Semiconducting Polymers: A New Class of Material for Electronic and Photonic Devices

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POLYMERS

Question: What is a polymer?

Answer: A polymer is a very large molecule comprising hundreds of thousands of Atoms formed by successive linking of one or two, occasionally more, types of Small molecules into a chain or network structure.

The concept of the polymer is one of the great ideas of twentieth century chemistry. The influence of the polymer (or macromolecule) concept spread into many areas of the natural sciences and technology.

Polymers can be synthesized to exhibit electrical properties that can be controlled over the full range from insulator to semiconductor to metal.
MOLECULAR STRUCTURE

Hydrocarbons and Hydrocarbon Polymers

Hydrocarbons are a class of substances containing only the chemical elements carbon and hydrogen (C and H) in combination. Petroleum and natural gas are complex mixtures of hydrocarbons.

A number of the most important polymers, including polyethylene (PE), polypropylene (PP) and polystyrene (PS) are also hydrocarbons: hydrocarbon polymers.

Difference between the individual hydrocarbon gases, liquids and solids (polymers) lies in “molecular structure”.

The simplest of all hydrocarbon molecules is that of methane, the main component of natural gas. The molecular formula is CH₄. The central carbon atom forms a single chemical bond with each of the four hydrogen atoms, arranged tetrahedrally about it. Methane is a compact five atom molecule.

C atoms may form chemical bonds between themselves giving rise to other hydrocarbon structures. The molecule of ethane (C₂H₆) comprises a pair of C atoms linked by a single C-C bond; each carbon atom is bonded in addition to three H atoms. Ethane is a C₂ hydrocarbon.

Higher hydrocarbons are formed by extending the chain of C atoms. Hydrocarbons of this kind are found in natural petroleum oils up to a maximum carbon chain length of about C₃₈.

There is a smooth change in the physical properties of the individual hydrocarbons as the chain length increases.

- C₁ – C₄ members of the series are gases at normal ambient temperature.
- C₆ – C₁₂ are volatile liquids
- C₁₃ – C₁₈ are higher boiling point liquids
- C₁₉ and higher are heavy oils and waxes

Polyethylene (PE) is a synthetic hydrocarbon polymer of chain length far greater than C₃₈. PE is composed of hydrocarbon chains containing hundreds or thousands of carbon atoms. The molecular structure of PE may be written as H₃C(CH₂)nCH₃ or, omitting the terminal atoms simply as (CH₂)ₙ. n is large but we cannot assign it a “unique” value.
Should we visualize the polymer chain molecule as a rigid or as a flexible entity?

Since both the C-C bond angle and the bond length are fixed, chain flexibility can arise “only” from rotational motions about the C-C bonds.

Ethane (C\textsubscript{2}H\textsubscript{6}) is the simplest hydrocarbon which possesses a C-C bond, in the liquid and gaseous state the relative rotation of the CH\textsubscript{3} groups is fairly free.

Higher liquid and gaseous hydrocarbons may be regarded as loosely jointed chains, continually changing their conformations through rotational motions about C-C chain bonds.

This is true also of the linear polymer chain molecule such as PE.

In the fluid state the molecule behaves as a loosely jointed chain and adopts a largely random arrangement in space, subject only to the bond angle restriction.

In the solid state, the situation is less clear cut. In some polymer solids the molecules adopt ordered crystalline arrangements; alternatively the solid polymer may be amorphous and lack long-range internal order.

ethylene molecule: \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

polyethylene molecule: \[
\begin{array}{cccccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H}
\end{array}
\]

ethylene mer
Polypropylene Heterochain Polymers

So far all the polymer chain structures are based on C chain backbones. Replacement of C atoms in the backbone itself by atoms of other elements produces “heterochain” polymers.

A structurally simple heterochain polymer is polyoxymethylene (POM)

-CH₂ – O – CH₂ – O – CH₂ – O -

POM may be thought of as a PE chain in which O atoms replace alternate CH₂ group. Other heterochain polymers include polyamide (PA) and polyimide (PI).

A number of “inorganic” polymers exists in which the backbone contains no carbon atoms at all. Among these are the polysiloxanes, linear Si – O polymers.
Further types of polymer structures arise when two or more kinds of “mer” are mixed in a single polymer chain.

For example, ethylene and propylene may be copolymerised to give a copolymer, with properties somewhat different from the parent homopolymers PE and PP.

To describe the copolymer chain structure it is necessary to know how the two types of mer are arranged within the chain.

Three possible distinct copolymer classes can be envisaged at once: the alternating copolymer, the random copolymer and the block copolymer.

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The polymer molecular structures are more or less complicated arrangements of atoms held together by primary chemical bonds.

The principal chain building bonds are C-C, C-O and C-N; and C-H, C-F, C-Cl, C=O, O-H and N-H occur frequently, attached directly or indirectly to the chain backbone.

