

MODERN MATERIALS

❑ LEARNING OBJECTIVES

❖ The goal of this section is to be familiar with the **structure and properties** of modern materials like:

- **Liquid Crystals**
- **Conducting Polymers**
- **Polyelectrolytes**
- **Ionic Liquids**

❑ LIQUID CRYSTALS: The Chemistry Behind Modern Electronic Displays

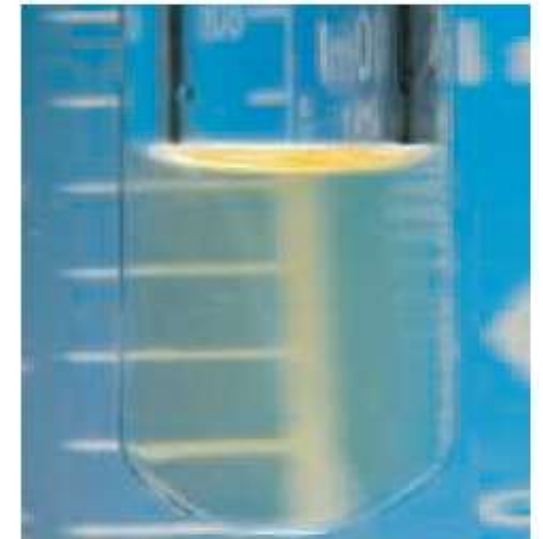
- One type of material that has **transformed electronic displays** is neither a solid nor a liquid, but something intermediate between the two. They are **liquid crystals**. Liquid crystalline materials are finding many applications in the electronics industry because they are responsive to changes in temperature and electric fields.
- ***Liquid crystals** are substances that flow like viscous liquids, but their molecules lie in a moderately orderly array, like those in a crystal. They are examples of a **mesophase**, an intermediate state of matter with the fluidity of a liquid and some of the molecular order of a solid. The molecules that form such liquid crystalline state are called **mesogens**.*
- When *heated*, most solids undergo a simple phase transition from an ordered crystalline solid (in which the molecules or ions are rigidly locked into place) to an isotropic liquid (in which the molecules are free to tumble and move past one another). In the *phase diagrams* for these substances, there are no regions between the liquid and solid phases. There are substances, however, that exhibit one or more phases intermediate between the liquid state and the solid state. In these ***intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid***. Hence they are called **liquid crystals**, and *their unusual properties* have found a wide range of commercial applications.

➤ The first documented example of a liquid crystal was reported by the Austrian botanist Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C. The transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C. **The 'liquid', later called a thermotropic liquid crystal,** was *anisotropic until the clearance temperature was reached.*

➤ Thermotropic liquid crystals are built from **form-anisotropic molecules** bearing the name *mesogens*.



$145\text{ }^{\circ}\text{C} < T < 179\text{ }^{\circ}\text{C}$
Liquid crystalline phase



$T > 179\text{ }^{\circ}\text{C}$
Liquid phase

Figure 11.31 Cholesteryl benzoate in its liquid and liquid crystalline states.

❑ Liquid Crystals

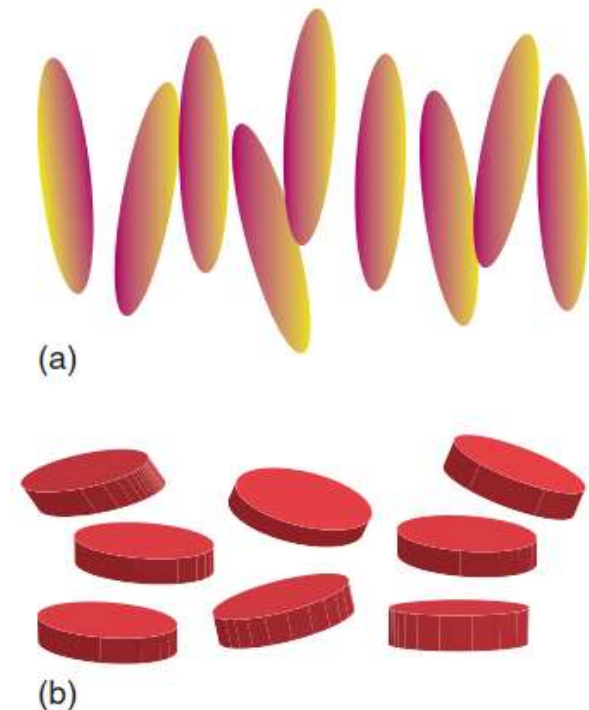
- A **liquid crystal** is a *thermodynamic stable phase* characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in the temperature range between the solid and isotropic liquid phase, hence the term ***mesophase***.
- ***Liquid crystalline, or mesogenic, compounds possess properties that lie between those of solids and liquids and include both.*** For instance, *they are fluid, but with positional order in at least one dimension.*
- Such materials have become widely *used in displays.*
- ***Ordinary fluids are isotropic*** in nature: *they appear optically, magnetically, electrically, etc. to be the same from any direction in space.* Although the molecules which comprise the fluid are generally anisometric in shape, this anisometry generally plays *little role in macroscopic behavior.*

❖ Characteristics of liquid crystalline molecules

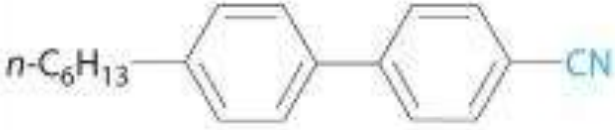
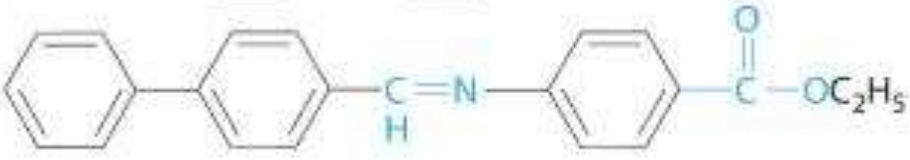
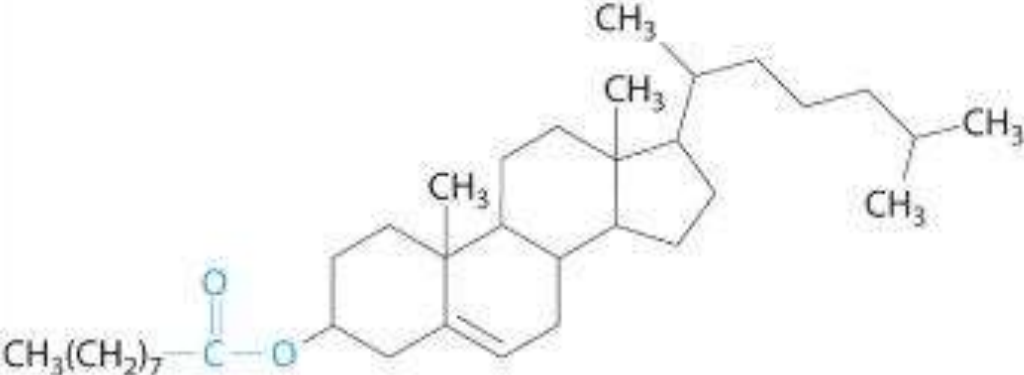
➤ A very large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical composition, these molecules have some common features in chemical and physical properties. Liquid crystal materials generally have several **common characteristics**. Among these are long, **calamitic (rod-like)** or **discotic (disc-like)** molecular structure (Figure 24.74), **rigidness** of the long axis, and strong **dipole and/or** easily **polarizable** substituents that offer dissimilar local structural regions that can interact in an organized way with their neighbors. Over a certain range of temperatures, these attractive forces can lead to a degree of self-organization in which crystal-like order persists in some directions even though it is lost in other directions. Although a large variety of molecules are known to form liquid crystals, the simplest and most common structures can be represented by the following generic scheme:

- 1) The molecule must be **elongated** in shape; *length should be significantly greater than its width.*
- 2) Molecule must have **some rigidity** in its central region.
- 3) The **ends** of the molecule are somewhat **flexible**.
- 4) There is strong **dipole and/or easily polarizable** substituent in the molecule.

Figure 24.74 Schematic diagram of liquid crystalline materials based on (a) **calamitic** (rod-like) and (b) **discotic** (disc-like) molecules.



➤ Some Typical examples of LC molecules

Structure	Liquid Crystal Phase	Liquid Crystalline Temperature Range (°C)
 $n\text{-C}_6\text{H}_{13}$ —C ₆ H ₄ —C ₆ H ₄ —CN	Nematic	14–28
	Smectic	121–131
 $\text{CH}_3(\text{CH}_2)_7\text{—C(=O)O—}$	Cholesteric	78–90

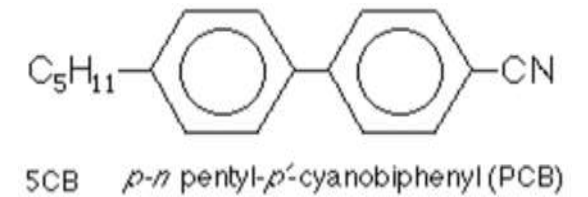
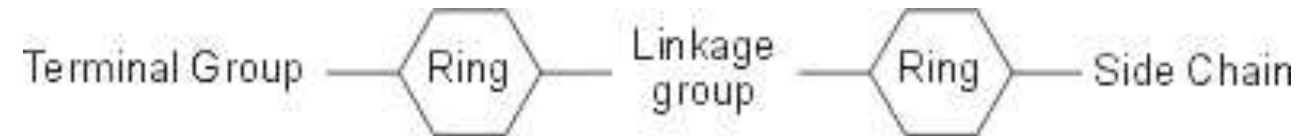


Figure 11.8.2 Structures of Typical Molecules That Form Liquid Crystals Polar or polarizable groups are indicated in blue.

❖ Typical representation of a LC molecule

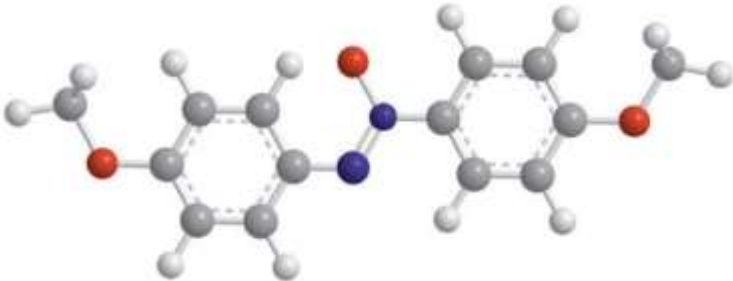
- The figure below shows the molecular structure of a **typical rod-like liquid crystal molecule**. It consists of two or more ring systems connected by a central linkage group. The benzene rings confer a degree of planarity on the molecule that promotes attractions between neighboring molecules. This planarity is enhanced when the linkage group contains a double bond such as $-(HC=N)-$ which keeps the rings in the same plane.



Typical shape of a liquid crystal molecule

- The **presence of the rings provides the short-range molecular forces needed to form the nematic phase** but **also affects the electrical and elastic properties**.
- The interconnecting group should cause the resulting compound to have a linear planar conformation. Linking units containing multiple bonds such as $-(CH=N)-$, $-N=N-$, $-(CH=CH)_n-$, $-CH=N-N=CH-$, etc. are used since they restrict the freedom of rotation. These groups can conjugate with phenylene rings, enhancing the anisotropic polarizability. This increases the molecular length and maintains the rigidity.
- **The chemical stability of liquid crystals, their resistance to, e.g., moisture or ultraviolet radiation, depends strongly on the central linkage group.** Compounds with a single bond in the center are among the most stable ones.
- At one side of the rings, there is a **long side chain**. The side chain is commonly a hydrocarbon chain that serves to elongate the molecule which strongly **influences the elastic constants and the transition temperature** of the liquid crystal phases.
- At the other end, **a terminal group is connected, which** is often (but not always) one that is somewhat polar, giving rise to intermolecular attractions along the long axis. The terminal group **determines the dielectric constant and its anisotropy**.
- A few examples of molecules that exhibit a liquid crystal phase are shown above/below.


Some liquid crystal forming molecules

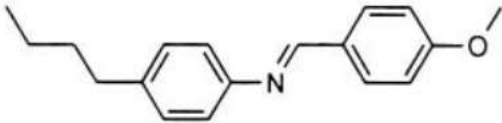


14 **p-Azoxyanisole**

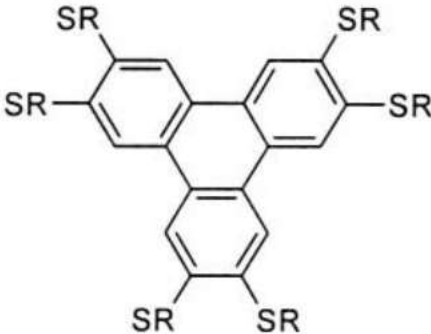


105a $R = \text{CH}_3$

105b $R =$ 

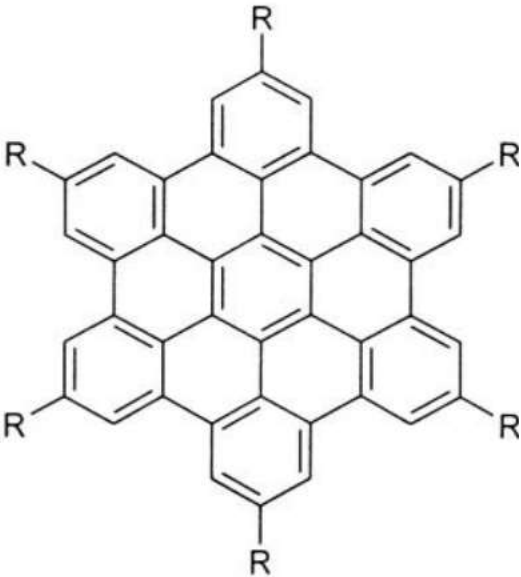


107



$R = \text{C}_6\text{H}_{13}$

108



106 ($R = \text{H}$)

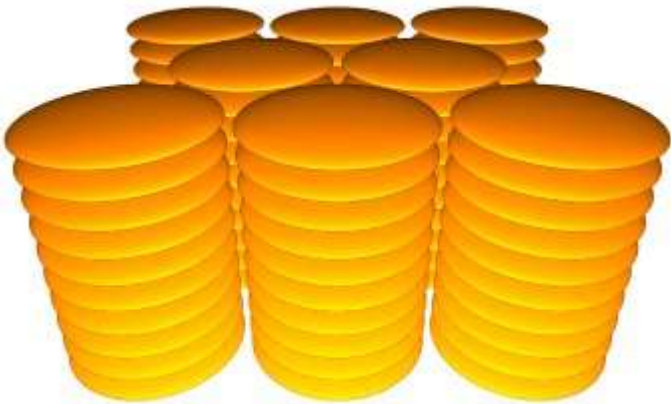
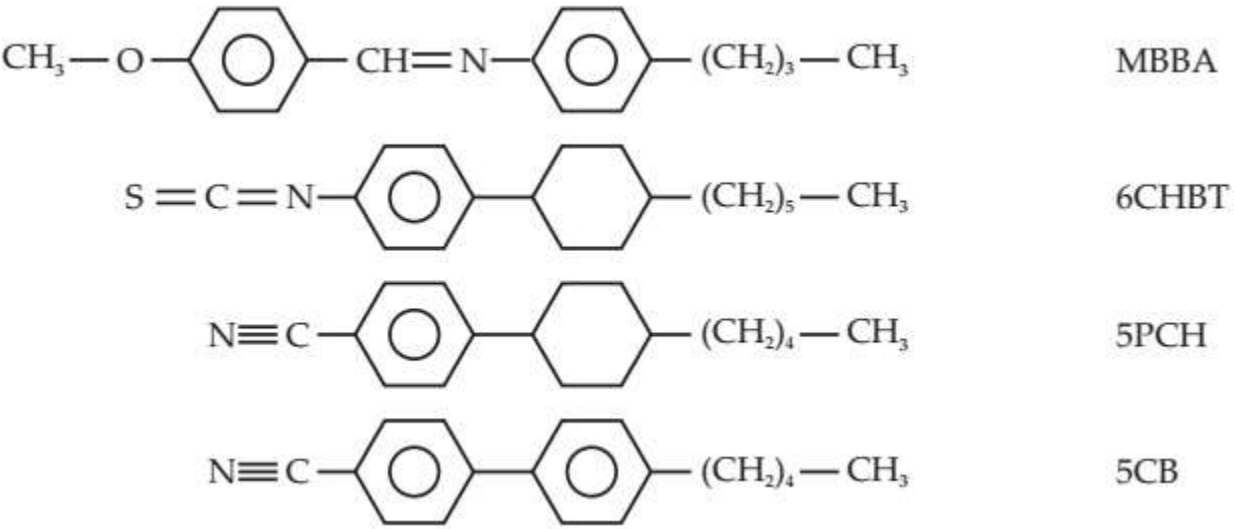
106a ($R = n\text{-C}_{12}\text{H}_{25}$)

106b ($R = n\text{-C}_{14}\text{H}_{29}$)

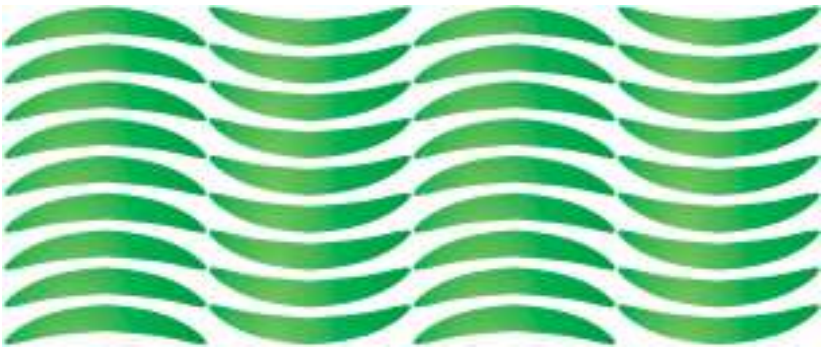
106c ($R = n\text{-C}_{16}\text{H}_{33}$)

Figure 2.4: The molecular structure of four liquid crystal materials:

MBBA (4'- methoxybenzylidene - 4 - butylaniline),
6CHBT (4- trans - n - hexyl - cyclohexyl - isothiocyanatobenzene),
5PCH (4 - (trans - 4' - pentyl - cyclohexyl) - benzonitril) and
5CB (4 - pentyl - 4' -cyanobiphenyl).



