

Review on the Prospect of Utilization of Polyacetylene Films as a Highly Conductive Material

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Abstract - Polyacetylene, is one of the simplest polyolefin, synthesized from acetylene. Due to its conjugated double bond structure, the pi-electrons keep on shifting between the repeat units in one direction replicating electron transport during conduction, becoming a conducting polymer by nature. In this review paper, we study the synthesis of highly oriented polyacetylene films as a material of high conductivity, which is achieved by doping of polyacetylene with halogen gases, the dependence of conductivity of polyacetylene upon doping concentration, draw ratio and structure of polyacetylene and some other miscellaneous factors like oxygen content and temperature.

Key Words: Polyacetylene, Conductivity, Orientation, Doping, Polymerization, Complex catalysts, Synthesis, Electron accepting species, Electron donating species, thin films.

1. INTRODUCTION

Linear Polyacetylene (CH)_x, is one of the most fundamental conjugated polymers and is therefore a great forerunner as a competitive conducting polymer. Polyacetylene has been extensively studied for two main reasons. First being the production of high strength Polyacetylene films and second being the discovery of a large increase in electronic conductivity due to doping with small quantities of electron-attracting species such as halogens. Various polymerization methods have been described in the fore coming sections wherein highly oriented polyacetylene films are directly produced from the polymerization reaction, eliminating any further secondary orientation processes like pulling. Several doping experiments conducted by C.K.Chiang et.al have shown that doping polyacetylene by halogenic vapors increased conductivity rapidly [1]. Highly conductive polyacetylene films prepared by K.Akagi et.al [2] has shown to have a conductivity as high as 10⁴ S/m . The studies conducted by H.Shirakawa et.al has shown that the conformation of the molecular chain has a direct influence on the conductivity of the polyacetylene films.

2. METHODS FOR THE SYNTHESIS OF ORIENTED HIGHLY CONDUCTIVE POLYACETYLENE FILMS

Over many years into the research of conducting polymeric materials, polyacetylene has proven to be one of the most promising due to its versatility but is highly unstable. The underlying three methods were highly successful in producing highly conductive polyacetylene.

2.1 LIQUID CRYSTAL POLYMERIZATION

As per K.Akagi et.al, this process uses a liquid crystal solvent with dissolved complex catalyst system. In order to keep the liquid crystals intact, the polymerization temperature was kept around 10-15 °C. The complex catalyst used was purified triethylaluminium (AlEt₃) and purified tetra-n-butoxytitanium (Ti(OBu)₄) in the ratio of 4. The liquid crystal solvent was an equimolar solution of 4-(trans-4-n-propylcyclohexyl)-ethoxybenzene and 4-(trans-4-n-propylcyclohexyl)-butoxybenzene.

The concentration of the catalyst solution was 0.01mol/l which was aged for 30 minutes at room temperature. In process, the catalyst solution was injected onto a flat bottom container held inside a schlenck flask with the help of a micro syringe (Fig. 1). The flask was degassed to ensure the removal of impurities. This setup was then placed inside a magnetic field of field strength 2-14 kGauss. At this stage of the experiment, acetylene gas was introduced onto the catalyst solution at a pressure of 600-700 torr for a time period of 60 minutes to ensure a high degree of polymerization and maximum yield. Due to the externally applied magnetic-force, the molecular chains got oriented thus yielding highly oriented polyacetylene films [2].

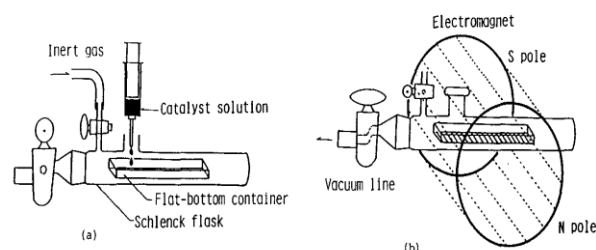


Fig. 1: Apparatus used for liquid crystal polymerization [2]

