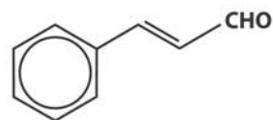


Lecture 22: Polymers and Biopolymers

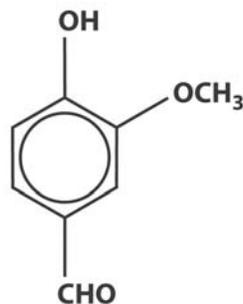
In the previous lecture we learned that by using carbon as the primary backbone, we can create a seemingly endless array of molecules built on covalent bonds to carbon. The simple concepts we learned at the beginning of the year about bonding—like structures being formed based on the number of valence electrons and the stability of filled shells, make it possible to rationalize why different structures are possible. We can even rationalize the reactivity that occurs by applying simple concepts like electronegativity or more sophisticated concepts in thermodynamics.

What should be most impressive is just how many different kinds of even relatively small molecules (molecular weights of a few hundred) we can build using carbon backbones and attaching all manner of functional groups. In fact most of the compounds we take for granted in our daily lives, like vitamins, and medications, and molecules that make it possible to see color or to smell or to taste, are built on even the smallest variations in organic molecules.

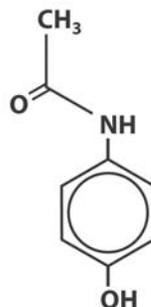
A few examples of these are shown below, not because you are expected to learn them, but more just to say, wow, this might actually be pretty interesting and make learning organic worthwhile.



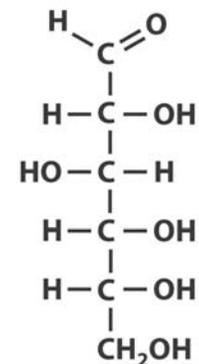
9 Cinnamadehyde



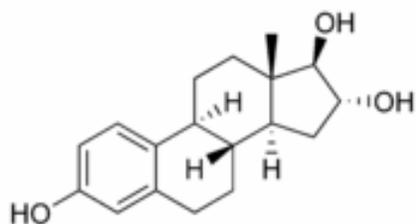
10 Vanillin



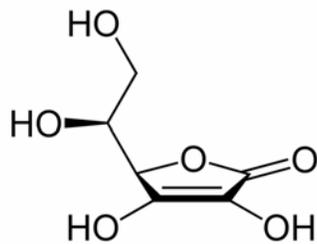
14 Tylenol



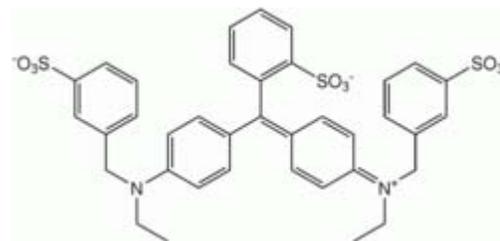
18 Glucose, $C_6H_{12}O_6$



Estrogen
Polymers



Vitamin C



brilliant blue food coloring

Now these small organic molecules are amazing given their complexity and diversity of function, but they are not really what is really important about organic molecules. Actually it is the ability of small organic molecules to polymerize that makes life really interesting (and possible.) The rest of this lecture describes this process by which small organic molecule units are able to form molecules that have molecular weights of millions and larger.

We will first look at the polymers built on very simple organic molecules that are responsible for the many products we use in our daily lives—like rubber or Plexiglass or Teflon. We will then look at biopolymers which are as they say, “the building blocks of life.” What I will want you to take away from this survey is a general appreciation for how these polymers are formed, and for the ones I lay out for you in the notes or the worksheets, the ability to identify what monomeric units are responsible for forming a specific polymer.

Addition Polymers.

We have learned that there are certain general classes of organic chemical reactions: substitutions, additions and eliminations. You can imagine that these can occur in such a way that a one or more small organic molecules can react to produce molecules of ever increasing size. For example, the polymerization of ethane to form polyethylene.