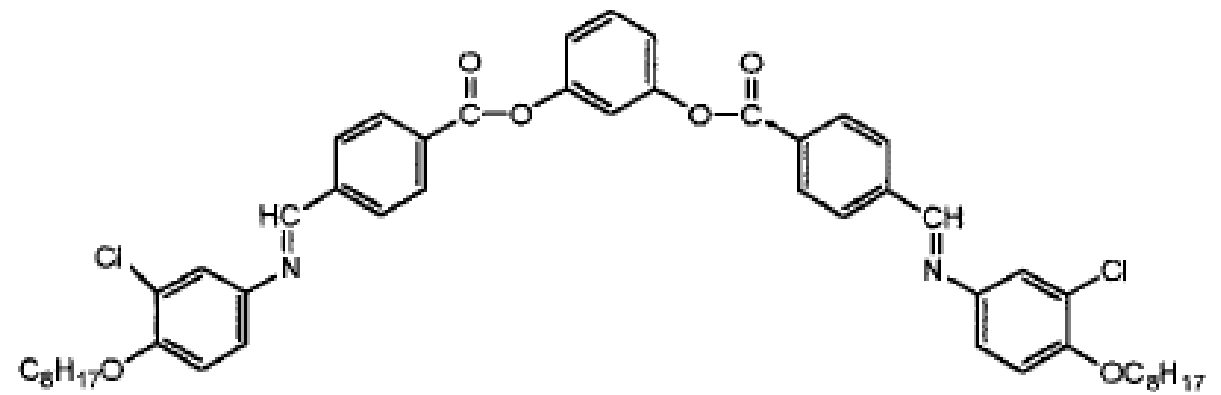
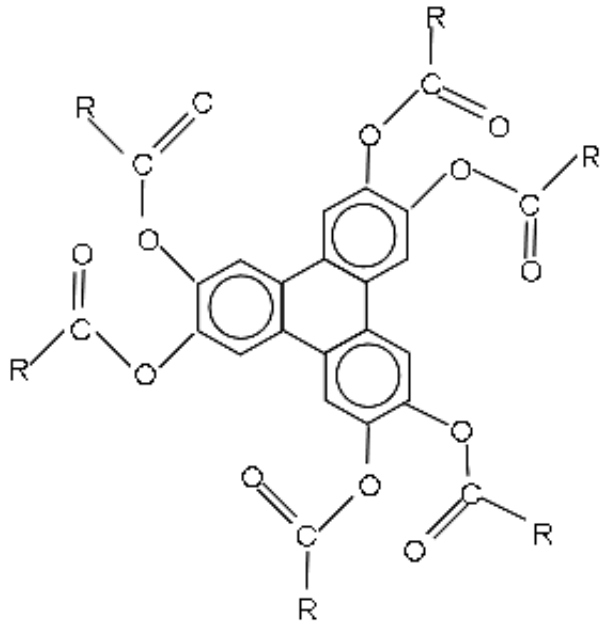
Discotic shaped liquid crystals



Banana shaped liquid crystals

➤ Beside these simple examples, ***more complicated ways of stacking are possible, giving rise to many other types of liquid crystals. Chiral molecules***, molecules without mirror symmetry, can give rise to helices comprising cholesteric liquid crystal phases. In *ferroelectric* or *antiferroelectric* liquid crystals, the *smectic layers possess a permanent polarization* which is constant or alternating between successive layers respectively. Apart from the rod-like molecules, more advanced-shaped liquid crystals are possible such as disk-like or banana-shaped liquid crystals which can give rise to other types of ordering. Discotic liquid crystals can be stacked a columnar phase, the bottom picture illustrates a possibility for stacking banana shaped liquid crystals. Examples of molecules which give rise to discotic and banana shaped liquid crystal phases are shown below.

**Discotic
shaped liquid
crystal
molecule**



Banana shaped liquid crystal molecule

- Although most liquid crystalline materials are totally organic, there is a growing number of inorganic liquid crystals based on the ***coordination compounds of metals and on organometallic compounds***. These metal-containing liquid crystals show similar properties to the purely organic systems but ***offer additional properties associated with a d-metal center, such as redox and magnetic effects***.

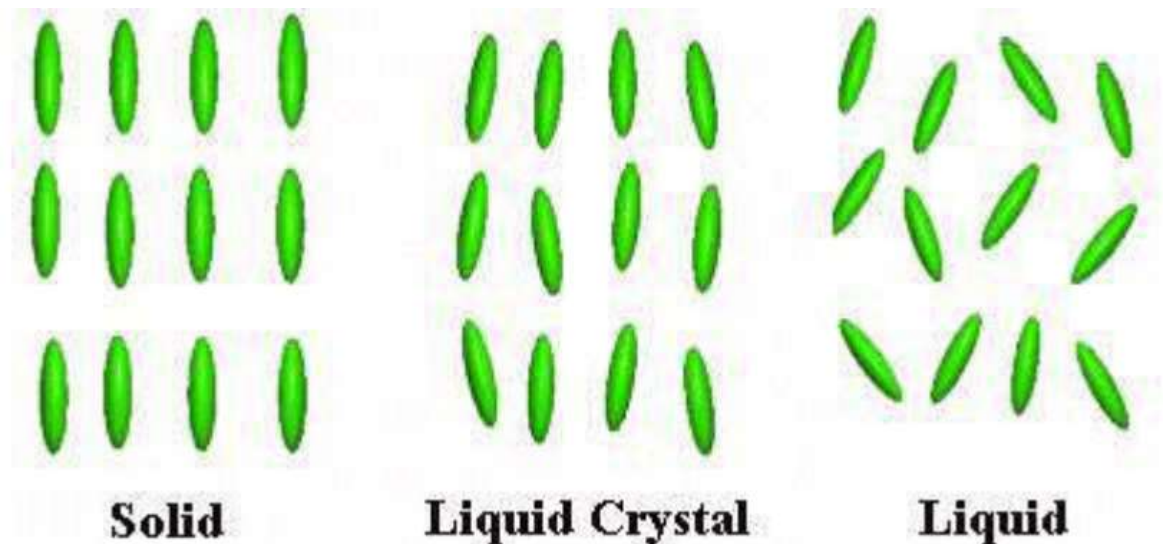
❑ Why Liquid Crystals Form?

- In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as isotropic, which means that it is equally disordered in all directions.
- Liquid crystals, in contrast, are anisotropic: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.
- In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.
- **Uneven distribution of electrons in the molecule gives rise to** the electrostatic contributions like *dipole–dipole interactions*, molecular hydrogen bonds, etc., in addition to van der Waals forces.
- **Intermolecular forces strong enough to cause the molecule line up in the same overall direction but not strong enough to hold them firmly in one place (over a certain range of temperatures).**
- Most substances that exhibit the properties of liquid crystals consist of long, rigid ***calamitic (rod-like) or discotic (disc-like)*** molecules that are easily polarizable and can orient themselves in ***a particular direction leading to the ordered liquid-type structures***. Their ***disc- or rod-like shape*** enables the molecules to ***stack together*** and ***lie parallel*** to one another but ***are free to slide past one another along their long axes***.

❑ Distinguishing Characteristics of Liquid Crystals

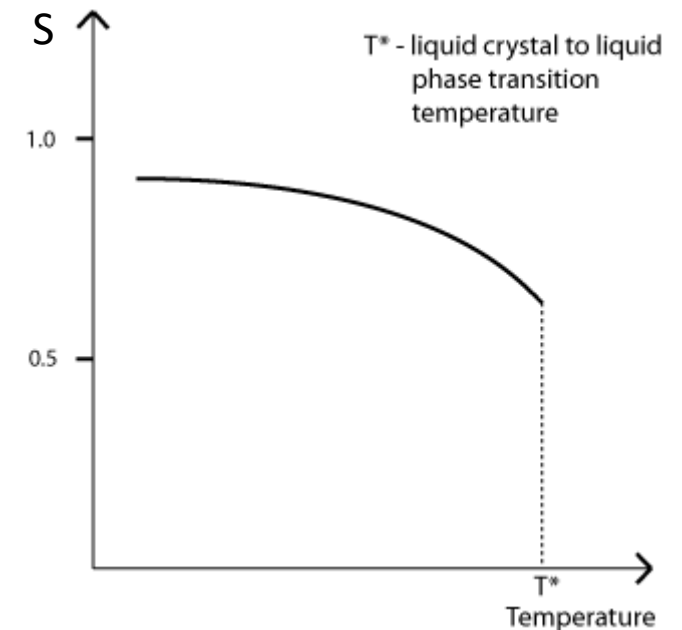
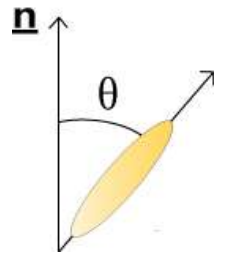
- The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (**mesogens**) to **orient** themselves **along a common axis, called the director** (the molecular direction of preferred orientation in liquid crystalline mesophases). This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. **The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases** and this is the origin of the term mesogenic state, used synonymously with liquid crystal state.
- Note the average alignment of the molecules for each phase in the following diagram.

- A **mesogens** are rigid rod-like or disc-like molecules which are components of liquid crystalline materials.



- It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state.
- Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic (having properties that are the same regardless of the direction of measurement. In the isotropic state, all directions are indistinguishable from each other) liquid has no orientational order. *Substances that aren't as ordered as a solid yet have some degree of alignment are properly called liquid crystals.* The term **crystallinity implies the presence of three-dimensional order on the level of atomic dimensions.**
- In polymers, the range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in at least one direction. Polymer crystals frequently do not display the perfection that is usual for low-molecular mass substances. Polymer crystals that can be manipulated individually are often called polymer single crystals.

- **To quantify** just **how much order** is present in a material, an order parameter (S) is defined. S describes the orientational order of liquid crystalline material, allowing for the individual **orientational deviation of the molecules from the director**, which **represents the average over the collection**.
- Due to their distinctive shape calamitic liquid crystal molecules undergo stronger attractive forces when arranged parallel to one another. They therefore tend to align themselves pointing along one particular direction; this is known as the **director** vector and is given the notation \underline{n} . The angle between individual liquid crystal molecules and the director gives an indication of the **orientational order** of the system, which can be calculated using the following formula:
- The **order parameter**, $S = (3 \langle \cos^2 \theta \rangle - 1) / 2$ where θ is the angle between the director and the long axis of each molecule. The brackets denote an average over all of the molecules in the sample.
- In an **isotropic liquid**, the **average of the cosine terms is zero**, and therefore the **order parameter is equal to zero**.
- For a **perfect crystal**, the **order parameter evaluates to one**.
- Typically, S ranges from 0.3 to 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion.
- This is illustrated below for a nematic liquid crystal material .



- The tendency of the liquid crystal molecules to point along the director leads to a condition known as ***anisotropy***.
- This term means that the properties of a material depend on the direction in which they are measured.
- For example, it is easier to cut a piece of wood along the grain than against it.
- The anisotropic nature of liquid crystals is responsible for the unique optical properties exploited by scientists and engineers in a variety of applications.

❑ Characterizing Liquid Crystals

The following parameters describe the liquid crystalline structure:

- ***Orientational order***: Measure of the tendency of the molecules to align **along the director** on a long-range basis.
- ***Positional order***: The extent to which the **position of an average molecule or group of molecules** shows translational symmetry.
- ***Bond orientational order***: Describes a **line joining the centers of nearest-neighbor molecules** without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short-range positional order along that line.

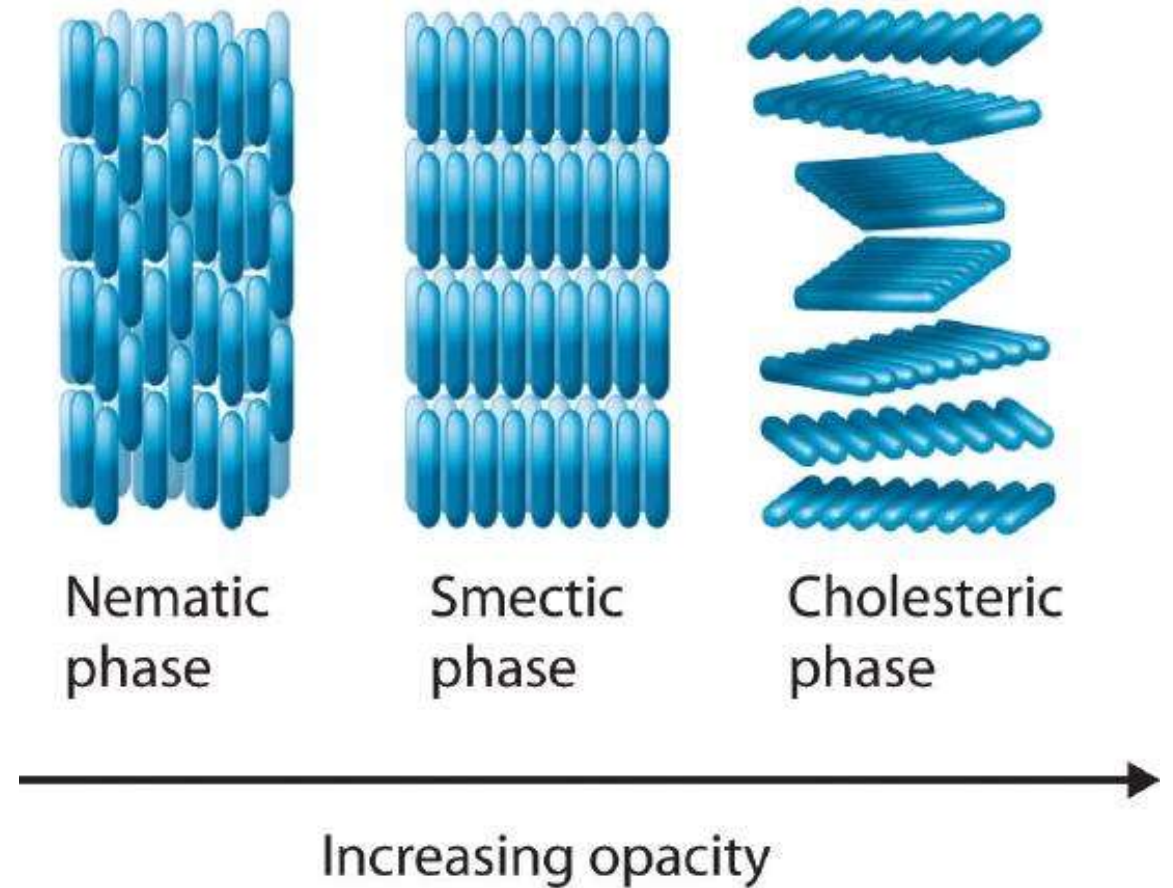
- Each of these parameters describes the extent to which the liquid crystal sample is ordered. **Positional Order** refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows).
Orientalional Order, as discussed above, represents a measure of the tendency of the molecules to align along the director on a long-range basis.
Bond Orientalional Order describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short-range positional order along that line.
- Most liquid crystal compounds exhibit **polymorphism**, or a condition where more than one phase is observed in the liquid crystalline state.
- The term **mesophase** is used to describe the "subphases" of liquid crystal materials. **Mesophases** are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion.
- The following section describes the mesophases of liquid crystals in greater detail.