2.2 NON-SOLVENT POLYMERIZATION METHOD

In correspondence to K.Akagi et.al^[3], the same catalyst solution as in section 2.1 was used. The difference lies in the fact that after the high temperature aging of the catalyst solution, the polymerization solvent was evaporated by dynamic pumping just before the introduction of acetylene gas (Fig. 2). The Polyacetylene films thus synthesized by this method had a young's modulus of 100 GPa and tensile strength of 0.9 GPa, while the electrical conductivity was found to be 2×10^4 S/cm and had a very high bulk density of 1g/cc. Thus, it can be inferred that by this method, the polyacetylene films thus obtained would have high strength, high density and high conductivity which can be further enhanced by the mechanical stretching of the films in order to induce molecular orientation.

2.3 GRAVITY FLOW METHOD

In this method, the catalyst solution used was like the solution used in section 2.1. The complex catalyst that is, $AlEt_3$ and purified $(Ti(OBu)_4)$ had a ratio of 3 as per H.Shirakawa et.al^[4]. The catalyst solution was first introduced along the sides of a glass flask by allowing it to flow with the help of gravity. Then acetylene monomer gas at a pressure of 450-470 torr was introduced wherein polymerization took place along the sides of the glass flask where the catalyst solution was initially made to flow.

The polyacetylene films obtained by this method had a highly oriented fibrillar morphology^[4] with the fibers oriented in the flow direction. Fig. 3 depicts a schematic representation of the flow method. Thus, we can say that the gravity flow method is the least expensive method of all, as it does not require the usage of vacuum pumps and other expensive equipment.

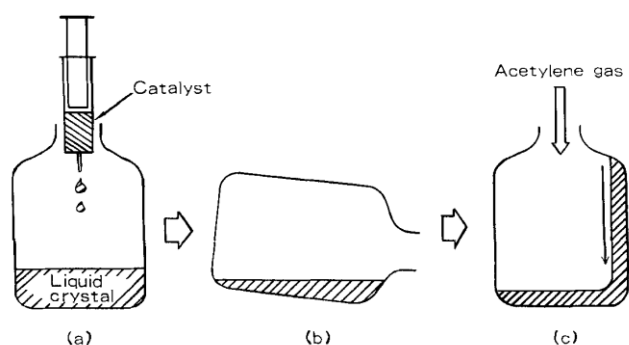


Fig. 3: Schematic representation of gravity flow method^[4]

2.4 ARA METHOD

With reference to the paper published by H.Naermann and N.Theophilou^[5], this method was successful in generating films of 5000 S/cm in doped, unstretched samples and

those of stretched and doped samples showed a conductivity of 10^5 S/cm. (ARA is an abbreviation for Addition of Reducing Agents, e.g., butyl-lithium)^[5]. This method uses a complex catalyst system (which contains dissolved ARAs). A thin layer of this catalyst system was applied over a supporting carrier film (like High density polyethylene film or polypropylene film). It was found that in order to produce a polyacetylene film of thickness $15\mu m$, 7 ml of the catalyst solution was required^[5]. At this stage of the experiment, Acetylene gas was introduced over the film, where it reacted with the catalyst and formed polyacetylene films. It has been reported in^[5] that using 3ml butyl-lithium ARA yielded a polyacetylene film of the highest conductivity. These films were then stretched along with the carrier film, removed from the carrier film, washed with toluene and finally, doped with an appropriate halogen solution.

3. EFFECT OF ORIENTATION, DOPING, PERCENTAGE CIS-TRANS CONTENT AND OTHER MISCELLANEOUS FACTORS ON THE CONDUCTIVITY OF POLYACETYLENE