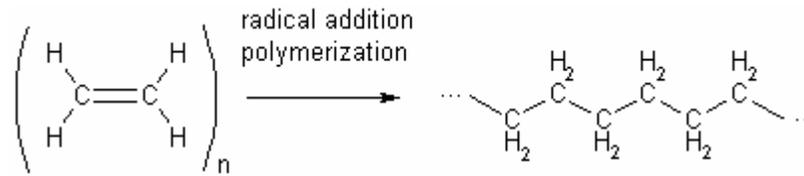
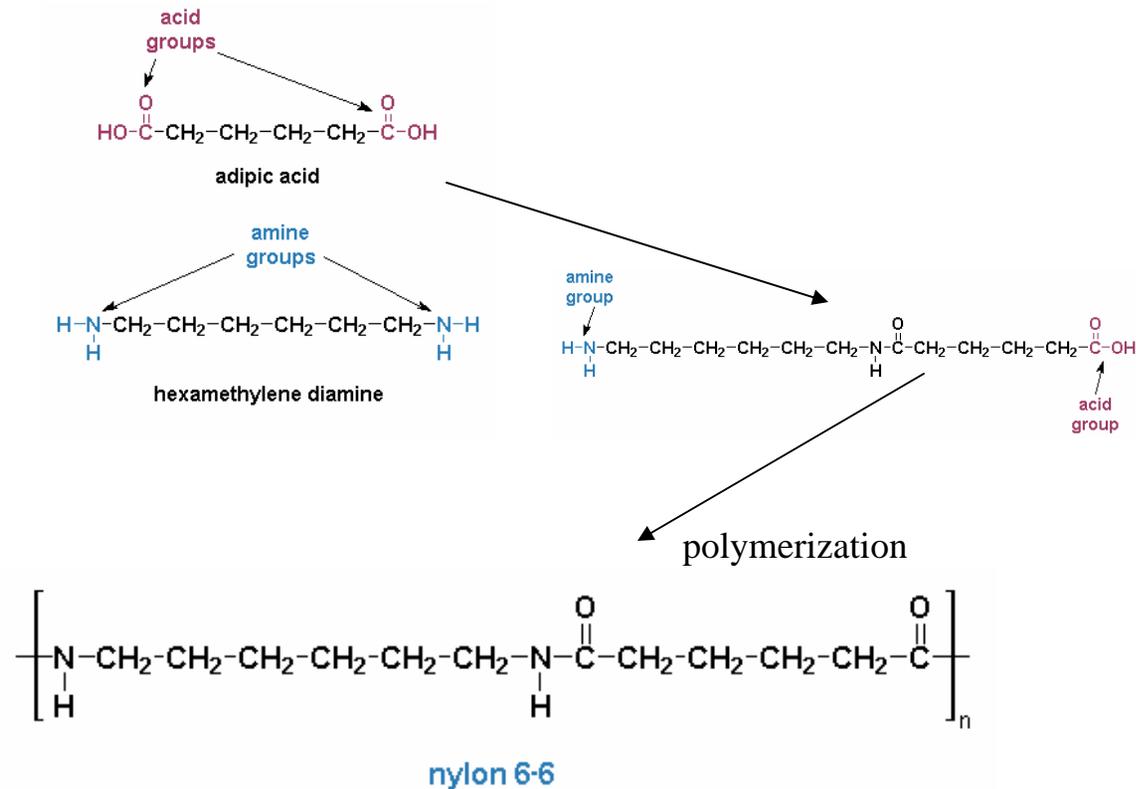


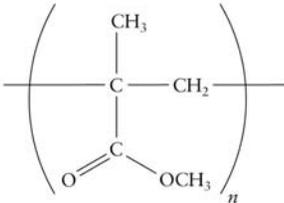
Fig 1: The polymerisation of ethene in to poly(ethene)

Another famous example, that is done as a demo just about everywhere, including this class, is the production of nylon from adipic acid and hexamethylene diamine. In the sequence below the two starting materials form the monomer that polymerize to form nylon



A table of some common monomers, their polymer formulas and their famous names is shown in the table below.