❑ Liquid Crystal Phases

- The liquid crystal state is a distinct phase of matter observed between the crystalline (solid) and isotropic (liquid) states. *There are **many types of liquid crystal states**, depending upon the amount of order in the material.* This section will explain the phase behavior of liquid crystal materials.
- Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, as shown in Figure 11.8.1.
- In the nematic phase, the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another.
- In the smectic phase, the molecules maintain the general order of the nematic phase but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smectic A phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another.
- In the cholesteric phase, the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it.
- As the degree of molecular ordering increases from the nematic phase to the cholesteric phase, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.

Diagrammatic representation of phases of liquid crystals.

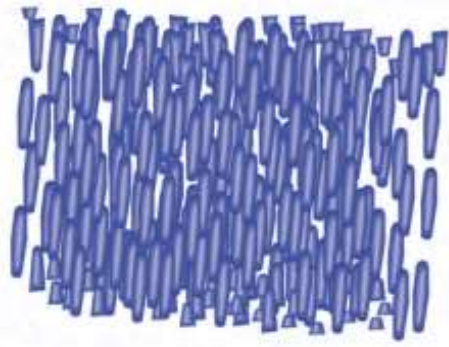
Figure 11.8.1 The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases In the *nematic* phase, only the long axes of the molecules are parallel, and the ends are staggered at random intervals. In the *smectic* phase, the long axes of the molecules are parallel, and the molecules are also arranged in planes. Finally, in the *cholesteric* phase, the molecules are arranged in layers; each layer is rotated with respect to the ones above and below it to give a spiral structure. The molecular order increases from the nematic phase to the smectic phase to the cholesteric phase, and the phases become increasingly opaque.



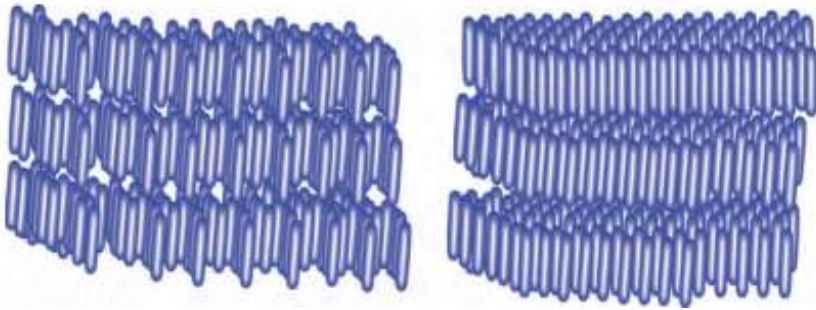
Different phases of a *thermotropic* liquid crystals.

- The *nematic phase (orientational order)*: The molecules tend to have the same alignment, but their positions are not correlated.
- *Smectic* liquid crystals: *exhibit some positional order*. In smectics, the molecular centers of mass are arranged in layers.
- The *cholesteric phase*: The molecules tend to have the same alignment which varies regularly through the medium with a periodicity distance $p/2$. The positions of the molecules are not correlated.

(a)



(b)



(c)

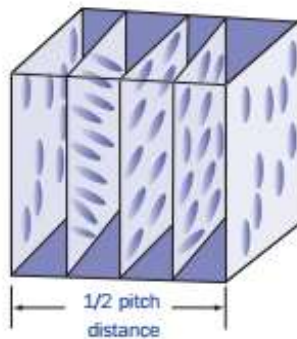


Figure 4.11 Diagrammatic representation of forms of **thermotropic** liquid crystals. (a) nematic, (b) smectic and (c) cholesteric liquid crystals.

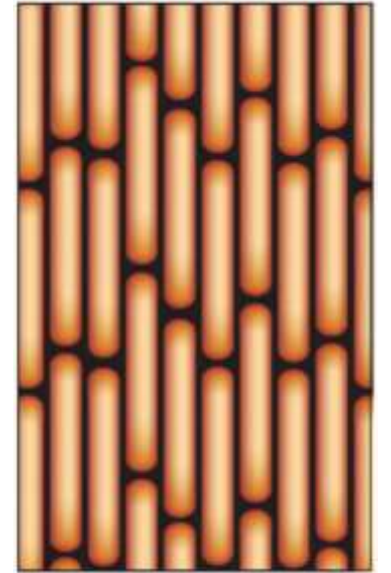
In the **nematic** phase all molecules are aligned approximately parallel to each other. In each point a unit vector can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighborhood.

Nematic comes from the Greek word for “thread”; **smectic** comes from the Greek word for “soapy”; **cholesteric** is related to the word cholesterol, which comes from the Greek words for “bile solid.”

❑ Liquid Crystal Phases

1. Nematic Phases

- The nematic liquid crystal phase is characterized by molecules that have ***no positional order*** but exhibit ***orientational order*** such that ***tend to point in the same direction (along the director)***. The molecules are still able to move around in the fluid, but their orientation remains the same. In the following diagram, notice that the molecules point vertically but are arranged with no particular order.



nematic

Note: *thermal disorder that upsets the regularity of the arrays to some extent.*

- Liquid crystals are anisotropic materials, and the physical properties of the system vary with the average alignment with the director. If the alignment is large, the material is very anisotropic. Similarly, if the alignment is small, the material is almost isotropic. Owing to their polarity, the alignment of the rod-like molecules can be controlled by applying an electric field; this is the physical basis for liquid crystal displays and certain other electrooptic devices.
- A special class of nematic liquid crystals is called chiral nematic. Chiral refers to the unique ability to selectively reflect one component of circularly polarized light. The term ***chiral nematic is used interchangeably with cholesteric***. Refer to the section on cholesteric liquid crystals for more information about this mesophase.

2. Smectic Phases

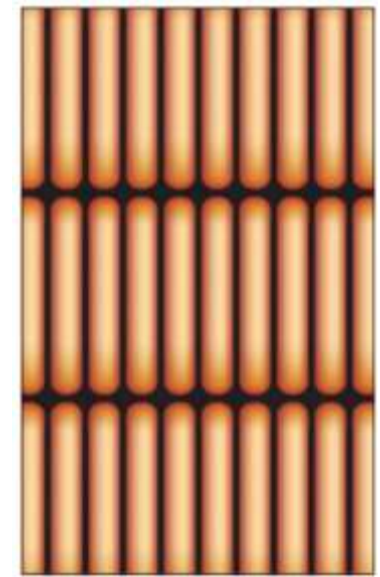
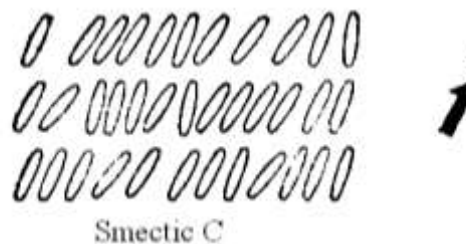
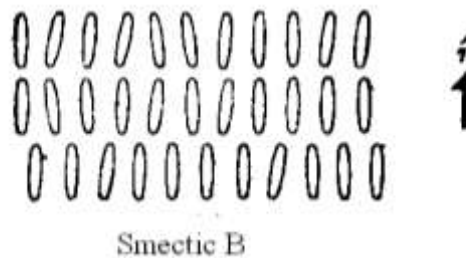
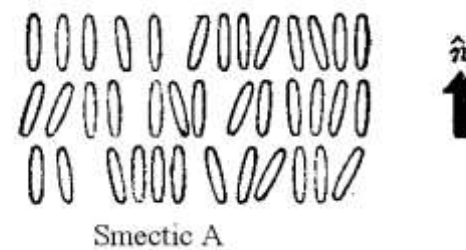
- The word "smectic" is derived from the Greek word for soap. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal.
- The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a ***degree of translational order not present in the nematic***. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to ***align themselves in layers or planes***. Motion is restricted to within these layers and the movement is mainly limited inside the layers. Separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic. Cell membranes are composed mainly of smectic liquid crystals.
- In smectics, the molecular centers of mass are arranged in layers In *smectic* ("soap-like") phases the molecules are arranged in layers, with the long molecular axes approximately perpendicular to the laminar planes. The only long-range order extends along this axis, with the result that individual layers can slip over each other (hence the "soap-like" nature) in a manner similar to that observed in graphite. Within a layer there is a certain amount of short-range order. There are a large number of sub-categories of smectic phases which we will not go into here.

- Many compounds are observed to form **more than one type of smectic phase**. As many as 12 of these variations have been identified, however only the most distinct phases are discussed here.
- In the **smectic-A mesophase**, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer.
- Similarly, the **smectic-B mesophase** orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer.
- In the **smectic-C mesophase**, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane.

A type: molecular alignment perpendicular to the surface of the layer, but **lack of order within the layer**.

B type: molecular alignment perpendicular to the surface of the layer, **having order within the layer**.

C type: having a **tilted angle** between molecular alignment and the surface of the layer.

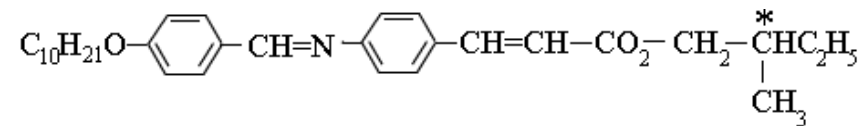


smectic

Note: thermal disorder that upsets the regularity of the arrays to some extent.

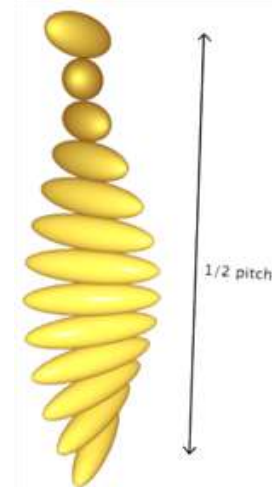
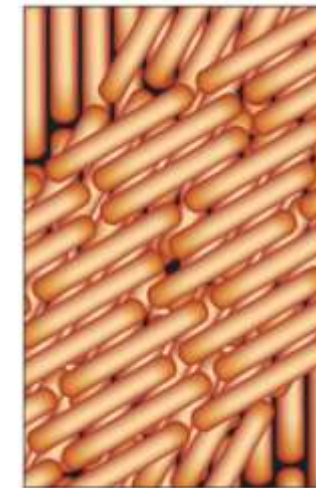
3. **Cholesteric or Chiral Nematic** phases

- Special cases of nematic and smectic phases are sometimes formed by molecules that display **chirality** — that is, they can exist in either left- or right-handed forms that cannot be superposed on each other. In the resulting **chiral phase**, successive molecules positioned along the long axis are rotated around this axis, giving rise to a periodicity that repeats itself at distances corresponding to a complete rotation. we see a helical structure, where the *director vector* is rotated slightly in each subsequent layer of molecules – the distance along the axis between two molecules with parallel director vectors is called the *pitch* of the liquid crystal. Historically, they were also known as *cholesteric* liquid crystals as the first molecules found to display these properties were those related to cholesterol. As we will later see, the different degrees of positional ordering lead to very different optical properties.
- These twisted phases are able to rotate the plane of polarized light that passes along the axis. If the molecules are polar, this twisting can be turned off by imposing an external electric field at either end of the long axis. Besides the very important application of this property (known as *ferroelectricity*) to liquid crystal displays, these materials can be used to make electrooptic shutters which can be switched open and closed in microseconds.
- A typical chiral molecule capable of exhibiting ferroelectric behavior is shown below. The chiral part of the molecule is indicated by the asterisk.



- In the **cholesteric phase** the molecules form ordered layers, but neighboring layers have molecules at different angles and so the liquid crystal **has a helical arrangement of molecules**. The molecules' alignment varies regularly through the medium with a periodicity distance $p/2$. The positions of the molecules are not correlated.

Note: *thermal disorder that upsets the regularity of the arrays to some extent.*



Cholesteric (Chiral Nematic)

❑ Liquid crystals are ***classified by their manner of preparation.***

- These two types of liquid crystals are ***distinguished by the mechanisms that drive their self-organization***, but they are also similar in many ways.
- ***Thermotropic*** transitions occur in most liquid crystals, and ***thermotropic liquid crystals*** are defined by the fact that the transitions to the ***liquid crystalline state are induced thermally***. That is, one can arrive at the liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a liquid. The highly viscous ***liquid-crystal phase exists over a short temperature range*** between the solid and liquid states. Thermotropic liquid crystals become isotropic liquids when they are heated above a ***characteristic temperature***, because then the molecules have enough energy to overcome the attractions that restrict their movement. ***p-Azoxyanisole is a thermotropic*** liquid crystal. Thermotropic liquid crystals are used in applications such as watches, computer screens, and thermometers.
- ✓ ***Thermotropic liquid crystals can be classified into two types: enantiotropic*** liquid crystals, which can be changed into the liquid crystal state from *either* lowering the temperature of a liquid or raising of the temperature of a solid, and ***monotropic*** liquid crystals, which can *only* be changed into the liquid crystal state from *either an increase* in the temperature of a solid *or a decrease* in the temperature of a liquid, but not both.
- ✓ In general, thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions.

