

CONDUCTIVE POLYMERS: WHY THEY WERE WORTH THE NOBEL PRIZE

By A. Brent Strong and Barry M. Lunt, Brigham Young University

Why was the Nobel Prize given for developing conductive polymers?

Three scientists have recently shared the Nobel Prize in Chemistry for their discovery and development of conductive polymers. These three men are: Americans Alan J. Heeger and Alan G. MacDiarmid and Hideki Shirakawa of Japan. The Nobel Prize was awarded because conductive polymers are so different from any other polymeric (plastic) material in their conductivity but are similar to other plastics in their weight, cost, moldability, and general physical properties. The advantages of plastics have always been associated with these typical plastic properties, and those properties included a very low electrical conductivity. For some applications, such as use in electronic packaging and as circuit board material, this low conductivity was favorable. However, there are many other applications where a conductive polymer would be highly advantageous. We will discuss some of these applications later in this article. When the potential of conductive polymers is seen, the reason for the awarding of the Nobel Prize to these men is quite evident.

We will give a brief introduction to what makes a material conductive. This will lay the foundation for understanding the importance of the discovery and development of conductive polymers. We will then look at how conductive polymers were discovered and will find that it

was a result of a combination of luck (or mistake), followed by insightful development, and also a clear basic understanding of chemistry. This is a classic story in how a serendipitous event can be made useful to the world.

What makes something conductive (or insulative)

To understand conductive polymers, it is first necessary to understand what makes any material a conductor or an insulator. And to understand this, we must first turn to the classical model of the atom. As shown in Figure 1, the center of classical atom is the nucleus, which is made up of protons with a positive charge, and neutrons, which are electrically neutral. The nucleus does not participate in electrical conduction or insulation. Outside the nucleus are the electrons, organized in shells or levels of energy. Each shell can only accommodate a specific number of electrons; the innermost shell can only accommodate 2, followed by a second shell which can accommodate up to 8. All three of the atoms shown in Figure 1 have both of these first two shells completely filled. As more electrons are added, they occupy additional shells, but fill only to the number each shell can accommodate, and no more. (Some of the shells in very large atoms are completed with 10 electrons and some with 14 electrons.) There is tremendous stability with a completed shell. Therefore, when more electrons are added to the atom, the new electrons start occupying another, more distant, shell.

The outermost shell, regardless of how many inner shells are complete, is the shell that determines the electrical conduction or insulation characteristics of the atom. This outer shell is known as the valence shell.

When an atom has only one or two electrons in its outer shell, it is quite easy for that atom to give up its electron and revert to the stable configuration of a complete outer shell. The

atoms that so easily give up their electrons are called the metals. When the material in question consists of only metal atoms (as would pure copper, for instance), the outer shell electrons have not particular place to go and are therefore free to move throughout the atomic structure. These free electrons form what is often called a sea of electrons. The sea of electrons can carry charge (which is really just more electrons) and transfer the charge throughout the material. Hence, atoms with free electrons, the metals, are electrically conductive. (Incidentally, when a material has a sea of electrons, light striking that material tends to be highly reflected but with a small amount of variation in the light. This results in the shiny or shimmery appearance that is typical of metals.)

On the other hand, some atoms lack only one or two atoms from achieving a full outer shell and the extra stability that goes with a completed shell. These atoms have a strong tendency to accept electrons. They are called the non-metals. There are no free electrons in non-metals. If some atom tries to give up its electron, it would quickly be drawn into some neighboring atom. Hence, non-metals are non-conductors or, in other words, are insulators. Most plastic materials are of the non-metal, non-conductor type.

The atoms between metals and non-metals, those in which the outer shell is about half full, are called the metalloids or semiconductors. Under some circumstances they can give up electrons and conduct, but under other circumstances they accept electrons and conduct in a different way. They are poor insulators, because they are semi-conductive.

Let's look at some examples of the three types of materials we have discussed. Take the example of a typical metal, sodium, which is represented as (a) in Figure 1. The sodium atom has only one electron in its valence shell. Because there is only one electron in this outermost

shell, it is not held tightly and is basically free to move about. When a little voltage (electrical pressure) applied, the free electrons move in a common direction. This is known as electrical conduction (or flow of current).