TABLE 19.2 Common Addition Polymers

Monomer name	Formula	Polymer formula	Common name
ethene*	$\text{CH}_2=\text{CH}_2$	$-(\text{CH}_2-\text{CH}_2)_n-$	polyethylene
vinyl chloride	$\text{CHCl}=\text{CH}_2$	$-(\text{CHCl}-\text{CH}_2)_n-$	polyvinyl chloride
styrene	$\text{CH}(\text{C}_6\text{H}_5)=\text{CH}_2$	$-(\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2)_n-$	polystyrene
acrylonitrile	$\text{CH}(\text{CN})=\text{CH}_2$	$-(\text{CH}(\text{CN})-\text{CH}_2)_n-$	Orlon, Acrilan
propene*	$\text{CH}(\text{CH}_3)=\text{CH}_2$	$-(\text{CH}(\text{CH}_3)-\text{CH}_2)_n-$	polypropylene
methyl methacrylate	$\text{CH}_3\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$		Plexiglas, Lucite
tetrafluoroethene*	$\text{CF}_2=\text{CF}_2$	$-(\text{CF}_2-\text{CF}_2)_n-$	Teflon, PTFE†

*The suffix *-ene* is replaced by *-ylene* in the common names of these compounds, hence the names of the corresponding polymers.

†PTFE, polytetrafluoroethylene.

Common sense tells you that the actual commercial production of polymers is not only staggeringly complicated but also staggeringly lucrative. So please don't leave this section thinking that heating up a couple of molecules to form a longer chain is all it takes to produce a product or that the simple formulas shown above are the actual structures of the products you buy. To achieve certain desirable properties, polymers are allowed to form in much more complicated ways, as seen in the picture below and in the example of rubber (polyisoprene below.)



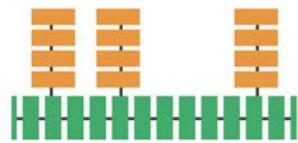
(a) Simple polymer



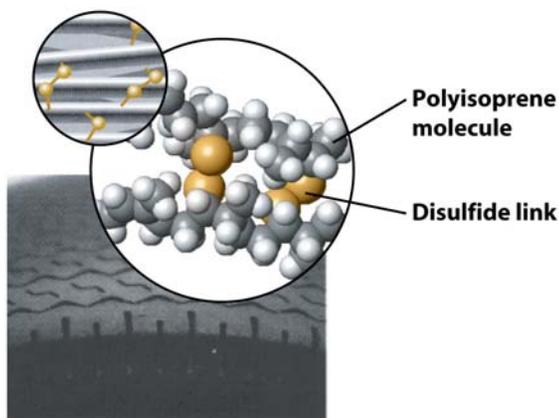
(b) Alternating copolymer



(c) Block copolymer



(d) Graft copolymer



Biopolymers.

This is not a biology class, or even a biochemistry class, but unless you have had your head in the sand most of your life, you already know that those folks define four basic categories of biopolymers. Biopolymers are similar to the polymers described above in that simple building blocks of monomeric units are used to create first, important classes of intermediately sized molecules, that are then linked to form the biopolymers that define what it means to be alive.

If you learn nothing else in the material below, you should walk away knowing that

- carboxylic acids combine with hydrocarbon groups to make **fatty acids**
- sugars that make polysaccharides that make the **carbohydrates** starches and cellulose
- amino acids that make polypeptides that make **proteins**
- the bases and phosphates and sugars that make nucleosides and nucleotides that make the nuclei acids **DNA and RNA**

I will briefly define each of these in terms of the simple units that form them and in terms of the important functions they have in our lives. What I want you to notice is that even those these are magnificently large, systematically defined structures, they are at root, a collect of bonds formed because an atom wanted to satisfy the octet rule, and the reactions that created these polymers were simple acid base or redox reactions based upon the thermodynamic and kinetic concepts that we have been learning.

Fatty Acids.

Fatty acids are the simplest of the biopolymers in that they can consist simply of a carboxylic acid functional group with a hydrocarbon chain. We can divide these into two categories. The saturated hydrocarbons that are made with alkane groups (no double bonds.) These saturated fatty acids are the bad guys that do damage to your cardiovascular system, but fast food places love them because they don't go rancid.