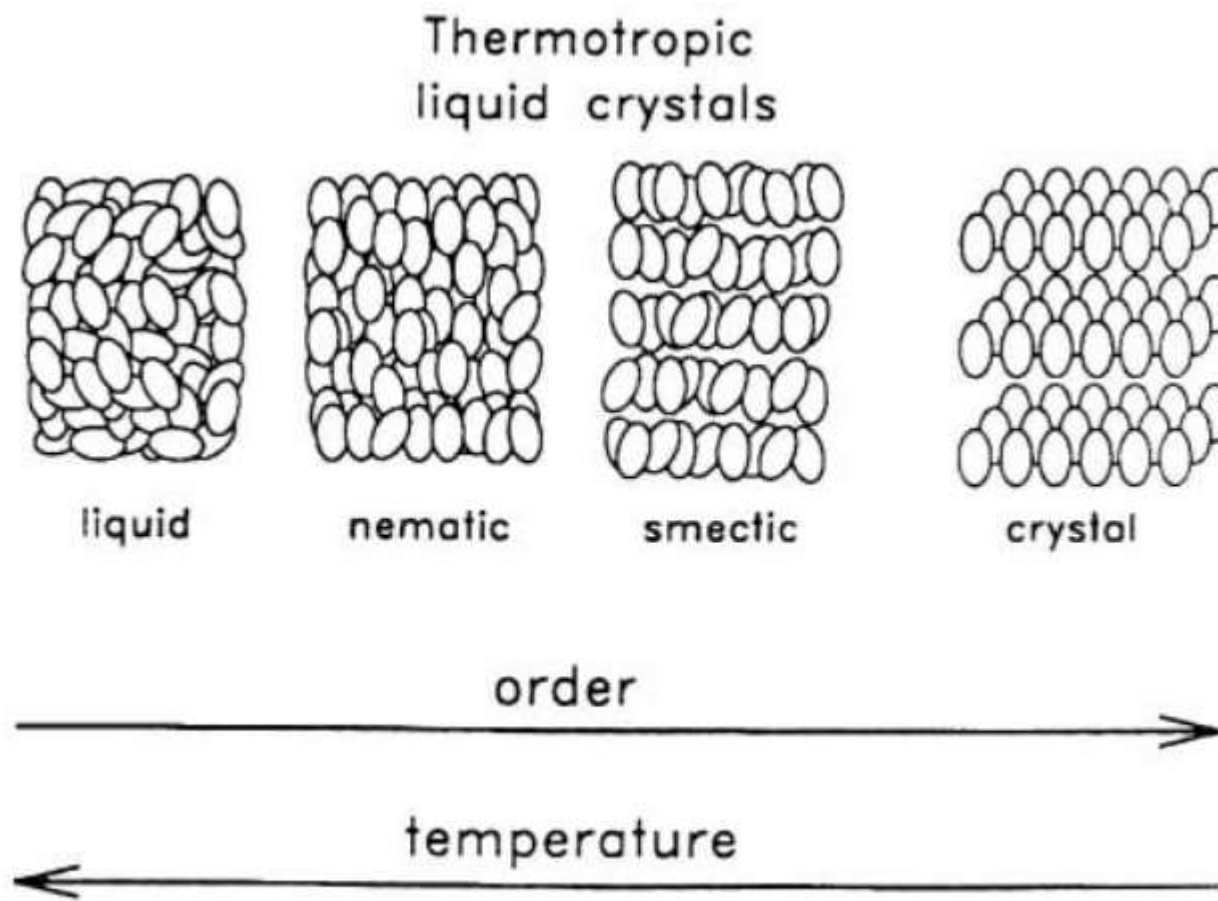
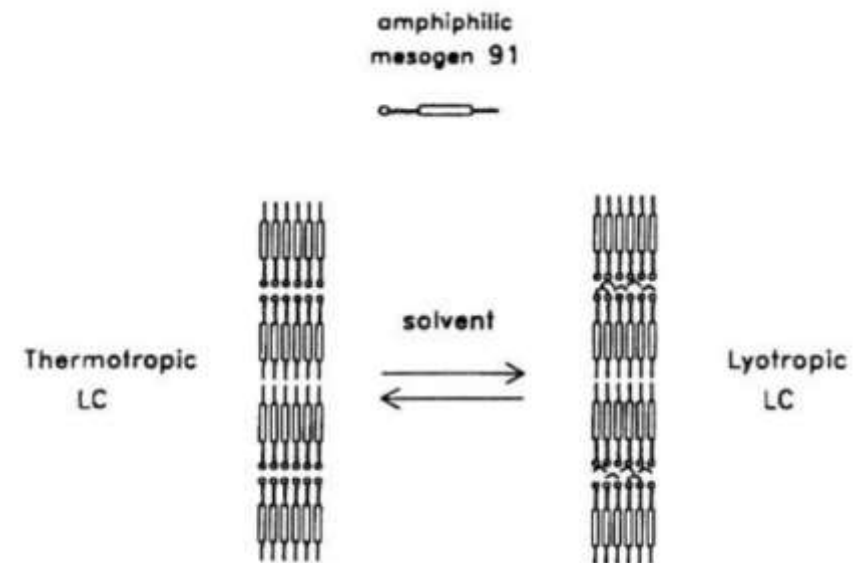
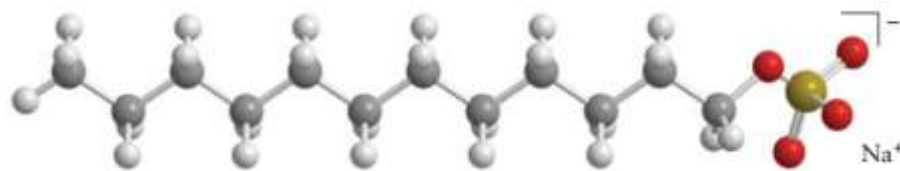


Figure 4.14. Schematic presentation of ordering in liquid, liquid crystal, and crystal.

- By varying the temperature between those corresponding to the *crystalline and liquid* phases one can generate a **nematic phase with a preferred orientation of the longitudinal molecular axis** and one of the **smectic phases characterized by a layered arrangement of mesogens orientated perpendicularly or at an angle to the layers**.

- **Lytotropic liquid crystal** transitions occur with the *influence of solvents* on a solid or liquid, *not by a change in temperature*.
- ✓ Lyotropic mesophases occur as a result of solvent-induced aggregation of the constituent mesogens into micellar structures.
- ✓ Lyotropic mesogens are typically amphiphilic, meaning that they are composed of both lyophilic (solvent-attracting) and lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophilic ends extend outward toward the solution. As the concentration of the solution is increased and the solution is cooled, the micelles increase in size and eventually coalesce. This separates the newly formed liquid crystalline state from the solvent.
- ✓ Examples are cell membranes and aqueous solutions of detergents and lipids (fats). These molecules, like the detergent **sodium lauryl sulfate (SLS or sodium dodecyl sulfate, SDS)** have long, nonpolar hydrocarbon chains attached to polar heads (15). When the lipids that form cell membranes are mixed with water, they spontaneously form sheets in which the molecules are aligned in rows, forming a double layer, with their polar heads facing outward on each side of the sheet. These sheets form the protective membranes of the cells that make up living tissues.
- The kind of liquid crystal requiring a solvent for formation bears the name **lyotropic liquid crystals**.

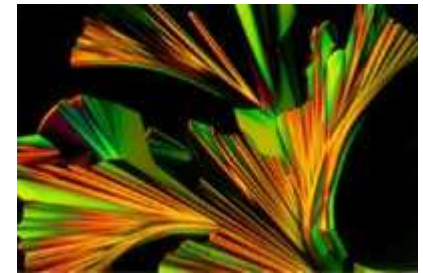
15 Sodium lauryl sulfate



- ***One type of liquid crystal molecule can exhibit many different liquid crystal phases.*** The phase in which a pure liquid crystal (with only one type of molecule) exists depends on the temperature. *Pure liquid crystals, or mixtures of them, in which the phase is controlled by temperature are called **thermotropic** liquid crystals.* The Brownian motion of the molecules increases with the temperature, reducing the order in the material. At high temperature, orientational order is lost and the material changes to the isotropic phase.
- ✓ When ***decreasing the temperature***, the material changes to the ***nematic*** phase. **The temperature at which the phase transition occurs, is specific for each material and is called the *nematic-isotropic transition temperature* or *clearing point*.**
- ✓ *By further lowering the temperature, the phase can change to the smectic A phase, the smectic C and finally to the solid state.*
- ✓ Each of the phase transitions occurs at a specific temperature, but depending on the material additional phases can appear or some can be missing.
- *Beside the thermotropic liquid crystals, a different class of liquid crystals is called **lyotropic**. These are mixtures of rod-like molecules **in an isotropic solvent** and **the concentration of the solution** is primarily **responsible** for the occurring phase.* Lyotropic liquid crystals are mainly of interest in biological applications and exhibit a considerable number of different phases.

❑ Properties of Liquid Crystals

- Liquid crystals are ***anisotropic*** because of this ordering. ***Anisotropic materials*** have *properties that depend on the direction of measurement*.
- For example, the *viscosity of liquid crystals is least in the direction parallel to the long axis of the molecules*: it is easier for the long rod-shaped molecules to slip past one another along their axes than to move sideways.
- *Isotropic materials have properties that do not depend on the direction* of measurement. Ordinary liquids, like water, are isotropic: their viscosities are the same in every direction.
- Liquid crystal phases are generally cloudy in appearance, which means that they scatter light in much the same way as colloids such as milk. This light scattering is a consequence of fluctuating regions of non-uniformity as small groups of molecules form and disperse.
- The anisotropy of liquid crystals causes them to exhibit *birefringence*. That is, light that enters the crystal is broken up into two oppositely-polarized rays that travel at different velocities. Observation of a birefringent material between crossed polarizing filters reveals striking patterns and color effects. The colors arise from interference between the *ordinary ray* and the *extraordinary ray*; the latter traverses a slightly longer path through the material and thus emerges later (and out-of-phase) with the former.
- Liquid crystals, like all other kinds of matter, are subject to thermal expansion. As the temperature rises, the average spacing between the aligned molecules of a nematic phase (see below) increases, thus causing the e-ray to be increasingly retarded with respect to the o-ray. If a suitable liquid crystal mixture is painted onto the surface of a patient's body, it can often reveal the sites of infection or tumors, which cause increases or reductions in local blood flow giving rise to temperature anomalies. Inexpensive *thermometers* can be made by printing a succession of suitably formulated LC mixtures on a paper or plastic strip which is held in contact with the surface whose temperature is to be measured.



❑ Applications of Liquid Crystals

- Liquid crystal technology has had a major effect many areas of science and engineering, as well as device technology. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems. ***Liquid crystals have a degree of order characteristic of solid crystals, but they can flow like viscous liquids. They are mesophases, intermediate between solids and liquids; their properties can be modified by electric fields and changes in temperature.***
- **Liquid Crystal Displays**
 - The most common application of liquid crystal technology is liquid crystal displays (LCDs.) This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made.
- **Optical Imaging**
 - An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research.
- **Liquid Crystal Thermometers**
 - Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the helical structure of the cholesteric liquid crystals unwinds slightly as the temperature, the twist of the helical structure affects the optical properties of the liquid crystal, such as its color. Therefore, these properties change with temperature. The effect is utilized in ***liquid-crystal thermometers***. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer. By mixing different compounds, a device for practically any temperature range can be built.

➤ Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color (Figure 11.8.4) and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

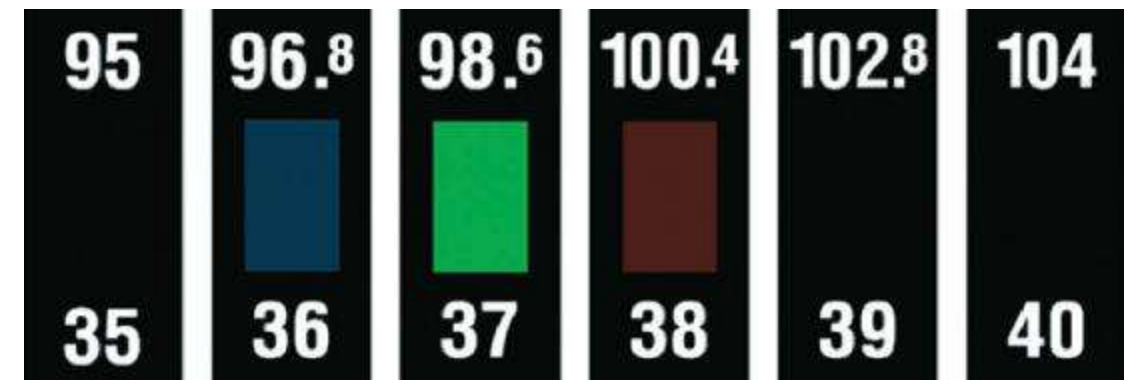


Figure 11.8.4 An Inexpensive Fever Thermometer That Uses Liquid Crystals Each section contains a liquid crystal sample with a different liquid crystalline range. The section whose liquid crystalline range corresponds to the temperature of the body becomes translucent (here shown in green), indicating the temperature.

▪ **Other Liquid Crystal Applications**

- Liquid crystals have a multitude of other uses. They are used for nondestructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full color "electronic slides" for computer-aided drawing (CAD), and light modulators for color electronic imaging.
- As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications.

❑ Applications

- For almost 80 years studies of these and other substances exhibiting similar behaviour were thought to be a mere curiosity of no practical significance.
- The situation has changed rapidly with the development of the first compound **exhibiting liquid crystal behaviour at room temperatures** 4-methoxybenzylidene-4'-n-butyraniline (**107**).
- The *nematic liquid crystal phase is by far the most important phase for applications*. At present there are huge industrial application of liquid crystals *in wrist watches and high contrast computer displays*.
- Many other applications of ferroelectric liquid crystals as sophisticated optical computing systems, flat panels for high-definition computer and video displays, and materials exhibiting nonlinear optical properties are foreseen in the near future.
- Notably, some high strength polymeric materials, such as the famous Kevlar, are spun out of lyotropic liquid crystal.

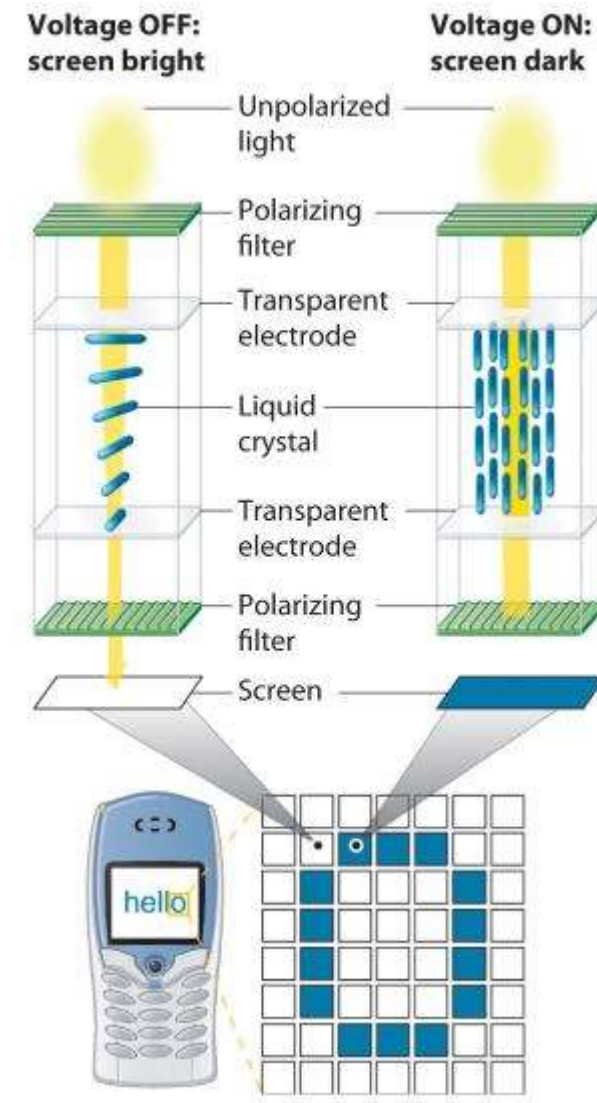
Applications

➤ **Electronic displays** make use of the ***anisotropy of the nematic phase*** and the changes in *orientation of liquid-crystal molecules caused by **an electric field***. In an **LCD (liquid-crystal display)** television or computer monitor, layers of a liquid crystal in a nematic phase lie between the surfaces of two glass or plastic plates. The long axis of the molecules twists from the orientation governed by grooves in one plate to the perpendicular orientation governed by the grooves in the second plate. The light from the lamp is polarized, and as it passes through the twisted liquid crystal its plane of polarization changes too, and it is able to pass through the second polarizer. However, where a potential difference is applied between the electrodes (the second being in the shape of the characters it is intended to display, in this case, a simple numerical display), the twist is lost, and so too is the change of polarization of the light. As a result, a dark spot forms on the screen. In a “super-twist” LCD screen, the twist of the resting liquid crystal has more than one turn.

➤ Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure 11.8.3.

Figure 11.8.3 Schematic Drawing of an LCD Device, Showing the Various Layers

Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.



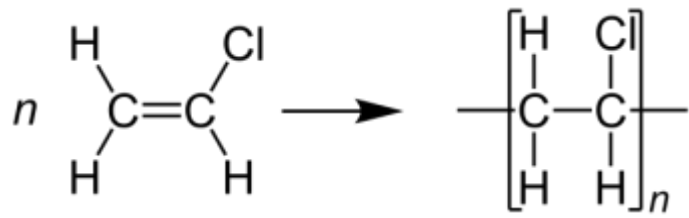
Two properties of liquid crystals make them ideal sensors: the sensitivity to changes in their surroundings, and visual effects. Because of these properties, we can use liquid crystal sensors to see what our eyes can't.

Some liquid crystals can measure temperature, while others can sense movement, pressure, chemicals and electricity. Brainstorm some potential inventions that could use liquid crystal sensors.