Chemical bonds are formed by rearranging valency electrons from the outer regions of the participating atoms into new spatial distributions which embrace both atoms.

If the two atoms forming the bond are “dissimilar” (except C-C) the sharing of the vacancy electrons is unequal. The electron distribution is not symmetrical and the bond has a definite “electrostatic polarity”, which arises because one atom is able to draw electron charge more strongly to itself than the other.
The electronegativity difference of the two atoms of the bond is a good guide to bond polarity.

Electronegativity differences of more than about 0.8 indicate a strongly developed bond polarity. C-C and C-H are effectively non-polar; in C-O, C-F and C-Cl the carbon atoms are at the positive ends of the polar bonds. In O-H and N-H, the hydrogen atoms are likewise situated at the positive ends of polar bonds.

All primarily chemical bonds (polar or not) are strong and stable, the polymer molecules built from them can generally be broken down or modified only by the action of thermal or chemical forces.

In the solid state, the individual polymer molecules lie close together, and the properties of the bulk material depend as much on forces acting between the molecules as on the chemical bonds within them.

What are the forces that operate between atoms which are in contact but not Joined by primary chemical bonds?

Collectively these secondary interactions are known as van der Waals’ forces. Unlike primary chemical bonding, they do not involve sharing or transfer of electrons between atoms.

The weakest of the interactions is a feasible force of attraction known as a dispersion force resulting from rapid fluctuation of the atomic electron distribution.

The dispersion force between each pair of adjacent –Ch2- mers on two polyethylene chains lying side by side is about 200 times weaker than the force acting within each C-H bond.

Somewhat stronger than the dispersion force is the van der Waals’ force acting between suitably orientated polar bonds. A particularly strong and important type of polar force is the “hydrogen bond”

The hydrogen bond is formed between a markedly electronegative atom and a hydrogen atom already bonded to another electronegative atom.

N-H….O bonds are formed between PA molecules
The strength of a hydrogen bond depends on the identity of the electronegative atoms involved and on their exact relation to other atoms.

The hydrogen bond is often as great as one length of the strength of a typical primary chemical bond. Hydrogen bonds are sufficiently strong to survive the forces arising from molecular thermal motion at normal temperatures.

N-H….O hydrogen bonds also link the two antiparallel macromolecular chains forming the double helix of DNA, the properties of the hydrogen bond lie at the roots of molecular biology.

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**Conducting Polymers**

Polyacetylene (CH)$_x$, a model system

Polyacetylene is the simplest conjugated polymer.

Polyacetylene has a planar structure and alternating single and double bonds along carbon backbones indicating delocalization of Pi-orbitals over the polymer chain.

We will be concerned mainly with trans – (CH)$_x$, which is the thermodynamically stable isomer form of polyacetylene.

Its uniqueness consists in the double degeneracy of the chemical structure with respect to the sequence of bond alteration.
The chain like structures with one Pi-electron per carbon atom suggests that (CH)x is an example of a covalent organic polymer in what has grown to become a wide class of quasi-(1D) conductors.

An anisotropic electronic structure is implied by comparison of the interaction and interchain electronic overlap, strong Pi overlap along the chain with weaker interchain coupling since the intrachain carbon-carbon bond length is about 1.4Å whereas the interchain spacing is about 3.6Å.

**Electronic Structure**

The unsaturated bonds which characterize the polyenes have an important effect on their electronic structure and the corresponding electronic properties.

In a polyene “three” of the “four” carbon valence electrons are in the sp2 Hybridized orbitals;

Two of the the sigma-type bonds are links in the backbone chain while the third forms a bond with some side group (e.g., H)

The remaining valence electrons has the symmetry of the 2pz orbital and forms a Pi bond in which the charge density is perpendicular to the plane of the molecule.

In terms of an energy-band description, the sigma bonds form “low-lying” completely filled bands, while the Pi bond would correspond to a half-filled band.

The Pi bond could be “metallic” provided there is negligible distortion of the chain.
Studies of the $\pi-\pi^*$ transitions in short-chain polyenes show that the frequencies do not fall as n-2 as expected for free-electron picture, but do appear to saturate at $\Delta E_{\pi-\pi^*} \sim 2$ eV.

Bond alternation can serve as a possible explanation for the energy gap in long-chain polyenes.

In a tight binding calculation, the band gap due to bond alternation would be

$$\delta B = \delta x \left( \delta B / \delta x \right)_{xo}$$

Where the $\delta x$ is the difference in the bond lengths and $xo$ the average bond length; $\beta(x)=\beta_o \exp (-x/a)$ in the transfer integral between successive sites where a is a characteristic atomic distance (a $\sim 0.7\text{\AA}$) describing the fall-off of the carbon 2p$_\pi$ wavefunction ($\beta(x)\sim 2.5\text{eV}$). If we assume $dx$ takes the maximum value, equal to the difference in bond lengths between a “single” bond (1.51\text{\AA} as in ethane) and a “double” bond (1.34\text{\AA} as in ethylene), we estimate $E_g \sim 0.6\text{eV}$.