Butyric (butanoic acid): $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ C4:0
Caproic (hexanoic acid): $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ C6:0
Caprylic (octanoic acid): $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ C8:0
Capric (decanoic acid): $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ C10:0
Lauric (dodecanoic acid): $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ C12:0

Myristic (tetradecanoic acid): $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ C14:0
Palmitic (hexadecanoic acid): $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ C16:0
Stearic (octadecanoic acid): $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ C18:0
Arachidic (eicosanoic acid): $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ C20:0
Behenic (docosanoic acid): $\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$ C22:0

The unsaturated hydrocarbons include at least one double bond.

Myristoleic acid: $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C14:1 Palmitoleic acid: $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C16:1 Oleic acid: $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C18:1 Linoleic acid: $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C18:2 Alpha-linolenic acid: $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C18:3 Arachidonic acid $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$

C20:4 Eicosapentaenoic acid C20:5 Erucic acid: $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$

C22:1 Docosahexaenoic acid C22:6 _____

The two essential fatty acids that you must eat to survive

C18:1 Linoleic acid: $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

C18:2 Alpha-linolenic acid: $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

_____ are unsaturated. _____

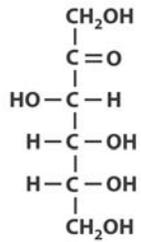
And you can turn on the TV without someone trying to get you to eat as much fish oil as possible because it is the source of omega-3-fatty acids.

C20:4 Eicosapentaenoic acid C20:5 Erucic acid: $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$

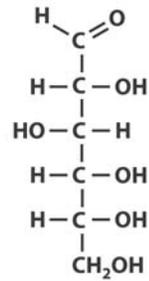
C22:1 Docosahexaenoic acid C22:6 _____

Carbohydrates.

Carbohydrates are polymers formed from simple sugars (monosaccharides) that contain large numbers of hydroxyl groups. For example. Fructose and glucose are the two monosaccharides with which you are most familiar, no doubt because they can combine to form the disaccharide loved by all, table sugar (sucrose.)



19 Fructose, $\text{C}_6\text{H}_{12}\text{O}_6$



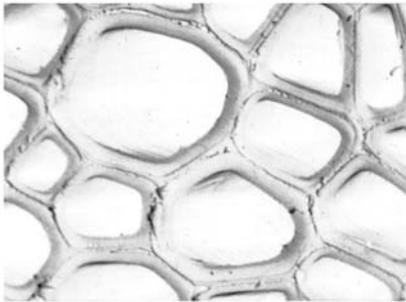
18 Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$

→ table sugar

The chemical reaction that produced table sugar is the formation of a glycosidic bond between the sugars, a process that can continue on to form thousands of linkages in what are polysaccharides known as carbohydrates.



(a)



(b)

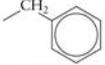
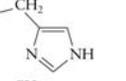
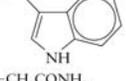
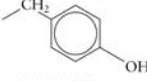
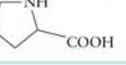
Before you start thinking that carbohydrates are not as important as the two biopolymers we are about to consider, the fact is that carbohydrates are the most common living thing of the earth and include

- starch which is the way we store energy in the body
- cellulose (the picture above) which is the basic structural unit of plants.

Proteins.

Proteins are a biopolymer formed when peptide bonds are created between amino acids. Amino acids, as the name implies, consist of a simple carbon-based structure that has a carboxylic acid and amine function group (note the switch hitting acid and base nature of amino acids) along with an organic substituent group. The 20 naturally occurring amino acids are listed below—not the X group is the attached organic substituent.