❑ POLYMERS - CONDUCTING POLYMERS

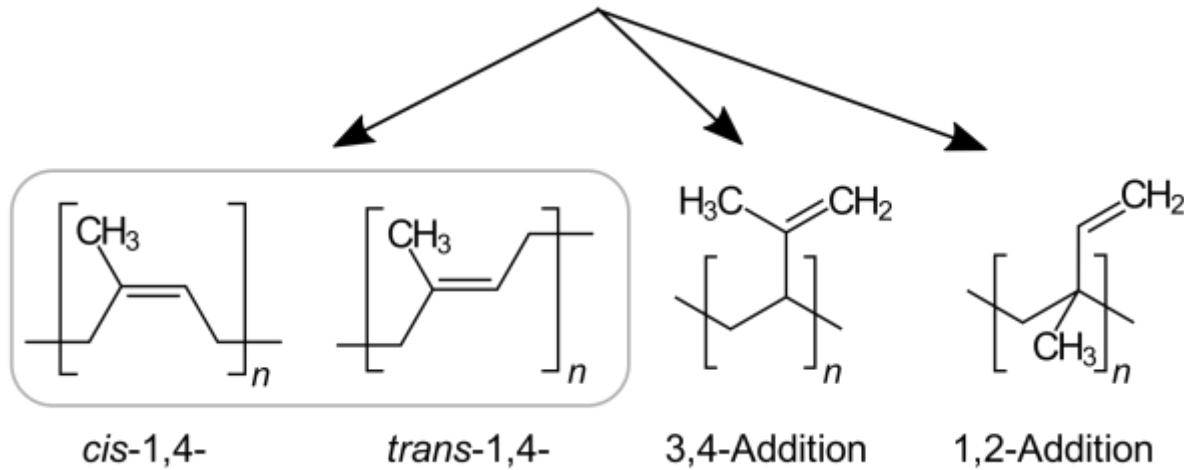
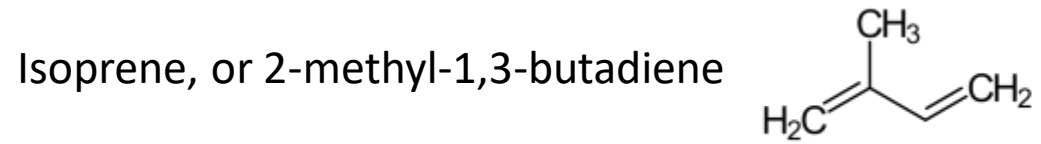
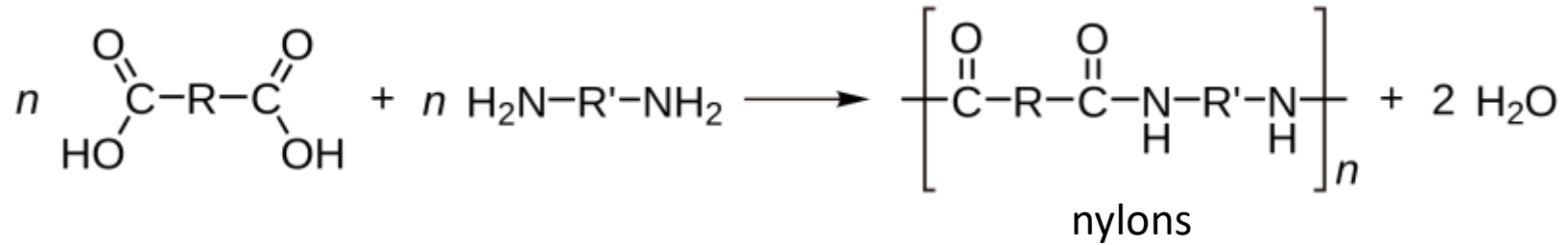
- The chains of carbon atoms in organic compounds can reach enormous lengths and give rise to *macromolecules*. **Polymers** are macromolecular compounds in which chains or networks of small repeating units form giant molecules, such as polypropylene and polytetrafluoroethylene (sold as Teflon).
- Polymers are made by two main types of reactions, *addition reactions* and *condensation reactions*.
- Which type of reaction is used depends on the functional groups present in the starting materials.
- Most of the raw material for polymers comes from petroleum, but some polymers are made from agricultural products such as corn and soybeans.
- The original alkene, such as ethene, is a small molecule called the ***monomer***. Each monomer becomes one ***repeating unit***, the structure that repeats over and over to produce the polymer chain. The product, the chain of covalently linked repeating units, is the ***polymer***.

- The simplest addition polymer is polyethylene, $-(\text{CH}_2\text{CH}_2)_n-$, which is made by polymerizing ethene ($\text{H}_2\text{C}=\text{CH}_2$) and so consists of long chains of thousands of repeating $-\text{CH}_2\text{CH}_2-$ units.
- Many addition polymer molecules also have a number of branches, which are generated as new chains sprout from intermediate points along the “backbone” chain.
- The plastics industry has developed polymers from a number of monomers with the formula $\text{CHX}=\text{CH}_2$, where X is a single atom (such as the Cl in vinyl chloride, $\text{CHCl}=\text{CH}_2$) or a group of atoms (such as the CH_3 in propene).
- These substituted ethenes are used to make polymers of formula $-(\text{CHXCH}_2)_n-$, including polyvinyl chloride (PVC), $-(\text{CHClCH}_2)_n-$, and polypropylene, $-(\text{CH}(\text{CH}_3)\text{CH}_2)_n-$.
- They differ in appearance, rigidity, transparency, and resistance to weathering.



Vinyl chloride (VC)

Polyvinyl chloride (PVC)



❑ **Copolymers**, polymers *made from more than one different monomeric subunit*, are also possible.

➤ These may appear in any of a variety of forms, each with different macroscopic properties and different synthetic procedures.

- **Alternating copolymers** are formed with each monomer bonded to a different monomer.
- **Random copolymers** have no order to the appearance of one type of monomeric unit over another.
- **Block copolymers** have large isolated groups of each monomer, and the groups are then bound together.

Different types of polymers:

- 1) homopolymer
- 2) alternating copolymer
- 3) random copolymer
- 4) block copolymer
- 5) graft copolymer.



❑ Polymers **encompass a wide range of physical properties**, including:

- **plastics**: Compounds that distort under stress, such as polyethylene.
- **elastomers**: Compounds that distort under stress but return to their original structure when the stress is removed, such as rubber.
- **fibers**: Essentially one-dimensional polymers, forming long, thin strands, such as nylon.

❑ Bulk polymers may be either ***crystalline*** or ***amorphous***, or ***a mixture of both***.

➤ The *crystalline regions* within the bulk are called *crystallites*.

✓ The fraction of the bulk that exists in crystallites depends on the *regularity of the polymer chain* but can also be controlled in some cases by *the rate of solidification*.

✓ *Stressing a polymer tends to increase the size and number of crystalline regions*, because external forces tend to push or pull the polymer units into line with one another.

➤ *The amorphous regions allow the polymer to yield to stress, giving the substance **plasticity***.

➤ *Crystallites, on the other hand, will resist any stress that opposes alignment of the molecules, and may fracture if the stress force exceeds the bonding force.*

❑ CONDUCTING POLYMERS

One day, if you want to check your e-mail in a remote location, you might unroll a plastic sheet with a tiny microprocessor embedded in it. When you activate the microprocessor, your messages will appear, and you might reply by writing on the screen with a special pen or by speaking to it. The remarkable material of this flat computer already exists: one form of it was discovered by accident in the early 1970s when a chemist who was ***polymerizing ethyne (acetylene)*** ***added a thousand times too much catalyst***. Instead of a synthetic rubber, he made a thin, flexible film. It looked like metal foil tinted pink (see the photograph), and—very much like a metal—it ***conducted electricity***.

This flexible polyacetylene sheet was peeled from the walls of the reaction flask in which it was made.

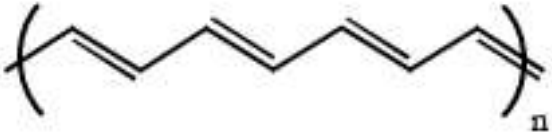
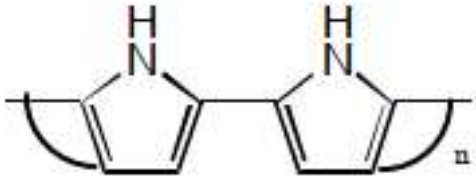

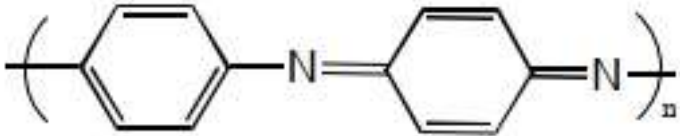
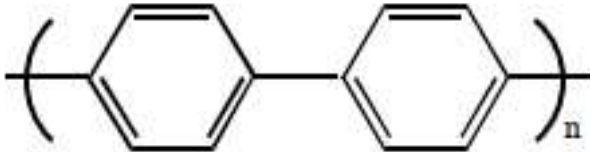
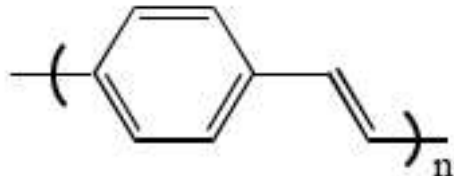


❑ Conducting Polymers (CPs)

- Polymers are typically utilized in electrical and electronic applications as **insulators** where advantage is taken of their **very high resistivities**.
- Typical properties of polymeric materials: Strength, flexibility, elasticity, stability, mouldability, ease of handling, etc.
- There are polymers which are good conductors of electricity. They are called (*intrinsically*) ***conducting (conductive) polymers or organic metals (synthetic metals)***.
- ✓ The chemistry Nobel prize in 2000 was awarded to Alan J. Heeger, Alan G MacDiarmid, and Hideki Shirakawa for the discovery and study of conducting polymers.
- ✓ We are going to discuss **those conducting polymers whose backbones are responsible for the generation and propagation of charge carriers**.
- Here we are **not** considering the “conductive polymer *composites*” which are polymers ***filled with the conductive materials*** such as carbon black, metal flakes or fibers, and so on.
- ✓ In these materials, the major practical function of the *polymer matrix is to serve as a “glue”* to hold the conductive elements together in a solid entity. The interest in such material derives from the *low cost, lightweight, mechanical durability, and ease of processability of the polymer component, in concert with reasonably good bulk conductivity*.

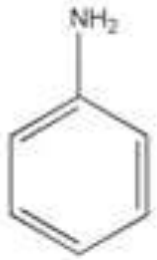
Examples of Conducting Polymers

- ***Polyacetylene***, in view of possessing the simplest molecular framework, has attracted the most attention, especially of physicists, with an emphasis on understanding the mechanism of conduction. However, its *insolubility, infusibility* and *poor environmental stability* has rendered it rather *unattractive* for technological applications.
- The technologically relevant front runners belong to essentially four families: **polyaniline** (PAni), **polypyrroles** (PPy), **polythiophenes** (PT) and **polyphenylene vinylenes** (PPV).
- *Polyaniline is rather unique as it is the only polymer that can be **doped by a protic acid** and can exist in **different forms depending upon the pH of the medium**.*
- While polyaniline is soluble in the neutral emeraldine form in highly polar aprotic solvents like, N-methyl pyrrolidone (NMP), all other polymers are insoluble.
- However, *laterally substituted derivatives of the remaining three classes are soluble in pristine form and are solution processable.*

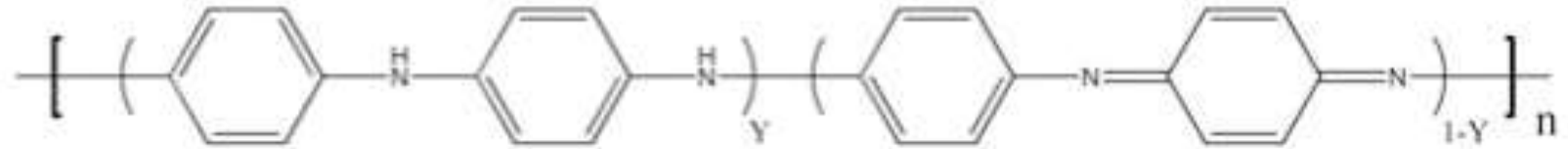
	Structure	Maximum conductivity S/cm	Stability	Processability
Polyacetylene		1.5×10^5	Reacts with air	Film not soluble or fusible
Polypyrrole		2000	Reasonably stable	Insoluble and infusible
Polythiophene		100	Stable	Insoluble and infusible
Polyaniline		10	Stable	Soluble in neutral form
Polyphenylene		1000	Stable	Insoluble and infusible
Polyphenylene-vinylene		1000	Stable undoped form	Soluble precursor route available

Precursor Monomer

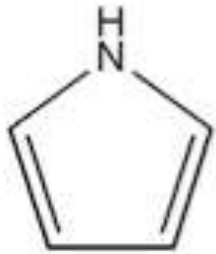
Polymer



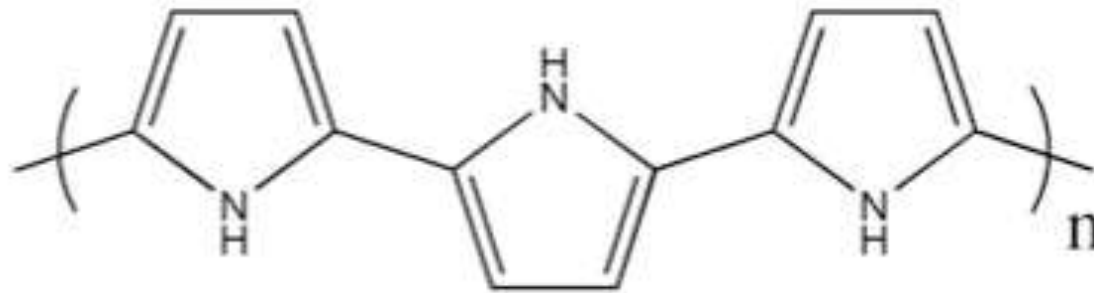
Aniline



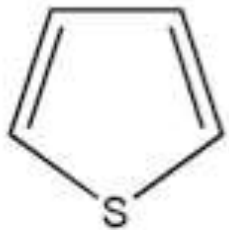
Poly (aniline), PANI



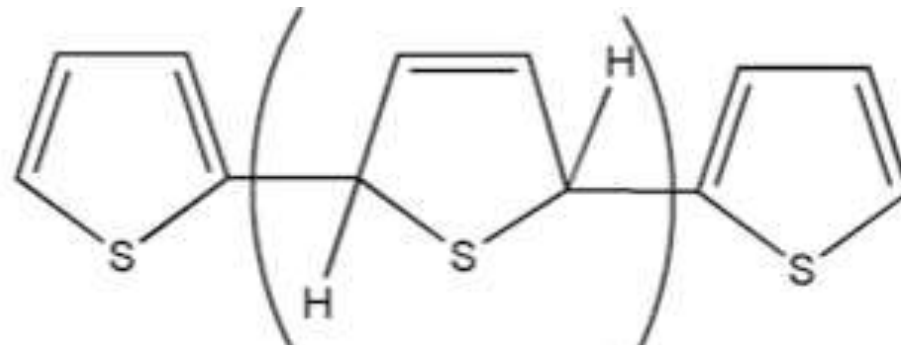
Pyrrole



Poly(pyrrole), PPy



Thiophene



Poly(thiophene), PTh

❖ Conduction Mechanism

- Metals conduct electricity because their valence electrons move easily from atom to atom. Most covalently bonded solids do not conduct electricity, because their valence electrons are locked into individual bonds and are not free to move. Exceptions such as graphite and carbon nanotubes have delocalized π -bonds in connected aromatic rings through which electrons can move freely because there are empty molecular orbitals close in energy to occupied orbitals. However, a disadvantage is that commercial graphite is fragile and brittle.
- **Conducting polymers** provide a new and exciting alternative. They are organic compounds that **do not rust and they have low densities**. They can be molded or drawn into shells, fibers, or thin plastic sheets, but they can still act like metallic conductors.
- They can be made to glow with almost any color and to change conductivity with conditions. Imagine cases of food labeled with polymer tags that change in conductivity when the cases are left unrefrigerated for too long.

