difficult because the bonds between them is very strong as it is formed by the some kind of an electrons sharing mechanism which means that the bond lengths are almost constant and there can be possibility of a small vibrations but more or less they are almost constant.

If we look at the particular angle, then there are some electron clouds overlapping over on one another and some kind of angle is formed which creates some sort of a balance between the electron clouds. In the case of most molecules the bond angles are really constant and the interactions between clouds are very strong. For example, in case of a water molecule ($H_2O$) the angle formed between H-O-H is 109 degrees which is relatively less but it still almost constant.

Let us consider 4 carbon atoms what we can observe is that the bond length and angles are same and If we try to rotate around the middle bond then it will give rise to torsion motion. We can apply some kind of a torsion where the angles between all the 3 adjacent carbons in the system will not change, the bond lengths will not change but we can rotate around the middle carbon. The torsion will have certain angle which is formed by the electron clouds sharing. These bonds are the strongest ones, bond lengths are most constant and bond angles are due to some kind of an interactions between the electron clouds in the neighbouring bonds and the torsion angle is now between a higher level correlations between 3 electron clouds. Thus torsion angle are relatively more flexible. Now let us extend this idea and think of like what really happens if we have many number of carbons on the polymer chain then first carbon and the other carbon 1 and 2 are of course correlated because they have a bond and some angle in between. This distant carbons are correlated by a lesser measure because there is a torsion angle in between and as we keep on going the correlation remains, but it becomes smaller and smaller, so the more I travel along the carbon chain the more we see that the correlation between the positions of carbon atom decades.

As we proceed further with this logic we have thousands of carbon atom in a polymer chain and if we look at 2 points far off on the carbon chain and we have large number of carbons in between then the position of the initial carbon and position of distant carbon is almost uncorrelated. For example in alkanes containing we have 4, 5 carbons so there will be more correlation which will not happen even in say oligomers containing 20 carbons they will still have like high degree of correlations. But when we have thousands of carbon in the polymer chain, in that case if we start from say one end of molecule and then start following the molecule like this at certain distances along the contour the positions between the 2 points at certain distance from contour become uncorrelated which give rise to a great amount of flexibility because since the one carbon does not depend on the other carbon.



Long Chain of Polymer depicting minimum Correlation between first and last carbon

Now if we really zoom-in into the polymer chain we will see that there is a sequence of carbons and they still have high degree of correlation at short distances along the contour it is locally very straight and locally very correlated but the overall structure is very flexible when we look at this particular polymer chain. This concept give rise to the polymer physics. Polymer physics really begins where with depart from the usual physical chemistry.

In a polymer chain we have many possible conformations and all these conformations will have different energies and the idea is that the energy gap between 2 conformations are not really very high, so by using the principles of kinetic theory of gases that every molecule every atom in the molecule has certain Kinetic energy and this can give rise to the thermal energy equivalent of kBT is comes from the equi-participant principle which implies the mean square velocity of molecules is proportional to kbt ( forget about the constant). The main point is that there is a thermal energy which is of the order of kbt,

kb = Boltzmann constant and T = absolute temperature in Kelvin.

So, In the polymer chain molecules have high energy so they keep on bumping with each other and gaining small thermal energies or packets of energies. If the energy gap between the 2 conformations are of kBt order, then we can easily switch from one confirmation to the other.

In this course we will later study how to find energies of a polymer chain and things of that sort. There can be some conformations which are less probable, there can be conformations which are more probable and then there can be some are never possible or they can be some which are like the maximum possible and so on.

In this course we will focus on the probability of conformations and at any given energy level how many conformations are really possible. We will consider large number of molecules, large number of entities we make to use of statistical mechanics there are certain laws and we will use that in this particular course So, we do not talk about a particular molecule or 10 particular molecules, we talk about an ensemble of molecules which possess a certain feature like a temperature pressure or a density. In statistical mechanics we try to build on the idea of large number of molecules which has many possible conformations which together give rise to some kind of an average property. For example, the pressure of a gas is not because of say 1 molecule of the gas, the pressure of a gas results from the collisions of molecules, density also is not a property of 1 molecule, it is property of the entire system. Similarly when we apply the concepts in the case of the polymer then we do not talk about the property of a particular confirmation of polymer chain. A property of an ensemble of possible conformations that a given energy or for a given energy range that we can access using the thermal fluctuations that occur the system

So, in next lecture we will discuss about like how polymers are made and why exactly we do polymer physics based on today's lecture.

Thank you