TABLE 19.4 The Naturally Occurring Amino Acids, X—CH(NH₂)COOH

X	Name	Abbreviation	X	Name	Abbreviation
—H	glycine	Gly	—CH ₂ (CH ₂) ₃ NH ₂	lysine*	Lys
—CH ₃	alanine	Ala	$\text{—CH}_2(\text{CH}_2)_2\text{NH—C}\begin{matrix} \text{NH}_2 \\ \text{NH} \end{matrix}$	arginine	Arg
	phenylalanine*	Phe			
—CH(CH ₃) ₂	valine*	Val		histidine*	His
—CH ₂ CH(CH ₃) ₂	leucine*	Leu			
—CH(CH ₃)CH ₂ CH ₃	isoleucine*	Ile		tryptophan*	Trp
—CH ₂ OH	serine	Ser			
—CH(OH)CH ₃	threonine*	Thr	—CH ₂ CONH ₂	asparagine	Asn
	tyrosine	Tyr	—CH ₂ CH ₂ CONH ₂	glutamine	Gln
—CH ₂ COOH	aspartic acid	Asp		proline†	Pro
—CH ₂ CH ₂ COOH	glutamic acid	Glu			
—CH ₂ SH	cysteine	Cys			
—CH ₂ CH ₂ SCH ₃	methionine*	Met			

*Essential amino acids for humans.

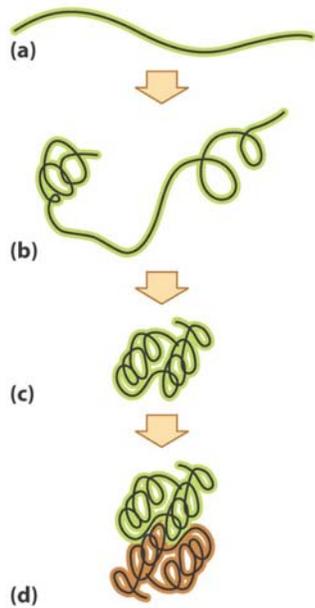
†The entire amino acid is shown.

So what can we build with these aminoacids?

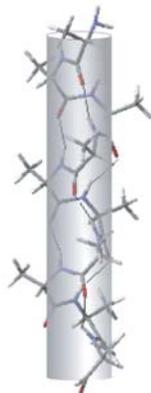
Polypeptides which are small assemblages are one example. And a famous representative is hemoglobin which includes four peptides chains surrounding a heme group which is a cyclic organic structure with an iron in it.



As amino acid sequences form, they take on ever increasing layers of multidimensionality shown in the picture below, that we like to refer to these as



- primary structure—the sequence of linked amino acids
- secondary structure—which is the three dimensional shape, usually a coil (helix) as shown below, or a sheet

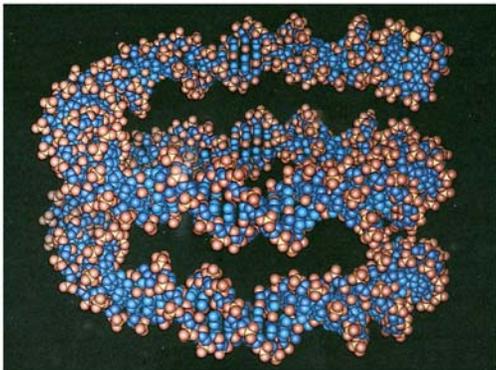


- tertiary structure—the folding that occurs in the larger protein as the sheets and coils come together and try to conform to each other (find the lowest energy way of arranging themselves structurally)
- quaternary structure—when neighboring peptides or proteins stack together, as is seen above when the four peptide units in hemoglobin arrange around each other.

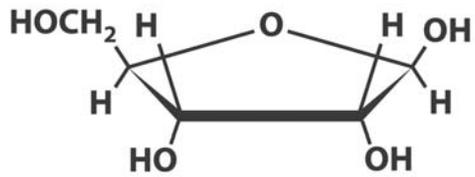
The impressive array of proteins that are the larger biopolymers formed from these original amino acids units are essential to cell function serving every role imaginable including most famously, enzymatic function as we discussed in kinetics (lowering the activation energy of a reaction).

Nucleic Acids.

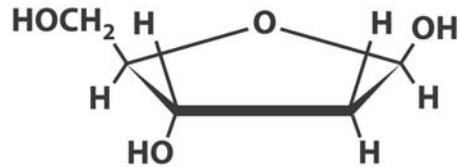
DNA and RNA, which are the molecule that stores the information that make a living organism unique, have to come from somewhere. And as the elaborate three-dimensional rendering below suggests, the building blocks are a but more complicated to unravel than what we have discussed above. There are famous stories about how the structure of DNA was discovered, and to give you a sense of its importance, most everyone knows that Watson and Crick figured out the structure I will describe below, but no one knows who figured out cellulose.