- All conducting polymers have ***a common feature***: a long chain of sp^2 hybridized carbon **atoms**, often with nitrogen or sulfur atoms included in the chains. Researchers have shown that certain classes of polymers, which are conjugated (those that possess an extended π -conjugation along the polymer backbone), ***exhibit semiconducting behavior***.
- The discovery of **doping** led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S/cm (compare Copper $\sigma_{\text{room temp}} = 10^6$ S/cm).
- ***Doping is a process by which the polymer is either oxidized or reduced to create charge carriers.***
- The chemical origins of such a remarkable difference in the material properties between various types of polymers can be readily rationalized.
- **Traditional polymers**, such as polyethylene or polypropylene, are made up of essentially **σ -bonds** and hence *a charge once created on any given atom on the polymer chain is not mobile*.
- ***The presence of an extended π -conjugation in polymers, however, confers the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting.***

- All conducting polymers have **a common feature**: a long chain of sp^2 hybridized carbon atoms, often with nitrogen or sulfur atoms included in the chains. Researchers have shown that certain classes of polymers, which are conjugated (those that possess an extended π -conjugation along the polymer backbone), **exhibit semiconducting behavior**.
- This **unique intrinsic conductivity of these organic materials**, which generally are comprised simply of C, H, and simple heteroatoms such as N and S, and the myriad of properties emanating from it **arise uniquely from π -conjugation**. That is to say, a sometimes fairly extended and delocalized conjugation originating in overlap of π -electrons. Such conjugation is illustrated somewhat simplistically in Fig. 27.1 for poly(acetylene), a prototypical CP.

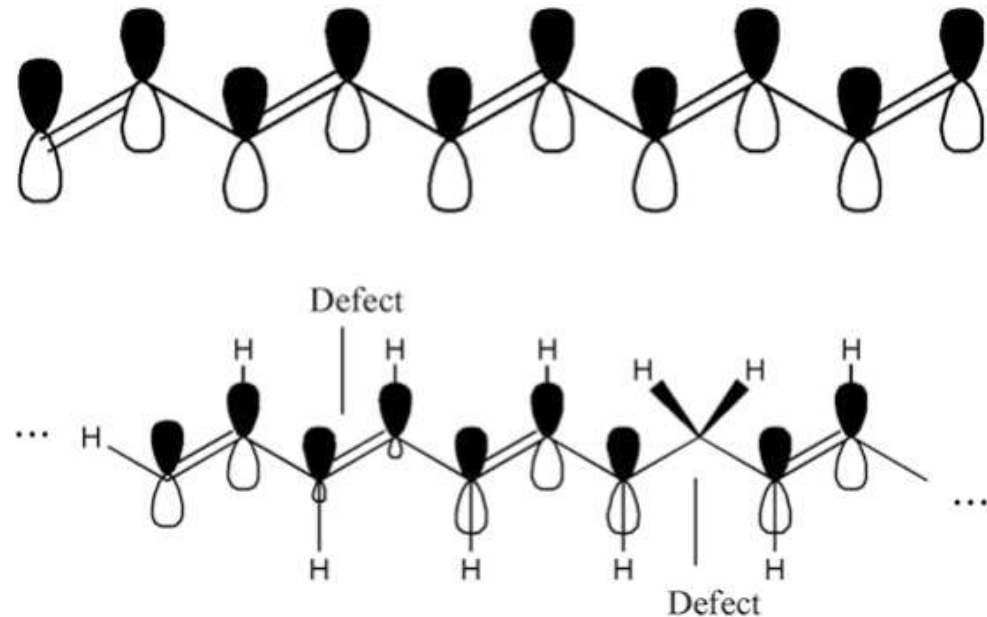
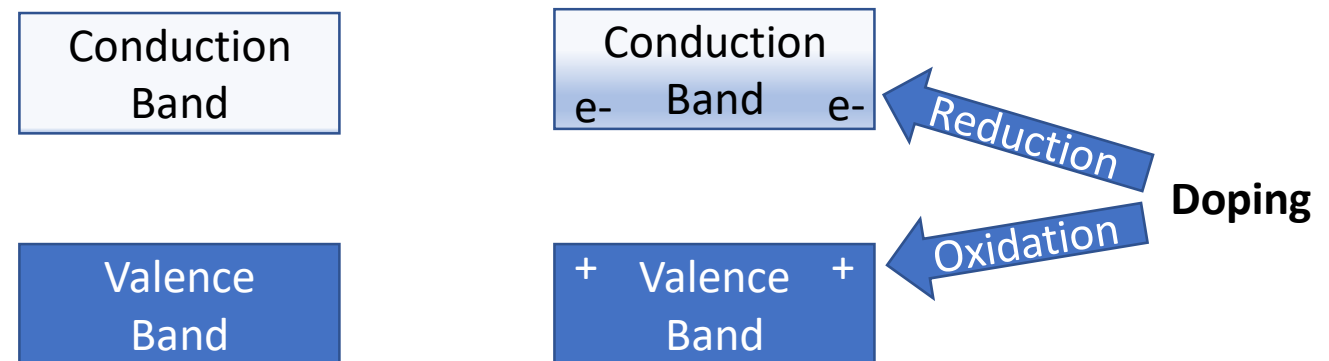


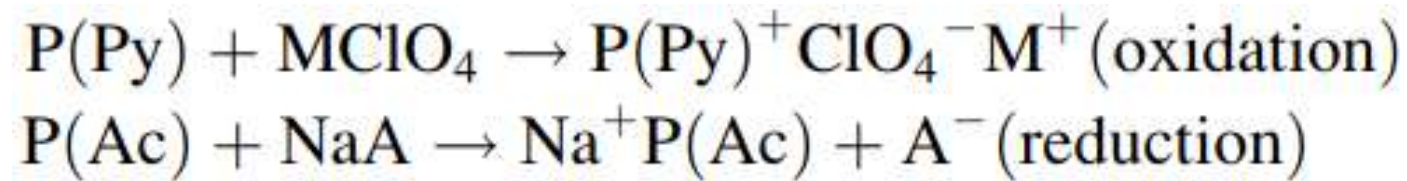
Fig. 27.1 Schematic representation of π -conjugation in the conducting polymer (CP) poly(acetylene).
Top: Basic schematic. Bottom: Three-dimensional, including defects

- The chemical origins of such a remarkable difference in the material properties between various types of polymers can be readily rationalized.
- *The **presence of an extended π -conjugation in polymers**, however, confers the required mobility to **charges that are created on the polymer backbone (by the process of doping)** and make them **electrically conducting**.*
- **Traditional polymers**, such as polyethylene or polypropylene, are made up of essentially **σ -bonds** and hence *a charge once created on any given atom on the polymer chain is not mobile.*
- The discovery of **doping** led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S/cm (compare Copper $\sigma_{\text{room temp}} = 10^6$ S/cm).
- **Doping** is a process by which the polymer is **either oxidized or reduced to create charge carriers**.
- This conductivity of CPs is achieved through simple **chemical or electrochemical oxidation**, or in some cases **reduction**, by a number of simple anionic or cationic species, **called dopants**.

- That is to say, the polymeric backbone of these materials needs to be *oxidized or reduced* to *introduce charge centers* before conductivity is observed, and the oxidation or reduction is performed by anions or cations somewhat misnamed dopants, a term borrowed from condensed matter physics.
- A better idea of the place of CPs among the three broad conductivity classifications of materials, i.e., ***insulators, semiconductors, and metals***, can be garnered from a comparison of conductivities, as shown in Fig.
- The semiconductor band structure of CPs permits electronic excitation or electron removal/addition, e.g., from the valence to the conduction band, leading to most of the properties that are of interest in CPs.
- Excitation of electrons from the valence band to the conduction band, e.g., by photons, yields typical excited state properties such as photoluminescence and nonlinear optical properties (e.g., third-harmonic generation).



- On the other hand, a chemical or other oxidation of the CP, i.e., essentially a removal of electrons from the valence band, *leads to the presence of charges on the CP*. These *charges are in general strongly delocalized*, over several monomer units in the polymer. These charges also cause a relaxation of the geometry of the (now charged) polymer to a more energetically favored conformation.
- A charge may also be donated to the conduction band of the CP, causing reduction of the CP.
- **Oxidation caused by a chemical species generates a positively charged CP and an associated anion.**
- **Reduction similarly generates a negatively charged CP and an associated cation.**
- ✓ Examples of these processes, also designated “doping/de-doping,” are, respectively, in very rough schematic, where M and A are any cation and anion, respectively:



- ***Both the above processes, oxidation and reduction, impart conductive properties to the CP. Doping is reversible*** to produce the original polymer with little or no degradation of the polymer backbone.

- Because of the analogy with impurities which cause the removal or addition of charges from the valence or conduction band and thence impart higher conductivity in inorganic semiconductors such as silicon or CdSe, the chemical oxidation of the CP by anions, or its reduction by cations, was originally called **doping**. The **associated anions/cations, i.e., the counterions**, were called **dopants**.
- A CP that is in its **undoped**, i.e., neutral, state is generally termed **pristine** (sometimes, *virgin*).
- During the doping process, **an organic polymer, either an insulator or semiconductor** having a small conductivity, typically in the range 10^{-10} to 10^1 S/cm, is converted to a polymer which is in the '**metallic**' conducting regime (1 to 10^4 S/cm).
- The **extent of oxidation/reduction**, i.e., doping, is called the **doping level** and *is generally measured as the proportion of dopant ions or molecules incorporated per monomer unit*. This is then generally expressed either as a fraction or as a molar percentage. For instance, a CP with *one dopant anion per four monomer units* would have a doping level of 0.25 or 25%.
- *The controlled addition of known, usually small (≤ 10 per cent) nonstoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer.*

Ag, Cu

 10^6

Fe

Bi

 10^4 Graphite,
poly(acetylene)

doped

TTF/TCNQ

 10^3

{Most

InSb

1.0

...

Ge

 10^{-2}

... doped CPs}

 10^{-4}

Si

 10^{-6}

AgBr

 10^{-8}

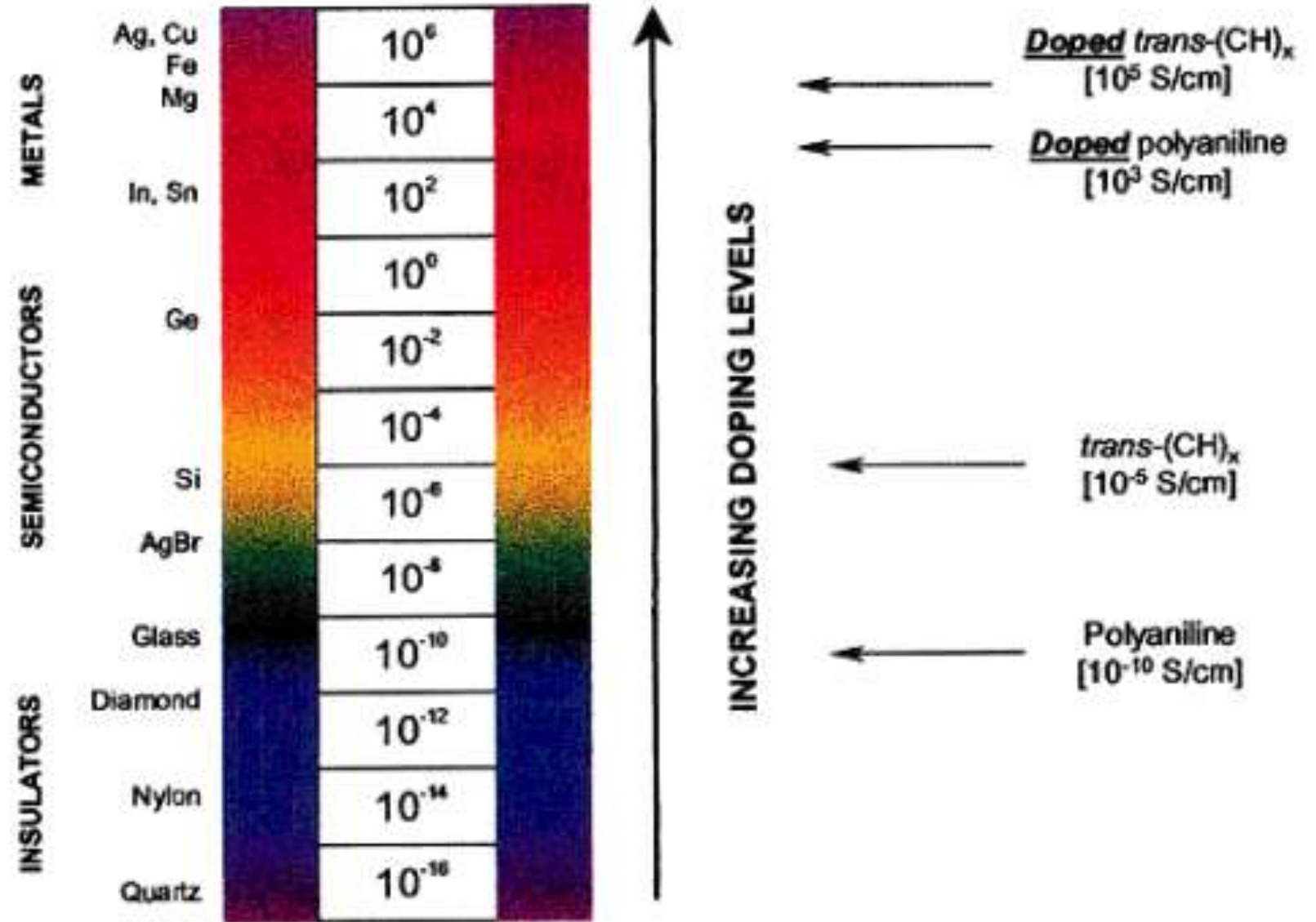
Glass

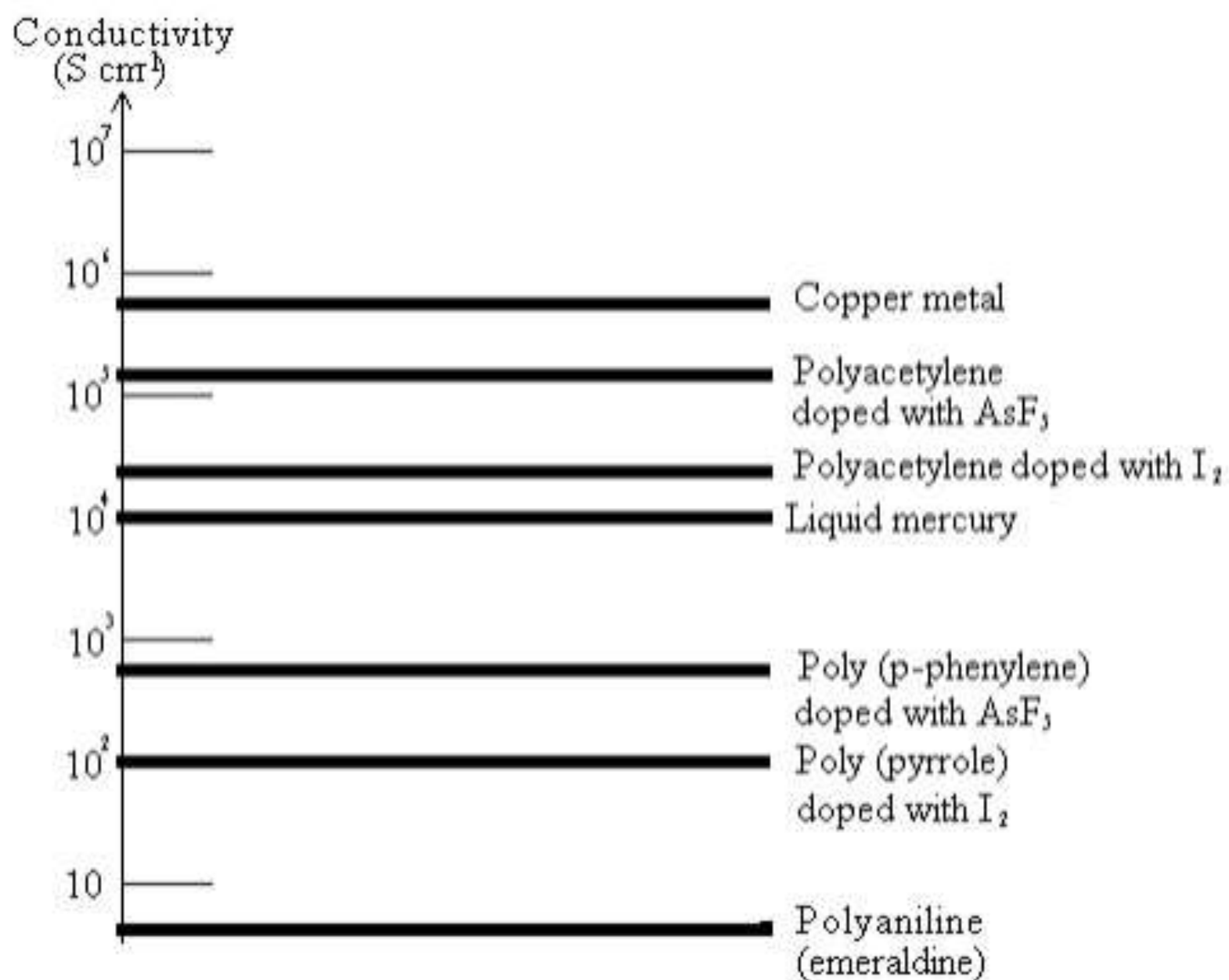
 10^{-10}

(S/cm)