The valence shell of argon contains 8 electrons, which makes it a full shell. In an atom with a full valence shell, the valence electrons are held onto very tightly, and are thus not free to participate in electrical conduction. It takes much more voltage (thousands of Volts) to force these electrons out of their valence shell to make them available for conduction. Argon is, therefore, a non-conductor. Argon is shown as (b) in Figure 1.

The valence shell of our third example, silicon, contains 4 of the 8 electrons the shell could hold; this shell is thus half full. We would predict that silicon, with its half-full valence shell, would be a half-good conductor (or half-good insulator); this is indeed the case, and is the reason silicon is known as a semiconductor.

The situation in all elements in the world is slightly more complicated than that which we have discussed. Some additional stability can also be achieved in large atoms that have half of their shell completed, thus suggesting that when an atom has one or two electrons more than half a shell, it can give up its electrons easily and be quite conductive. That is the situation with copper, a well known metallic conductor.

The conductivities of materials is, therefore, dependent on the tendency of the material to give up electrons (conductors) or to take on and retain electrons (non-conductors or insulators). The range of conductivities in these various types of materials is very large. As can be seen in Table 1, the conductivity of materials ranges by over 23 orders of magnitude. Near the very bottom of the list in terms of conductivity are polymers. They are insulators because the atoms

which make up polymers are non-metals and therefore take on and hold electrons. This causes the electrons to be firmly fixed in the bonds between the various atoms in the polymer molecules. (By fixing the electrons between the non-metal atoms, both of the atoms share the electrons, thus achieving some stability from a full shell at least part of the time.) Only a very high voltage (thousands of volts) can break the bonds that occupy these valence electrons, and then this only destroys the polymer. Teflon, is shown in Table 1 as the material having the lowest conductivity. That low conductivity is a direct result of the extremely strong bonds between carbon and the fluorine atoms which make up Teflon. The strong bonds indicate that the electrons are held very tightly and are fixed in their locations between the atoms.

Note that the metals are high in conductivity, as given in Table 1. Silicon and the two forms of pure carbon (graphite and diamond) are in the middle of Table 1, indicating the semi-conductive nature of these materials. The conductivity of diamond is much lower than graphite because the bonds in diamond are much stronger than the bonds in graphite. Diamond is, therefore, an insulator.

With this basic understanding of what makes a material conductive or non-conductive (or even semi-conductive), we must understand another process which is commonly used in modern industry to dramatically alter the conductivity of a material; this process is called *doping*. Doping is accomplished in several different ways, but the end product of doping is to insert a small number of atoms into a network of another atom. Generally, the inserted atoms have a different number of electrons in their valence shell when compared to the surrounding atoms of the native material. This doping is usually done by adding a slightly metallic material or a slightly non-metallic material to a semiconductor (metalloid) such as silicon. Even this very small change in

the atoms of the mixed material can raise the conductivity of the material by many orders of magnitude. This is perhaps best understood by using a metaphor of a pool table.

Consider a pool table completely filled with balls. The movement of the balls when in this packed condition is essentially impossible because there is no place for them to go. This is analogous to a stable polymer, with all its valence electrons fully occupied in the polymeric bonds. If we come along and remove a few balls from the pool table, movement suddenly becomes possible; this is because we have created holes, or places for the balls to move. If we dope a material with an atom with an electron deficiency, we have created holes, or places for the valence electrons to go, thus dramatically increasing the ability of the electrons to move and conduct electricity. Another type of doping adds another layer to the pool table, with only a few balls on it. The full layer is not free to conduct, but the balls on the additional layer move readily, because there is ample room for movement and ample balls to move about.

Doping is heavily used in the electronics industry for making transistors and integrated circuits, or computer chips. Although the physics behind it is still not fully understood, the process itself is well understood and widely used.

With this basic understanding of why materials are conductive, we can examine and appreciate the nature of conductive polymers.

How were conductive polymers discovered and developed?

Conductive polymers were discovered by mistake. But, like other materials that were found by chance or mistake (familiar examples being penicillin and Teflon), the ability to recognize the possibilities of the strange material is the heart of their discovery. As Louis Pasteur said, "Chance favors the prepared mind."

The mistake was made by a graduate student in Japan who was attempting to polymerize acetylene. This seemed to be a logical polymer to create because it is analogous to the already common polyethylene but might possess some interesting properties. The graduate student's purpose was simply to investigate the properties of this polymer, just as many other new polymers were being synthesized and studied back in the 1970s, when these experiments were done. However, something strange happened during one particular polymerization. Instead of getting the black powdery material that had been previously obtained by other chemists, this experiment resulted in the formation of a thin, silvery film that looked much like aluminum but was stretchy like polyethylene. (Its appearance could be compared to the aluminized Mylar balloons so commonly used for birthday greetings today.)