The backbone of DNA and RNA is a sugar called ribose. Note the number of hydroxyl groups that define it as a sugar. This monomeric compound can form repeating units built on the molecule deoxyribose.

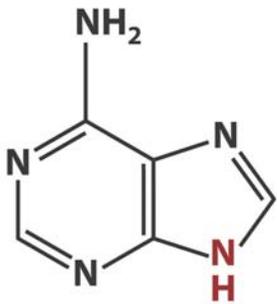


20 Ribose, $C_5H_{10}O_5$

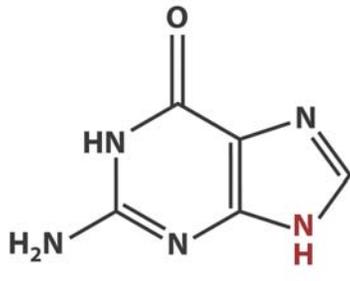


21 Deoxyribose, $C_5H_{10}O_4$

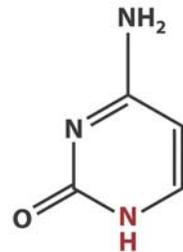
Attached to these sugar units are one of four bases (you can tell because they have amines on them, oh and uracil substitutes for thymine in RNA)



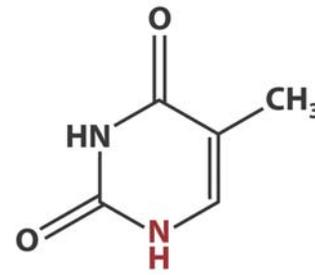
22 Adenine



23 Guanine

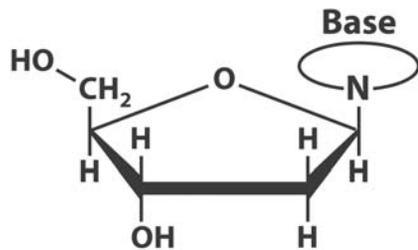


24 Cytosine

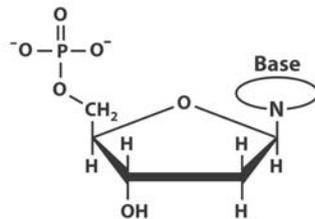


25 Thymine

A base attached to a sugar makes the compound called a nucleoside. And when we add a phosphate, we form the compound called a nucleotide.

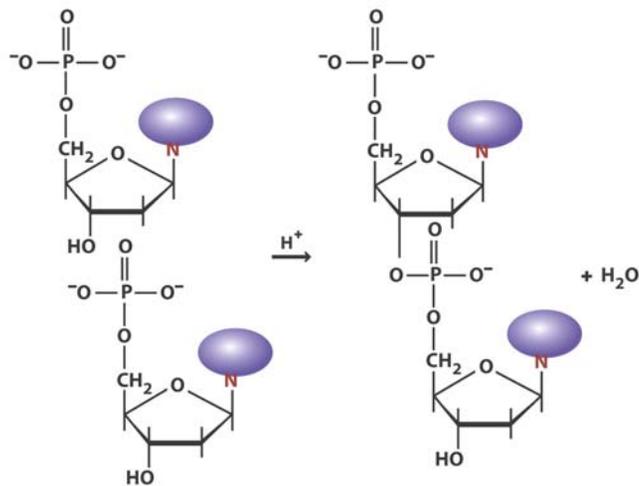


27 A nucleoside



28 A nucleotide

Polynucleotides are what you get when you form linkages of nucleotides. When nucleotides get large enough, they are called nucleic acids. And the most famous of these is DNA.



The great thing about DNA is that it can participate in a chemical reaction that allows for replication, which is good for making new people. So a sophisticated, and in fact, ingenious three-dimensional structure is needed to allow this to happen. Hence, the double helical structure that we all know and love. And I am through with biomolecules.

