C-3-6 (Invited) Polyacetylene - A Typical Semiconducting and Metallic Polymer

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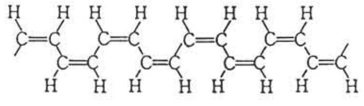
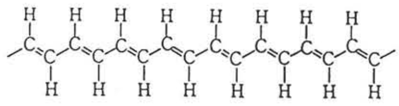
1 Introduction

Polyacetylene is the simplest linear synthetic polymer. Fundamental unit consists of one carbon and one hydrogen atoms, as has been called simply $(CH)_x$ recently. Each carbon is σ bonded by sp^2 hybrid orbital to one hydrogen and two adjacent carbon atoms to form a planar chain molecule. The remaining fourth valence electron of the carbon atom is in P_z orbital, π electron, which lies perpendicular to the molecular plane. Thus, the molecule forms a quasi-one-dimensional lattice of the π electrons. In an ideal infinite chain with equal carbon-carbon bond length, one would expect the π electrons to form a half-filled band leading to metallic conductivity. However, as shown below, alternately short (or double) bonds and long (or single) bonds causes the Peierls instability, separation of the half-filled band into valence band and conduction band with a gap of about 1.5 eV.

It can be prepared in the form of lustrous silvery films with thicknesses varying from 10^{-5} cm to 0.5 cm by catalytic polymerization of acetylene. It exists in two isomeric forms, *trans* and *cis*, or as a mixture of the two forms depending on the preparative conditions.



cis polyacetylene



trans polyacetylene

The *cis* form can be converted to the more thermodynamically stable *trans* form on heating to 150 - 200 °C for 30 min. The room temperature DC conductivity of the films and the activation energy of the conduction depend on the *cis-trans* content, varying from 10^{-9} S/cm and 0.5 eV for the *cis* isomer, and 10^{-5} S/cm and 0.3 eV for the *trans* film, respectively. As-grown films consist of randomly oriented fibrils of *ca.* 200 Å diameter, highly crystalline extended chain bundles. The bulk density of the films is 0.3 - 0.5 gm/cm^3 depending on the preparative condition compared with 1.15 gm/cm^3 of the fibrils as obtained by floatation method. Therefore, the fibrils fill only one-third to half of the total volume of the film. Because of its unique solid structure, the films have a quite high surface area, 40 - 60 m^2/gm. The films can be stretch oriented in excess of three times their original length with concomitant partial alignment of the fibrils.

2 Chemical doping

Polyacetylene films can be doped chemically or electrochemically with a variety of electron attracting chemicals (acceptors) and electron donating chemicals (donors) to form n- and p-type semiconductors, $[CH(A^-)_y]_x$ and $[CH(D^+)_y]_x$ where A and D represent acceptor and donor dopant species, respectively, and y is the dopant concentration. The electrical conductivity increases with increasing the dopant concentration resulting in a semiconductor-metal transition at y = 0.01 to 0.02. It can be varied over twelve orders of magnitude through the chemical or electrochemical doping. The highest value observed so far is greater than 3×10^3 S/cm with a stretch-oriented film doped by AsF_5.

Figure 1 and 2 show the electrical conductivity of iodine doped films as a function of doping time under various iodine vapor pressure and dopant concentration, respectively.

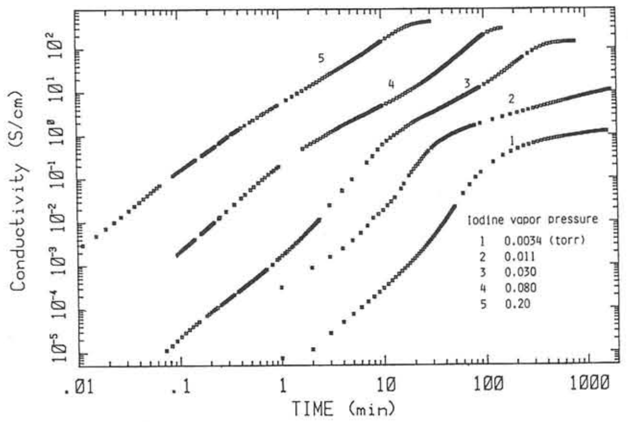


Figure 1 Electrical conductivity of iodine doped films as a function of doping time.

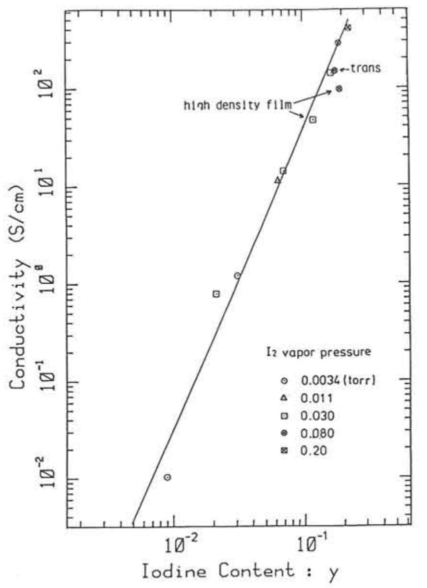


Figure 2 Electrical conductivity as a function of iodine concentration (y).

3 Device application

The doped polyacetylene as a new class of semiconducting and metallic materials has generated considerable interest from the point of view of potentially low cost and light-weight devices such as solar cell and rechargeable batteries. The figures shown below are preparative method of p/n junctions (Fig. 3), I/V characteristics of p/n junction (Fig. 4), and solar cell chataceristics of p-$(CH)_x$/n-Si junction.

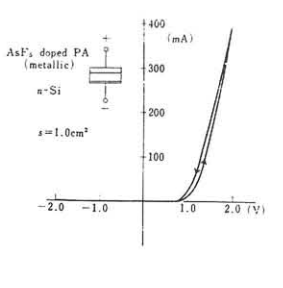


Figure 3 →

Figure 4 ←

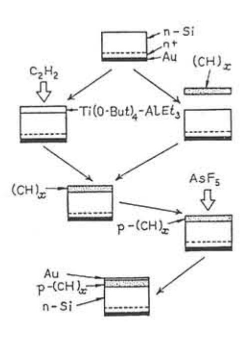


Figure 5 →