Units: S/cm

Figure 2. Effect on conductivity of polyacetylene and polyaniline after doping (figure taken from Nobel Lecture, 2000 by Alan G. MacDiarmid)





Logarithmic conductivity ladder locating some metals and conducting polymers

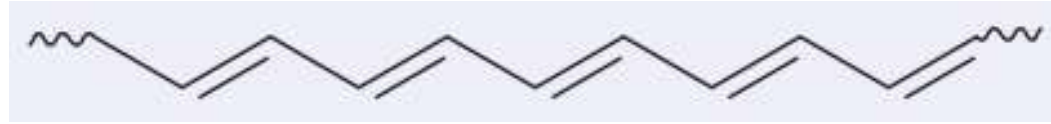
- One *problem* is that, ***due to the presence of this extended conjugation along the polymer backbone, the chains are rigid and possess strong interchain interactions resulting in insoluble and infusible materials.*** These **conjugated polymers, hence, lacked** one of the most important and useful properties of polymers, namely their **ease of processability**.
- More recently, however, it was demonstrated that when ***lateral substituents were introduced***, even ***conjugated polymers can be made soluble*** (hence, processable) without significant loss in their conductivity.
- One other *problem* that plagued this field from its inception, is the ***inherent instability of these polymers (especially, in the doped form) to ambient conditions***. Today, conducting polymers that are stable even in the doped form have been prepared.
- We shall highlight some specific examples of their potential applications.

❖ Conducting Polymers: Applications

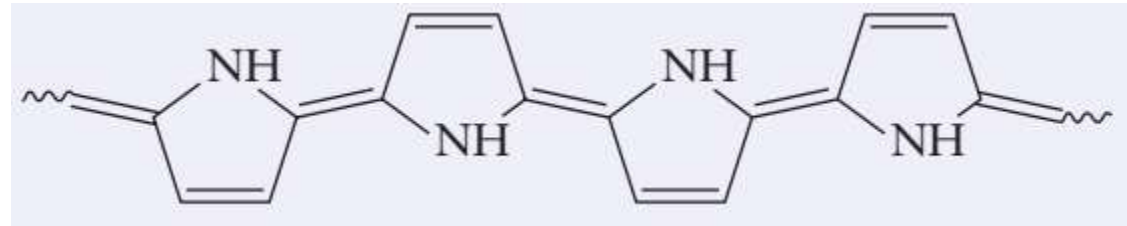
Although several conducting polymers have been prepared, it was soon realized that they cannot compete with metals in traditional electrical applications, like wiring, transmission cables etc. Researchers have, therefore, focused on other applications that exploit the existence of extended conjugation in these polymers. A few interesting possibilities are mentioned below.

- Potential ***advantages*** include variable conductivity by controlling the extent of oxidation or reduction, the ability to dictate the nature of the majority carriers, and facile cycling between conductive and insulating states.
- Can be used as hole injecting electrodes for OLEDs (organic light-emitting diodes)
- Usage in electroluminescent displays (mobile telephones)
- In use as emissive layer in full-color video matrix displays
- Some are promising for field-effect transistors (Usage in supermarket checkouts)
- Can be used as antistatic coating material to prevent electrical discharge exposure on photographic emulsions
- Can provide electromagnetic shielding of electronic circuits
- Some absorb microwaves: stealth technique

- Polyacetylene, the first conducting polymer, is also the simplest, consisting of thousands of —CH=CH— units:



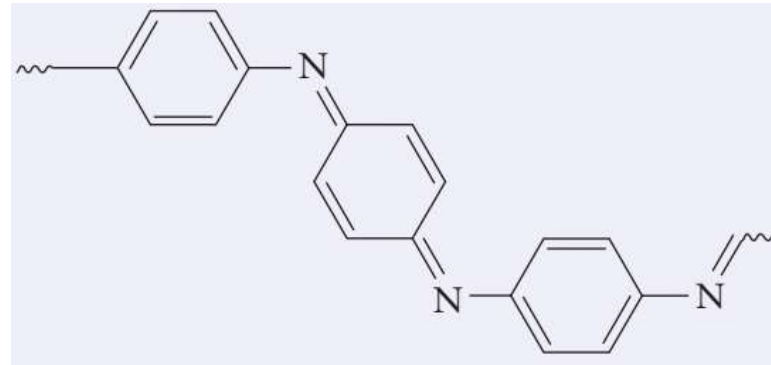
- The alternation of double and single bonds means that each C atom has an unhybridized p-orbital that can overlap with the p-orbital on either side. This arrangement allows electrons to be delocalized along the entire chain like a one-dimensional version of graphite.
- One conducting polymer, polypyrrole,



has been used in smart windows, which darken from a transparent yellow-green to a nearly opaque blue-black in bright sunlight.

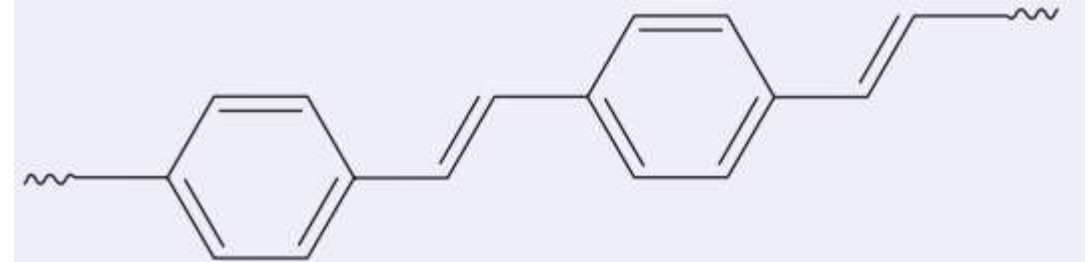
- ✓ *Fibers of polypyrrole are also woven into radar camouflage* cloth that absorbs microwaves. Because it does not reflect microwaves back to their source, the cloth appears on radar as a patch of empty space.

➤ Polyaniline, which has the structure



is being used in flexible coaxial cable; rechargeable, flat, buttonlike batteries; and laminated, rolled films that could be used as flexible computer or television displays.

➤ Thin films of poly-p-phenylenevinylene, PPV,



give off light when exposed to an electric field, a process called ***electroluminescence***. By varying the composition of the polymer, scientists have coaxed it to glow in a wide range of colors. Such ***multicolor light-emitting diode (LED) displays*** can be as bright as fluorescent ones.

❖ ***Light Emitting Diodes***

- Other exciting phenomena that have caught the imagination of both scientists and technologists alike are the phenomena of ***photoluminescence and electroluminescence*** in conjugated polymers.
- Emission of light upon irradiation is termed as *photoluminescence*, while the emission on application of a voltage is termed ***electroluminescence***.
- *Light emitting diode* is an example of *utilization of the electroluminescence*.
- It was recently demonstrated that PPV (**Poly(*p*-phenylene vinylene)**) films can be used as the emissive layer in electroluminescent devices.
- Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e., after thermal elimination of the precursor).
- Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap.
- Polymer light-emitting diodes (PLEDs) have been become the topic of intense academic and industrial research. PLEDs based on PPVs are now coming out as commercial products.

❖ ***Electrochromic Displays***

- Electrochromic display is another interesting application that utilizes the ***electrochemical doping and undoping*** of conducting polymers.
- The basic idea, in such devices, is to effect a ***significant change in the color (both the wavelength of absorption and its intensity) upon application of an electric potential.***
- ***Depending on the conducting polymer chosen, either the doped or undoped state can be essentially colorless or intensely colored.***
- In general, ***the absorption of the doped state is dramatically red-shifted (moves to longer wavelength) from that of the undoped state.***
- Because of their *very high absorption coefficients* (ca. 10^5 cm^{-2}) in the visible range of the electromagnetic spectrum, ***only very thin films are required to provide display devices*** with *high contrast and a very broad viewing angle.*
- Polyaniline, polypyrrole, polythiophene, and their derivatives have been successfully used to prepare such display devices.

- However, for successful commercial utilization of these materials in display devices, one important aspect is again the cycle life, which should be $> 10^7$. A maximum of about 10^6 cycles has been achieved using 50 nm thick polyaniline films, wherein the switching occurs between transparent yellow and green in less than 100ms.
- Thus, while these materials are yet to achieve the set target (in terms of their life cycle) for use as electrochromic displays, *other interesting and innovative applications, such as electrochromic windows and other applications in the automotive industry are being actively pursued.*
- *Electro-chromic windows*, for instance, are windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential.

- Most polymers contain sp^3 -hybridized carbon atoms lacking delocalized p electrons, so they are usually electrical insulators and are colorless (which implies a large band gap). However, if the backbone of the polymer has resonance, the electrons can become delocalized over long distances, which can lead to semiconducting behavior in the polymer. Such “plastic electronics” are of great current interest for lightweight and flexible organic solar cells, organic transistors, organic light-emitting diodes, and other devices that are based on carbon rather than inorganic semiconductors like silicon.
- When a light source is viewed through graphene it absorbs 2.3 per cent of the light, which makes a single film visible to the naked eye. However, the high overall light transmission, in conjunction with the high electrical conductivity, leads to potential applications in displays, particularly flexible electronic displays and ‘**smart windows**’. In a smart window of this type, a layer of polar liquid-crystal molecules is sandwiched between two flexible electrodes comprised of graphene and a transparent polymer.
- ✓ With no voltage applied to the device the random alignment of liquid crystals scatters light and the smart window is opaque. Application of a voltage across the graphene layers will align the polar molecules, allowing some light to pass through the device, and the smart window turns transparent.

❖ ***Conducting Fabric***

- When a fabric that is impregnated with an aqueous catalyst solution is brought into contact with pyrrole vapor, a thin coating of polypyrrole is formed in the surface of the fibre – leading to the formation of a conducting fabric.
- The chemical oxidation of pyrrole is often carried out by using ferric chloride, FeCl_3 . It has been shown that the growth of the polymer can be made to occur even at a liquid-liquid interface, such as one of water and an organic solvent. Thus, in an unstirred system, when aqueous FeCl_3 and chloroform solution of pyrrole are brought into contact, it leads to the formation of a polypyrrole film at the interface.
- The ***unique electromagnetic shielding and microwave absorbing properties*** of such a fabric are expected to find many interesting applications.
- Similarly, other materials such as paper, microporous membranes etc., have also been coated with a conducting polymer using this chemical oxidation route.
- It should be noted here that the oxidation potential of the monomer would be less than that of the dimer, which would in turn be less than that of the polymer. Hence, the polymer generated by this oxidative polymerization approach will be in the oxidized (doped) conducting form, which is also generally true in the case of all oxidative polymerization approaches (both chemical and electrochemical) for the preparation of conjugated polymers.

❖ **Polymeric Batteries**

- One of the first applications of conducting polymers, that was the focus of attention worldwide, was that of **light-weight batteries**.
- While a lot of the conjugated polymers were tried most of them failed to exhibit the desired properties, specifically with respect to stability. However, **batteries made using either polypyrrole or polyaniline as the positive electrode (cathode)** and *lithium–aluminium* alloy as the *negative electrode (anode)* exhibited much more respectable properties.
- ✓ The *electrolyte in these cases* were either LiClO_4 or LiBF_4 in propylene carbonate (a highly polar aprotic solvent, which is also fairly resistant to oxidation).
- ***During the battery discharge***, electrons move from the lithium alloy (which gets oxidized) to the polyaniline cathode (which gets reduced), as Li^+ from the anode and the anion, say, BF_4^- from the cathode enter the electrolyte.
- One **major drawback of this battery** is that the ***energy density or energy storage capacity is low*** and *its recyclability* (charging–discharging cycles) is *relatively poor*.

- More recently, however, some composites of an ***alkali metal alloy and polyphenylene*** have been very effectively used ***as anode materials*** in batteries that exhibit much higher energy densities, of around 65mWH/g (compare with standard nickel–cadmium batteries which have about 39mWH/g).
- In these cases, the conducting polymer serves as a binder for the alkali metal alloy, forming a multiply connected electronically and ionically conductive network within which the alloy particles are held. The mixed ionic and electronic conductivity of the conducting polymer binder allows the alloy particles to continue the electronic and ionic processes associated with the charge-discharge cycles, consequently extending the battery cycle life. Thus, the prospect of a polymeric battery is still promising and is awaiting further technological refinement.

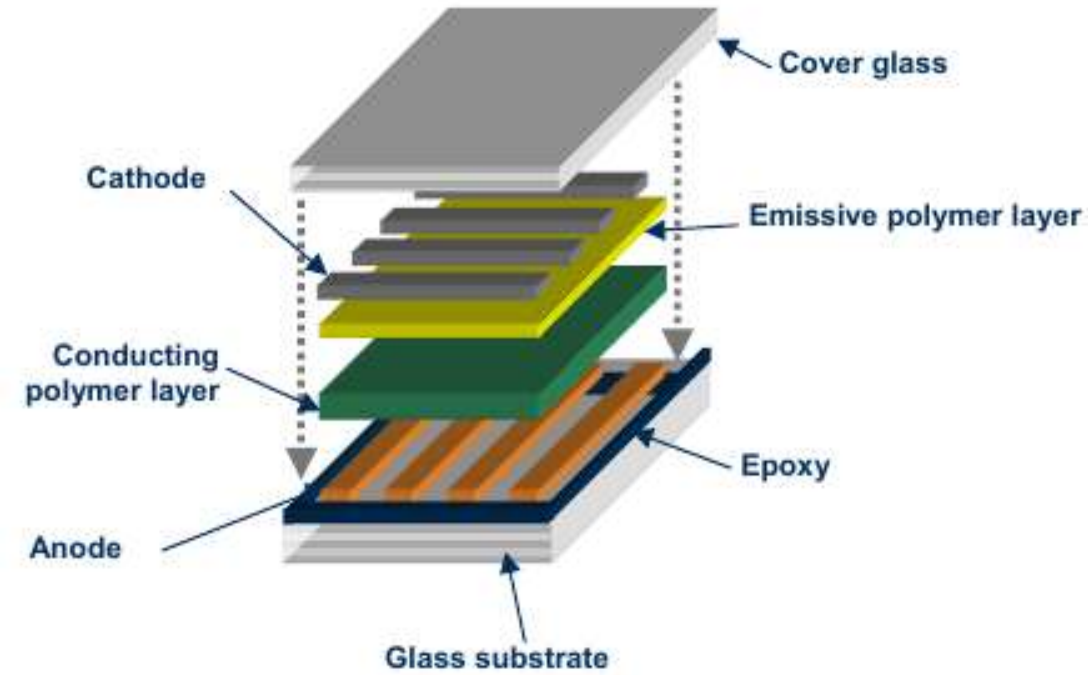
❖ ***Field Effect Transistors (FET)***

- Conducting polymers' advantages over conventional materials, such as silicon and germanium, include low cost and ease of processing.
- Organic or polymer-based semiconductors have been applied to fabricate field-effect transistors (FETs) since 1983. There have been many ongoing efforts to form organic or polymer-based FETs.
- Organic or polymer-based transistors have already found their application, such as in smart pixels and sensors.