The graduate student was shocked at the unusual appearance of this polymer. No other polymer had ever had this shiny look. (Remember that the Mylar in the balloons is a clear plastic – it is actually the same plastic as soda bottles – that is simply coated with metal on its surface. The metal imparts the shiny appearance.) The graduate student and his advisor recognized that this material might be a good candidate for making synthetic metals. They also theorized that the metallic appearance of the polymer might result from the same source that gives metals their shiny appearance – highly mobile electrons which move freely within the metal structure. Dr. Shirakawa then tested the new polymer for conductivity and found that it was much more conductive than any polymer previously made. The conductivity of polyacetylene is also listed in Table 1.

The graduate student then investigated the changes in his procedures that resulted in this unusual shiny polymer. He discovered that he has used 1000 times too much catalyst. (Those of

us who work in micrograms and milligrams can appreciate how easy this type of mistake could occur.)

Dr. Shirakawa was then invited to the University of Pennsylvania where he worked with Alan MacDiarmid and Alan Heeger – two experts already investigating the field of synthetic metals. Together, these three had the insight to make the next significant improvement in the development of synthetic polymers. That improvement was called doping.

As was explained previously, doping is used in making transistors to control their conductivity. The three professors reasoned that polyacetylene was like the billiard table that was full of balls. It was slightly conductive but could be made much more conductive if a few electrons (billiard balls) could be removed. This would give the electrons more mobility. The professors added iodine to the polyacetylene matrix to create this effect. Iodine lacks one electron from having a full electron shell and therefore has a place (hole) into which the electrons of polyacetylene can move. When the polyacetylene electrons move into the iodine holes, the movement of all of the electrons becomes much greater. Therefore, conductivity is increased. The professors found that the conductivity of doped polyacetylene was about a billion times greater than non-doped polyacetylene. This dramatic improvement in conductivity came from insightful developments based upon a clear understanding of the basic nature of polymers. The insight into the nature of polymers can be understood by referring to Figure 2, a representation of polyacetylene. Note that the bonds between the carbon atoms along the chain alternate from single to double. The double bonds are really a combination of a single bond and a pair of highly mobile electrons that are spread out between the carbons. When an adjacent carbon atom also is bonded with a double bond, the mobile electrons can freely move over the

entire set of carbon atoms. This property is called delocalization. Clearly, the electrons have the potential to move along the entire length of the chain where single and double bonds are the pattern. When doped, polymers containing these delocalized electrons gain tremendous conductivity. (The dopant atoms probably lie along the chains, thus creating holes for the some electrons and imparting mobility to the rest.)

Referring to Table 1 shows that this increase of one billion times in conductivity moves doped polyacetylene from the realm of insulators into the realm of conductors. It is better than many metals, but not quite as good as the best conductors such as copper. However, in the two decades or so of development of conductive polymers, the conductivity has been improved to be nearly equivalent to copper.

From the time of this development, the professors, and many others, have capitalized on the inherent advantages of the new conductive polymers. With these polymers we now have available materials that are highly conductive, but are also light weight, low in cost, highly moldable, and other common advantages of plastic materials.

Conductive polymers other than polyacetylene

Polyacetylene is not the only polymeric material having delocalized electrons. Some other polymers that have conductive natures include: polyparaphenylene, polypyrrole, polythiophene, and polyaniline. All of these have the alternating single and double bonds that delocalize electrons along the chain as is illustrated with two examples shown in Figure 3. With doping, the conductivities of all these polymers are quite high. Several of these conductive polymer types have been commercialized and are sold by a variety of polymer manufacturers.

NASA realized the potential of conductive polymers for aerospace applications and has announced the synthesis of a conductive polyimide film. This film has the advantage of very high (for polymers) thermal stability. Applications seen are those typical of other conductive polymers, with the added benefit of resistance to the extreme environmental conditions of aerospace. This polymer might also be used as a coating for airplanes to provide resistance to lightning strikes.