**Fundamental Mechanism of Doping**

In the traditional semiconductor picture of doping, an impurity donates an electron (or hole) to the conduction (or valence) band of the solid and “no” structural change of the solid occurs.

In (CH)$_x$, one must consider whether the state of lower energy is a free electron (or hole) as in the semiconductor picture, or a “charged soliton”.

Within one-electron theory, one concludes that the transfer of an electron to or from the polymer does “not” result in a hydrogenic impurity state or even an unbound carrier in the valence or conduction bands.

The excess carrier is predicted to be accommodated in a “soliton” (or Pi phase kink), an extended lattice defect across which the sign of the bond alternation is reversed.

Such a defect may be shown to introduce a half-filled state at midgap when neutral, which may the accommodate the excess electron or hole and becomes non-magnetic but electrically charged, as depicted in the figure.
From the enhanced mid-gap adsorption upon doping concurrent within the appearance of characteristic infrared active vibrational modes it has been concluded that doping in trans-(CH)x would proceed through the injection of electrons (or holes) and the relaxation of the carriers into solitonic states.

For examples, the observed features in the absorption spectra upon doping with AsF5 can be explained if the doping proceeds through formation of positive charged solitons (S+) and the low energy alpha is associated with the transition from the valence band into the S+ level to form a neutral soliton (So).

As the number of S+ increases with AsF doping, the strength of the low-energy transition (S+ + e -> So) grows proportionally.

The interband transition is suppressed with the introduction of soliton kinks.

On reacting with NH3, the S+ level is compensated, and the low-energy band decreases accordingly. On the other hand, the interband transition does not recover to its initial strength on compensation, since the Pi-electron kinks remain on the chain; only the charge center is compensated.

Obviously, the observed features in the optical spectra may also be explicable in terms of impurity states involving the dopant molecules.

Calculations show that in the presence of an electron-hole pair the lattice is unstable and (in a time on the order of the reciprocal of an optical phonon frequency, i.e., of order of 10^-13 sec) distorts to form a soliton-antisoliton pair.

Phototransport experiments are of direct relevance to the study of “solitons” in (CH)x and avoid the possible complexities associated with carrier generation by chemical doping.
Conjugated Polymers as Laser Materials

Polyacetylene is the simplest of the conducting polymers; however, it does not have very strong photoexcitation in the visible region.

Other materials have gained favor for applications as laser hosts, including the widely studied poly(phenylene vinylene) (PPV)

The PPV chain consists of alternating benzene rings and vinyl groups.

A number of related derivative compounds based on this central conjugated monomer have been used for stimulated emission; their side chains of varying composition both affect the electronic structure and may serve as steric hindrance to minimize the interchain interactions which have been postulated to quench stimulated emission.

Stimulated Emission:

To detect stimulated emission in a small system requires a simple technique; the method of choice for polymer laser is gain narrowing, the narrowing of the energetic peaks in the gain profile as optical pumping energy is increased.

If no stimulated emission is occurring, then increasing the intensity of a monochromatic pumping source with no change in the spectral distribution of the entering photons “should not” affect the spectral distribution of the light exiting the material.

If stimulated emission does occur in the material being probed, then those frequencies corresponding to the energy transitions that allow stimulated emission will selectively exhibit gain, and the peaks on a plot of gain versus frequency will grow taller and narrower as the pump intensity is increased, hence the name “gain narrowing”
Building a Working Polymer Laser

Amplification is proportional to the net number of photons created by stimulated emission, gain is proportional to the path length traveled by photons through a pumped material.

Laser gain is generally expressed as the number of additional photons generated through stimulated emission per unit length.

With a constant source of energy pumping a given material having fixed stimulated emission cross section, the only way to increase gain and thus output intensity is to increase the length traveled by the photons.

Resonator Geometries Realized with Conjugated Polymers

Mirrors create a resonant cavity for these photons for which an integral multiple of half-wavelengths is equal to the distance between the mirrors. These wavelengths are known as the set of longitudinal modes.

Developing resonance depends upon both properly sizing the cavity and minimizing energy losses via the mirrors.

A novel way to achieve optical feedback is the use of a nanostructured substrate providing distributed feedback (DFB) in the direction of propagation by a periodic modulation of the refractive index.
Figure 1.8: Schematic representation of the exciton dynamics in a disordered molecular solid. The picture shows a segment of the conjugated polymer poly(p-phenylene vinylene). 

a) A photon is absorbed by the molecules. 

b) An exciton, i.e. a bound electron-hole pair, is created on the molecule. 

c) The exciton migrates towards molecules with a lower exciton energy. 

d) The exciton recombines and a photon is emitted.
MEH-PPV/Glass 1% wt in THF

peak=633.5 nm
FWHM=11.0 nm