3.1 DOPING

Polyacetylene in its pure form has conductivity ranging from the order of 10^{-9} S/cm to 10^{-5} S/cm with the lower end of the range pertaining to cis-polyacetylene films and the higher end of the range pertaining to trans-polyacetylene films. However, polyacetylene films usually show conductivity in the order of 10^{-6} S/cm due to equal percentage of cis and trans entities in the film^[2]. As these films were subjected to doping by I_2 vapors, the conductivity of polyacetylene films increased to around 10^5 S/cm^[2], indicating a change in conductivity of polyacetylene by a magnitude of 10^{11} S/cm. Conversely, doping polyacetylene films with electron donor groups like ammonia (NH_3) had a negative effect on the conductivity of polyacetylene films. It was found that conductivity of trans-polyacetylene dropped by four orders in magnitude (that is, the conductivity of trans-polyacetylene was less than 10^{-9} S/cm)^[6]. The conductivity of polyacetylene films is also greatly dependent upon the concentration of the dopant group used. A graph relating the conductivity of polyacetylene films as a function of concentration of dopant was portrayed in^[6], wherein it can be clearly inferred that as the concentration of the dopant increases, conductivity also increases steadily given that the dopant is an electron accepting molecule like AsF_5 . However, this increase in conductivity occurs until a certain limit (reaches maximum) and then levels off. Pristine polyacetylene can therefore be called as a wide band gap semiconductor with a low intrinsic conductivity.

The studies conducted by T.C.Clark and G.B.Street^[10] have concluded that when pristine polyacetylene is doped with halogenic elements, trihalide or pentahalide moieties were formed on the polymer which was confirmed by

Resonance Raman Spectroscopy technique. It is also mentioned that the electron transfer from the dopant atoms to the polyacetylene molecule formed a bridge between the polymer chains itself. It has been further indicated by vibrational spectroscopy technique that doping of polyacetylene leads to weakening of the carbon carbon double bonds leading to an increase in electron delocalization relative to polyacetylene hence increasing the conductivity of pristine polyacetylene.

Furthermore, the studies conducted by H. Shirakawa and T. Kobayashi^[11] have suggested that doping of polyacetylene by some of the transition metal halides yield a highly conducting Polyacetylene. (Note: For the transition metal halide doping, it is essential to find a good solvent to increase dopant content in Polyacetylene, but controlled reaction is necessary to obtain maximum conductivity in metal halides).

Extensive studies on the doping of polyacetylene films by bromine has been conducted by C.K. Chiang^[15] wherein he observed that the conductivity of polyacetylene raised by six orders in magnitude within a few minutes into the doping process by bromine. This was followed by a very slow increase in conductivity to reach maximum conductivity.

Hence doping is an important parameter which affects the conductivity of polyacetylene.

3.2 ORIENTATION AND DRAW RATIO

Orientation has a very significant effect to play in influencing conductivity as it orients the fibrils and filaments within the molecular envelope of polyacetylene to increase the properties in the orientation direction. As published in ^[4], highly oriented polyacetylene films produced by the ARA method, doped with I₂ vapors showed a very high conductivity value of 120000 - 170000 S/cm. Thus, an inference can be drawn that orientation of the polyacetylene films accompanied by doping of the film by using electron accepting species like I₂, AsF₅ etc. has a significant effect in increasing the conductivity of polyacetylene to the point where it can be compared to that of the conductivity of metals, while doping of polyacetylene films by using electron donating species like ammonia has a negative effect on the conductivity of polyacetylene.

The conductivity was found to increase linearly with the draw ratio, the maximum conductivity was 2×10^4 S/cm at a draw ratio of $\lambda = 15$ for thick films, and 3×10^4 S/cm at a draw ratio of $\lambda = 10$ for thin films. When the plot of conductivity ' σ ' vs draw ratio ' λ ' was compared for thick and thin film samples, thin film samples showed a higher slope by a factor of 2 ^[9], than the thick film samples thus indicating that even thickness of the polyacetylene films play an important role in influencing the conductivity of

the samples. Hence, Yong Cao et al. have concluded by stating that if more homogeneous thin films can be prepared and stretched to higher draw ratios, higher conductivities can be achieved ^[9].