Graphite, which is not a typical polymer, consists of flat sheets of carbon atoms. Graphite is slightly conductive as can be seen in Table 1. In light of the concepts now understood from polyacetylene, the conductive nature of graphite is understood to arise from a small amount of contaminant atoms that act like electron donors, thus providing a few delocalized electrons which move freely about the carbon sheet. The same is true of carbon or graphite fibers which have small amounts of contaminants and are also slightly conductive.

Applications of conductive polymers

The following materials have either reached some minimal commercial viability or are on the verge of becoming commercial.

Static suppression. Electrostatic discharge (ESD) is a very serious problem in the electronics industry, since voltages as low as 50 Volts can readily damage sensitive electronic components, and this range of voltage is extremely common on equipment and personnel which are not properly protected. For example, if you have ever discharged yourself on something metal and found it to be a bit painful, you were discharging over 15,000 Volts! Today's equipment used for ESD protection is commonly made from polymeric materials which have been made somewhat conductive using fillers and weaving with metal or carbon fibers (for

fabrics). However, because these polymeric materials are inherently non-conductive, they must be tested regularly to assure their continued conductive properties. If future ESD protection equipment is made from conductive polymers, the native material will be conductive, and there will exist no need for periodic testing to assure its proper protective operation. Conductive polymers have been used to suppress static on computer screens, on films, and in windows. We can only hope that the conductive fibers are made inexpensive and durable enough to be used in carpets and eliminate their annoying static buildup.

Batteries. In the future age of massive portability for electronics, the need for improved batteries is critical. Modern society seems to be constantly moving and taking their electronics with them. Hence, we see tremendous growth in laptop computers, cellular phones, and personal digital assistants (Palm Pilots, etc.). Electronics are being put in every place that we might spend our time. Hence, being more portable is better. Therefore, replacing heavier metal components with light weight polymers would seem to be highly desirable.

The electrodes of all common batteries are made of metals. (Car batteries are lead, flashlight batteries are nickle/cadmium, and button cells are lithium.) By replacing these metals with conductive polymers, the following advantages have been shown: lower weight, lower cost, more charge/discharge cycles, lower toxicity, and improved recyclability. Hence, the promise of substituting conductive polymers for these metals is highly desirable and has already proven to be commercially successful. We should also note that originally obtaining the metals, usually from mines, is far more costly and damaging to the environment than is the obtaining of polymer raw materials from natural gas, deep oil wells, or now, increasingly, from residual plant materials.

Silicon replacement. As the director of solid-state physics at Lucent Technologies' Bell Labs said, "The hope is to get performance from plastic electronic components comparable to their silicon ancestors at a fraction of the cost." The ultimate goal is to make integrated circuits and other electronic devices for low cost applications by avoiding the use of silicon. The problem with silicon is that it must be highly purified and exist in an absolutely crystalline form before it can be doped for use in electronic devices. This need for purity and crystal exactness drive the price of silicon to about \$500 per pound. We believe that the price of polymeric conductors would, at large volume, be no more than \$10 per pound.

Light-emitting diodes. The conductive polymers have been made into devices that provide an alternate method to conventional backlit LCD displays. The devices using conductive polymers are sandwich-type structures where the active polymeric film layer lies between a semi-transparent anode and a back row cathode. The devices emit uniformly over the entire device. Such devices have already found application in cellular telephones, displays for home appliances, PDAs, and numerous industrial devices needing a readout display.

Microtools. One interesting property of many conductive polymers is that they swell when they conduct. This means that conductive polymers can change electrical signals into mechanical energy, similar to piezoelectric materials. However, in contrast to piezoelectric films, conductive polymeric films work well at low voltages (about 1/10 as much voltage), thus expanding the areas of applicability for such devices.

Solder. Solder is used heavily in the electronics industry to physically and electrically attach electronic devices to printed wiring boards which connect them together. The solder used is made of a mixture of tin and lead, and has served the industry extremely well for many

decades. However, in recent years there has been increasing concern for the lead in electronic products now ending up in our landfills, where it could eventually leach into the water supply. Although this is not presently a problem, wisdom dictates that we should proceed as quickly as possible to find alternatives. Many metal compounds have been investigated for this application, and much progress has been made. There is even a small niche of the electronics market which has begun to use conductive adhesives for a solder replacement. These adhesives are typically made from epoxies loaded with conductive filler material. One of the big disadvantages of such conductive adhesives is that they are thermosets, and are therefore not reworkable (repairable). The new class of conductive adhesives are generally thermoplastics; these have a great potential to replace presently used conductive adhesives, and perhaps to even replace a large part of the current market for solder in electronics.