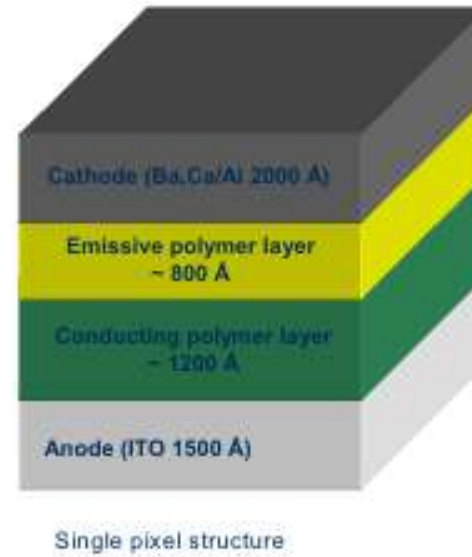
❖ **Light Emitting Diodes**

- Other exciting phenomena that have caught the imagination of both scientists and technologists alike are the phenomena of **photoluminescence and electroluminescence** in conjugated polymers.
- Emission of light upon irradiation is termed as *photoluminescence*, while the emission on application of a voltage is termed **electroluminescence**.
- *Light emitting diode* is an example of *utilization of the electroluminescence*.
- It was recently demonstrated that PPV (**Poly(*p*-phenylene vinylene)**) films can be used as the emissive layer in electroluminescent devices.
- Structures for electroluminescent devices are fabricated with the polymer film formed on a bottom electrode, which is deposited on a suitable substrate (such as glass), and the top electrode is deposited on the fully converted PPV film (i.e., after thermal elimination of the precursor).
- Electrode materials are chosen with a low work function for use as negative, electron-injecting contact, and with a high work function as the positive hole-injecting contact.
- At least one of these layers must be semi-transparent for light emission normal to the plane of the device. Both indium-tin oxide and thin aluminium films (7–15 nm) have been used as the transparent electrode.

Display

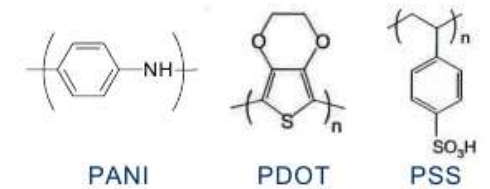


Pixel



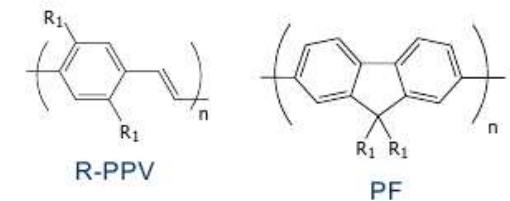
Conducting polymers

- Polyaniline (PANI:PSS)
- Polyethylenedioxythiophene (PDOT:PSS)



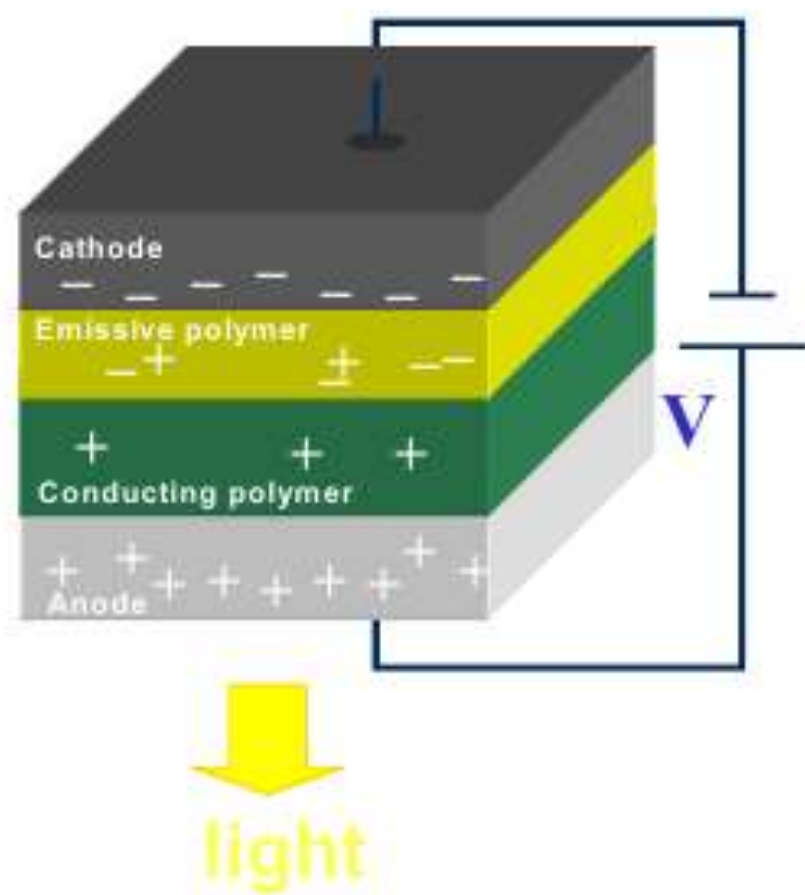
Emissive polymers

- Polyphenylenevinylene (R-PPV)
- Polyfluorene (PF)



Processed by :

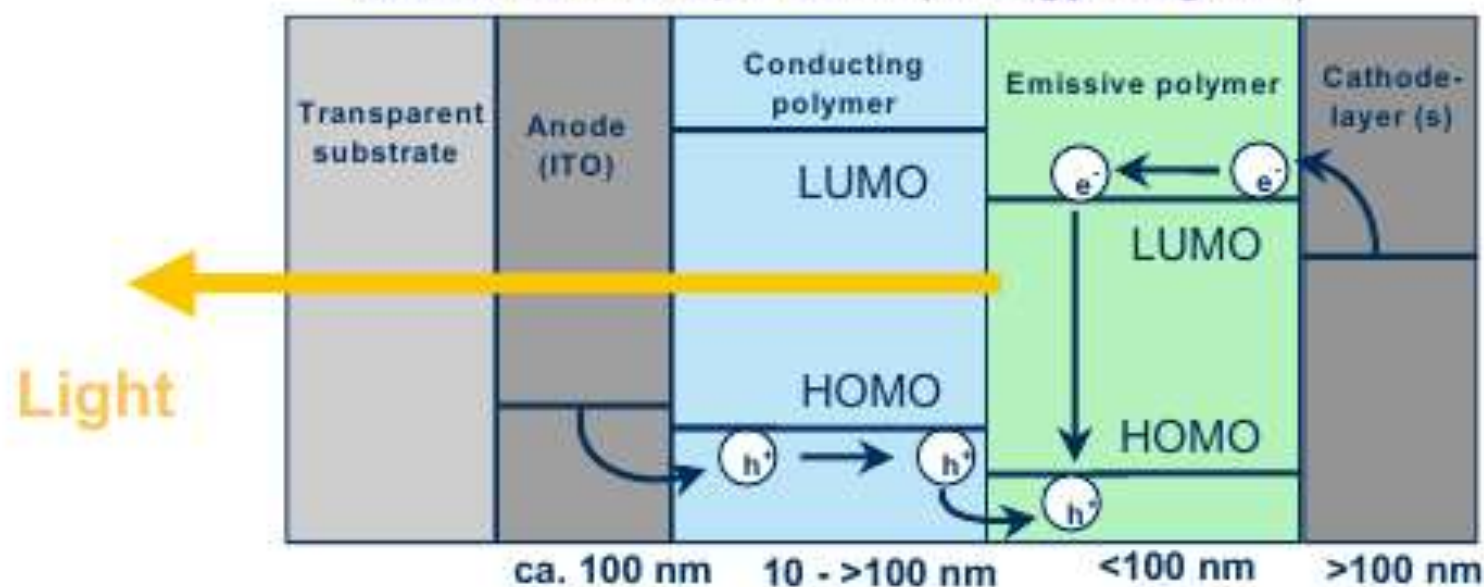
Spin casting, Printing, Roll-to-roll web coating



OLEDs rely on organic materials (polymers or small molecules) that give off light when tweaked with an electrical current

- Electrons injected from cathode
- Holes injected from anode
- Transport and radiative recombination of electron hole pairs at the emissive polymer

OLED device operation (energy diagram)



- These devices are believed to operate by double charge injection of electrons and holes from the negative and positive electrodes, respectively.
- These singly charged excitations combine to form excitons which can then decay by photoemission.
- Changing the band-gap of these conjugated polymers, by appropriate chemical modification, can result in a change in the wavelength of the photoemission: red-shifted upon reduction of band-gap and blue-shifted upon increasing the band-gap.
- For polymer films, of about 100 nm, the forward voltages were as low as 10 V. Further improvements, using soluble PPV derivatives such as 2,5-dialkoxy PPV's and lower work function metals, particularly calcium, as the electron-injecting contact layer, have resulted in a further drop in forward voltage to about 5 V, and an increase in the efficiency to about 1% (photons per electron injected).
- Enhancement of the photoemission efficiency and further lowering of forward operating voltage are two of the primary areas of current activity that is expected to lead to improved devices of greater technological relevance.

- Polymer light-emitting diodes (PLEDs) have been become the topic of intense academic and industrial research. PLEDs based on PPVs are now coming out as commercial products.
- When compared to inorganic or organic materials for LEDs, the main advantages of the polymer electroluminescence (EL) devices are their fast response times, processability, the possibility of uniformly covering large areas, low operating voltages, and the many methods were applied to fine-tune their optical and electrical properties by varying the structure.

❖ ***Field Effect Transistors (FET)***

- Conducting polymers' advantages over conventional materials, such as silicon and germanium, include low cost and ease of processing.
- Organic or polymer-based semiconductors have been applied to fabricate field-effect transistors (FETs) since 1983. There have been many ongoing efforts to form organic or polymer-based FETs.
- Organic or polymer-based transistors have already found their application, such as in smart pixels and sensors.

❖ ***Conducting Fabric***

- When a fabric that is impregnated with an aqueous catalyst solution is brought into contact with pyrrole vapor, a thin coating of polypyrrole is formed in the surface of the fibre – leading to the formation of a conducting fabric.
- The chemical oxidation of pyrrole is often carried out by using ferric chloride, FeCl_3 . It has been shown that the growth of the polymer can be made to occur even at a liquid-liquid interface, such as one of water and an organic solvent. Thus, in an unstirred system, when aqueous FeCl_3 and chloroform solution of pyrrole are brought into contact, it leads to the formation of a polypyrrole film at the interface.
- The ***unique electromagnetic shielding and microwave absorbing properties*** of such a fabric are expected to find many interesting applications.
- Similarly, other materials such as paper, microporous membranes etc., have also been coated with a conducting polymer using this chemical oxidation route.
- It should be noted here that the oxidation potential of the monomer would be less than that of the dimer, which would in turn be less than that of the polymer. Hence, the polymer generated by this oxidative polymerization approach will be in the oxidized (doped) conducting form, which is also generally true in the case of all oxidative polymerization approaches (both chemical and electrochemical) for the preparation of conjugated polymers.

HOW MIGHT YOU CONTRIBUTE?

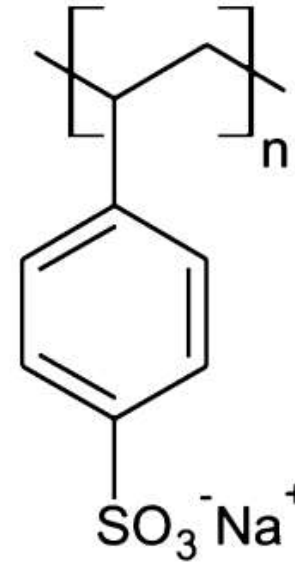
- ❖ *Current PPV displays last only about 10% as long as fluorescent displays.* If their longevity grows, however, they could replace the computer and television screens that we use today.
- ❖ Polyaniline could one day serve both as a nonmetallic solder for the printed circuit boards inside a computer and as electrical shielding for the case.
- ❖ All-plastic transistors and other electronic components can be miniaturized to an amazing degree, raising the possibility of nanoscale microprocessors and computers that could survive
- ❖ highly corrosive conditions, such as those in the body or at marine research sites.
- ❖ Because conducting polymers can also be designed to change shape with the level of electrical current, they could serve as artificial muscles or give flexibility of movement to robots.
- ❖ For these goals to be achieved, the characteristics of these polymers must be known and their responses to various conditions have to be studied.

□ Polyelectrolytes

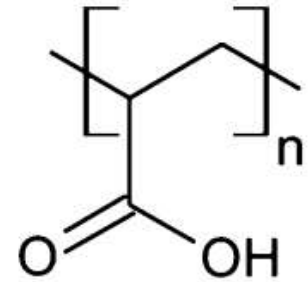
Polyelectrolytes are polymers with ionizable groups along their chains. One example of their use in nanotechnology is for the preparation of thin films by layer-by-layer (LbL) deposition. Some examples of the polyelectrolytes are (Fig. 13.11):

(i) Polyacids such as poly (acrylic acid), poly(methacrylic acid), poly sodium styrene sulfonate.

(ii) Polybases such as poly(vinylamine), poly(4-vinyl pyridine), nucleic acids and proteins.



PSS



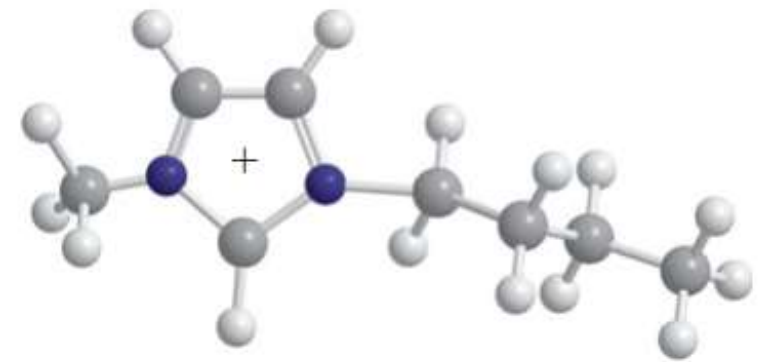
PAA

Fig. 13.11. Chemical structures of two synthetic polyelectrolytes. To the left is poly(sodium styrene sulfonate) (PSS), and to the right is poly(acrylic acid) (PAA). Both are negatively charged polyelectrolytes when dissociated. PSS is a 'strong' polyelectrolyte (fully charged in solution), whereas PAA is 'weak' (partially charged).

- The polyelectrolytes get ionized in aqueous solutions.
- The *repulsion between the similar charges on a chain causes the chain to expand much more than the normal polymers do in good solvents.*
- Furthermore, *the degree of ionization depends on the concentration of the polymer as well as that of any added salts.*
- Due to these factors, the *properties of polyelectrolytes such as viscosity and the intensity of light scattering behave quite differently as compared to the normal polymers.*
- The polyelectrolytes behave as a normal polymer in nonionizing solvent as well as in ionizing solvents containing large amount of salt so that the double layer around the polyelectrolyte chain is completely screened.

❑ Ionic Liquids

- We have seen that molecular substances tend to have low melting points, whereas network, ionic, and metallic substances tend to have high melting points. Therefore, with a few exceptions, such as mercury, a substance that is liquid at room temperature is likely to be a molecular substance. Liquid solvents are heavily used in industry to extract substances from natural products and to promote the synthesis of desired compounds. Because *many of these solvents have high vapor pressures and so give off hazardous fumes*, **liquids that have low vapor pressures but dissolve organic compounds have been sought**.
- A new class of solvents called **ionic liquids** has been developed to meet this need.
- A typical ionic liquid has a relatively small anion, such as BF_4^- , and a relatively large, organic cation, such as 1-butyl-3-methylimidazolium (Fig.).
- Because **the cation has a large nonpolar region and is often asymmetrical, the compound does not crystallize easily and so is a liquid at room temperature**. It can also dissolve nonpolar organic compounds. However, **the attractions between the ions reduce the vapor pressure** to about the same as that of an ionic solid, thereby reducing air pollution.



1-Butyl-3-methylimidazolium ion

- ***Ionic liquids are compounds in which one of the ions is a large organic ion that prevents the liquid from crystallizing at ordinary temperatures. The low vapor pressures of ionic liquids make them desirable solvents that reduce pollution.***
- Because different cations and anions can be used, solvents can be designed for specific applications.
- For example, one formulation can dissolve the rubber in old tires so that it can be recycled.
- Other solvents can be used to extract radioactive waste from groundwater.