3.3 PERCENTAGE CIS-TRANS CONTENT IN THE MOLECULAR STRUCTURE

The molecular structure of polyacetylene in the films play a very important role as a variable for the property of conduction. Since it is known to us that regular molecular structures provides a smooth path for electrical conduction, it can be deduced that trans-polyacetylene films would have a higher conductivity than cis-polyacetylene due to its structural regularity. This is further confirmed by the paper published by Hideki Shirakawa et al.^[7] wherein they conclude that the resistivity of polyacetylene films decreased with increasing trans content up to compositions containing 80% trans conformations. They have further discovered that the resistivity of polyacetylene films having more than 80% trans content show an increasing trend up to an extent. They mention that upon characterization of polyacetylene samples by using X-ray diffractometry (XRD), the diffraction patterns revealed that the nature of the polyacetylene film was crystalline irrespective of the cis-trans composition within the molecular structure ^[7]. This indicates that the percentage cis-trans composition within the molecular structure does not have any effect on the crystallinity of the polyacetylene films.

3.4 MISCELLANEOUS OTHER FACTORS

We would like to indicate that the conductivity of polyacetylene films not only depend upon the above mentioned three factors, but also on various other factors. However this review is mainly based around the above three parameters.

D.J. Berets and D.S. Smith ^[8] conducted experiments to determine the effect of oxygen on conductivity of polyacetylene samples and have reported that as oxygen content in the polyacetylene sample increased, the resistivity of the sample also increased linearly. They also found out that initially oxygen got adsorbed reversibly to the surface of the polyacetylene molecules which reduced resistivity but as oxygen content increased, oxygen reacted with the polyacetylene molecule irreversibly and thereby lead to an increase in resistivity of the polyacetylene sample^[8]. Further they also speculate that, it was not only the amount of impurities like oxygen affecting the conductivity but also the crystallinity of the sample. They deduce that since highly crystalline polyacetylene samples had long molecular chains, they showed higher conductivity than the ones with lower values of crystallinity. Also, electrical conductivity at room temperature does not depend on the dopant species rather depends on the dopant content in the doped

polyacetylene^[11]. Hence, dopant concentration is also a key characteristic feature when synthesizing highly conductive polyacetylene films.

The studies conducted by Y.Nogami^[12] have shown that the conductivity of polyacetylene depends upon temperature wherein heavily iodine doped polyacetylene reached conductivities of 10^5 S/cm at room temperature. They also conclude that the electrical conductivity of such a heavily doped polyacetylene film becomes independent of temperature for temperatures below 10K upto 0.06K.

The studies conducted by J.Tsukamo^[14] also arrived at a similar conclusion that the conductivity of doped polyacetylene decreases as the temperature decreases.

Siegmar Roth and Maria Filzmoser^[13] have reviewed that for all doping levels, conductivity of polyacetylene decreases as the temperature decreases. They have also reviewed that the conductivity of polyacetylene decreases drastically if the conjugation length decreases.

The synthesis conditions like catalyst ageing temperature, molar ratio, film thickness also play an important role in the formation of highly conductive polyacetylene. Z. Skanderia, A. Djebailia, Y. Bouzahera, M. Bellouma, M.J.M. Abadie performed various experiments on this matter and have concluded that a more fibrillar structure morphology yields better conductivity of polyacetylene. Higher density of these fibrillar structures also contributes positively in yielding a higher conductivity of polyacetylene^[17]

We would like to indicate that the above-mentioned factors play a key role in tweaking the properties of polyacetylene films in order to synthesize polyacetylene films having very high conductivities. Such highly conductive polyacetylene films if synthesized will find applications in solar cells, batteries, conductive tapes, cables, wires etc.

4. PROCESSING OF POLYACETYLENE

Polyacetylene is thought of to be one of the best material in the class of conducting polymers due to its exceptional versatility and ease of synthesis. But the main drawback of polyacetylene is its processability. It was thought of to be a material which could not be processed due to its unstable nature. The highly conjugated planar structure makes it highly insoluble in organic solvents and its thermal properties prohibits its processing via thermoplastic methods like extrusion, injection molding, blow molding and so on. To make polyacetylene processable, grafting process proved to be successful^[16].

Johannes Huber and Stefan Mecking processed polyacetylene from aqueous nanoparticle dispersions^[16] wherein they have processed polyacetylene by dispersion

of sub-micron level polyacetylene particles (obtained by catalytic polymerization) in emulsions. These emulsions are suitable for further processing methods like dip coating, ink jet printing and so on.

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