Printed circuit boards. Today's electronic devices are attached to "printed" circuit boards made from a composite of epoxy and fiberglass, to which a thin layer of copper has been attached and etched to form the appropriate conductive patterns. This process involves the use of expensive photographic equipment, along with much additional processing equipment for the many hazardous materials used in the process. The end product is very reliable and reasonably inexpensive, but there is much room for improvement. With conductive polymers, the possibility exists to make circuit boards which are truly printed (current ones are actually etched, not printed). Changing to a printing technology would dramatically lower the costs associated with making these boards, allowing many applications which today are only ideas without a way to be realized.

Limitations of conductive polymers

The best currently available conductive polymers do not have the precision in conductance and other electrical applications that we have come to expect from metallic and semi-conductive (silicon) materials. Also, conductive polymers do not conduct electricity at the same speed as silicon chips. Polymers are therefore limited to those applications where gross changes occur. The conductive polymers are, at least at present, to be viewed as complementary to silicon and metal devices rather than competitive.

Conductive polymers are still polymers. While that has some significant advantages in moldability and elongation, to name just a couple, the polymer nature also has some disadvantages. For instance, the conductive polymers are still much weaker in mechanical strength when compared to metals, although the polymers are better than silicon-based devices. Also, the polymer materials are softer and, therefore, more likely to be damaged by scratching and abrasion when compared to metals. Moreover, many of the conductive devices are currently encased in glass to prevent physical scratching or handling damage. Hopefully, this abrasion problem will be solved in other ways (new polymers?) as glass sometimes makes the devices quite fragile.

Lastly, the polymeric devices are mostly conductive in only one or two dimensions whereas metals are fully conductive in three dimensions. The dimensionality restriction of the polymers is because polymers are linear or, occasionally, planar structures and the delocalized electrons follow the shape of the polymer network. Designers need to be aware of this difference in directional conductivity. It can be a problem but, in some applications, it might also be an

advantage to have a significantly reduced conductivity in the vertical dimension (as would be the case in minimizing insulation at some connections).

The future of conductive polymers

Some envisioned applications for conductive polymers seem too strange to be possible but are being reported widely by the American Plastics Council. (See reference 12.) For instance, researchers see the possibility of “electronic paper.” This would be flexible plastic sheets that conduct electricity and would be capable of displaying information the same way a laptop computer screen does. This would, of course, make laptops (and conventional desk computers) much thinner. It might also mean that flexible sheets of this conductive polymer paper could be updated with data via computer (perhaps using a PDA) linked to the Internet or some wireless communication device, and then rolled up and carried to a presentation or wherever else displays might be useful. You could, of course, have several of these mounted in your home and then, at your whim, change the display from one painting to another to fit your mood.

Medical researchers are excited about possibilities they see in conductive polymers. Scientists at the University of Texas reported in a recent meeting of the American Chemical Society some encouraging success in mending damaged nerves by fitting the severed ends into an electrically conductive plastic sleeve packed with sugar. The sugar apparently encourages blood vessel growth, which in turn stimulates nerve regeneration. The electrical properties of the plastic, which dissolves over several weeks, appear to have a beneficial effect on the nerves.

Some researchers have embarked on a study of conductive polymers as a new method for storing electronic information, perhaps optically. These could be developed into very fast

storage and retrieval devices. Other see conductive polymers as light detecting devices that could be configured into large arrays for military and commercial applications.

Surely conductive polymers are exciting developments. As they become more common, they may enter many of the fiberglass composite products we currently make. We may find that the labels on our products are electronically displayed or that the veil coat of a boat can change the color of the boat to meet a customer's particular desires and that the change can be made in the sales office of the boat dealer. Make ours with red stripes.

Bibliography:

1. Yaukey, John, *USA Today*, August 15, 2000.
2. Kaner, Richard B. and Alan G. MacDiarmid, "Plastics That Conduct Electricity," *Scientific American*, p. 106, 1988.
3. De Gaspari, John, "New alternatives In Conductive Plastics," *Plastics Technology*, p. 13-15, November 1997.
4. "Conductive Polymers Spark New Ideas," *Technology Edge*, p.13, April 1993.
5. "Electrically Conductive Polyimide Films," NASA Tech Briefs, p. 57, August 1993.
6. Shirakawa, Hideki, et al, J.C.S. Chem. Comm., 1977.
7. Ito, Takeo, Hideki Shirakawa, and Sakuji Ikeda, *Journal of Polymer Science: Polymer Chemistry Edition*, Vol. 12, p.11-20, 1974.
8. Chiang, C. K. et al, *Physical Review Letters*, Vol. 39, No. 17, October 24, 1977.
9. <http://www.uniax.com/index.htm>
10. <http://nobelprizes.com/nobel/chemistry/chemistry.html>
11. <http://nobel.sdsc.edu/announcement/2000/chemreading.html>

12. <http://www.ameriplas.org>

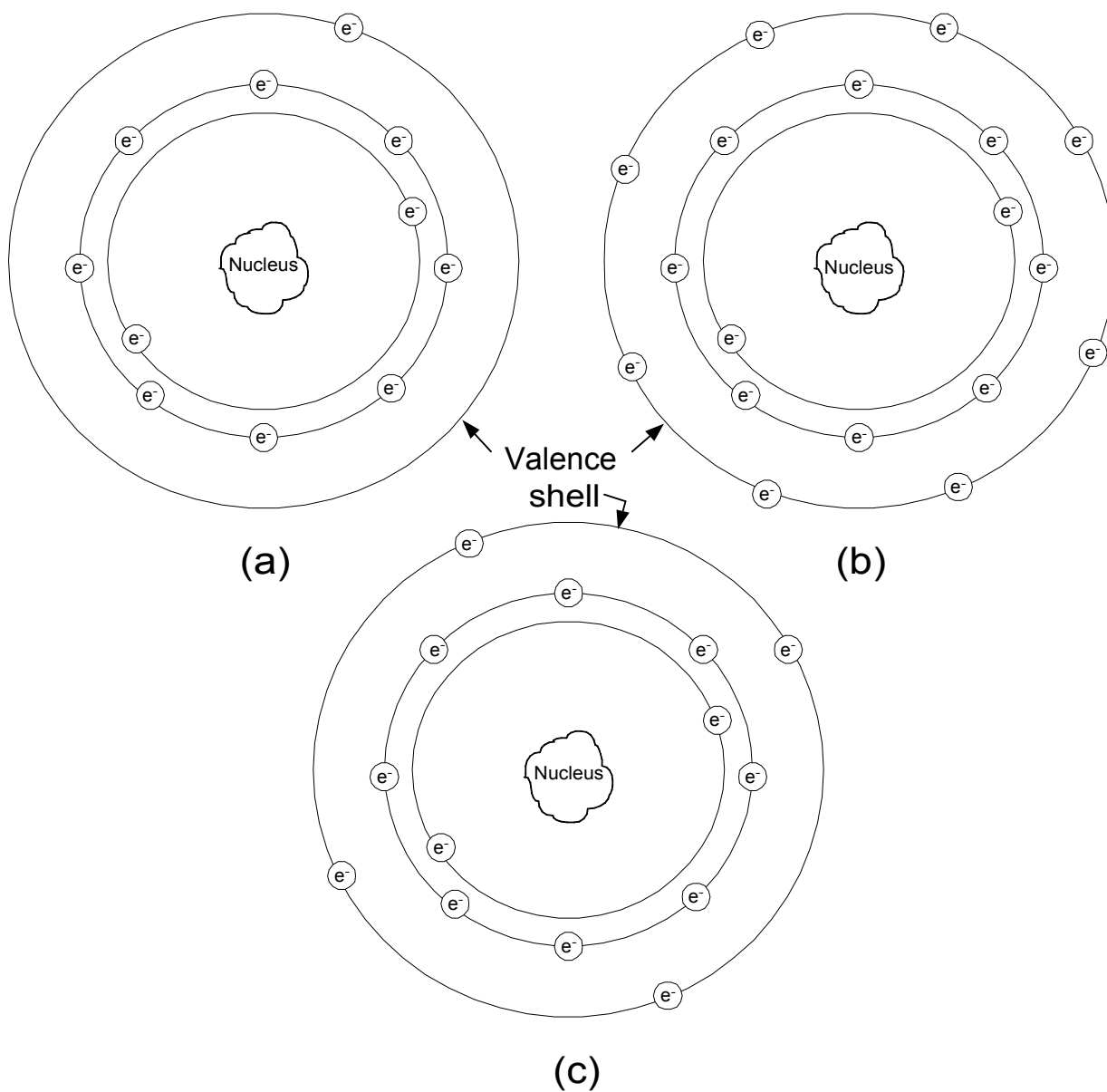
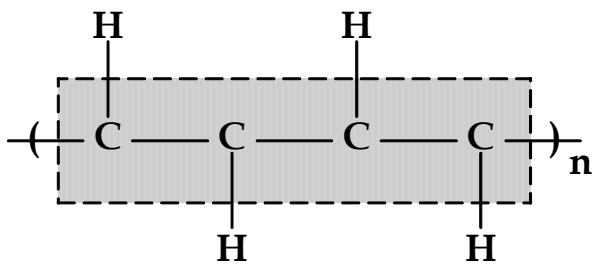
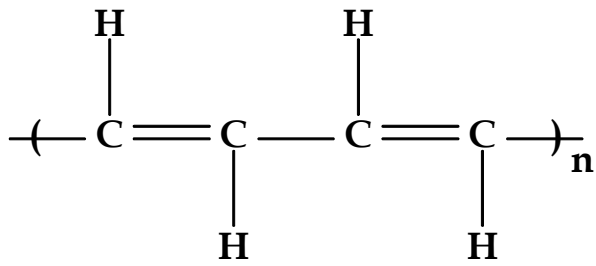


Figure 1: Classic structure of the atom, showing (a) an atom with one valence electron, (b) an atom with a full valence shell (8 electrons), and (c) an atom with a half-full (4 of 8) valence

Table 1 Relative conductivity of several common materials

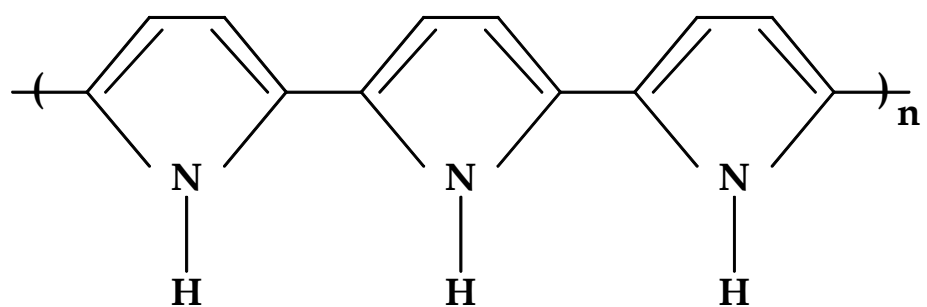
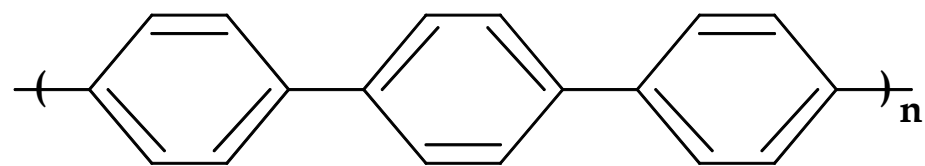
Material	Conductivity (Ohm-cm)⁻¹
Silver	6.25×10^5
Copper	5.85×10^5
Gold	4.44×10^5
Polyacetylene (doped)	$\approx 6.0 \times 10^4 - 1.5 \times 10^5$
Steel	$\approx 6.0 \times 10^4$
Silicon	1.56×10^{-3}
Carbon, graphite	$\approx 1.0 \times 10^{-3}$
Polyacetylene (unmodified)	$\approx 1.0 \times 10^{-11}$ to $\approx 1.0 \times 10^{-15}$
Carbon, diamond	$\approx 1.0 \times 10^{-14}$
Alumina ceramic	$\approx 1.0 \times 10^{-15}$
Epoxy	$\approx 1.0 \times 10^{-15}$
Polyethylene, medium density	$\approx 1.0 \times 10^{-16}$
Teflon	$\approx 1.0 \times 10^{-18}$



(a)

(b)

Figure 2: Acetylene polymer; (a) traditional representation showing alternating single and double bonds; (b) representation emphasizing the delocalized nature of the electrons.



(a)

(b)

Figure 3: Representative new conductive polymers, showing alternating single and double bonds; (a) paraphenylene, (b) polypyrrole.