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The bromine doping of polyacetylene

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Abstract

The original experiment of the bromine doping of polyacetylene performed by Chiang and Shirakawa is described. This simple, seminal experiment impacted physics and chemistry through the discovery of metallic conducting synthetic organic polymers and the verification and demonstration of the doping concept in organic polymers. Although the molecular formula of polyacetylene is simple, this molecule exhibits complex behavior and fueling significant work not only in polymer science, but also in quantum physics. The soliton theories used to describe polyacetylene's simple but unique 1-D structure inspired many new quantum concepts for more complicated conducting polymers. The continuing study of model complex conducting polymers could lead to a better understanding of quantum electronic devices at the molecular level.

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1. Introduction

The Nobel Prize in Chemistry 2000 was awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for their “Discovery and Development of Conducting Polymers” [1–4]. In their Nobel lectures, the Laureates summarized over three decades of research. The first lecture given by Shirakawa, described his work on the development of polyacetylene chemistry. He ended his lecture with a story of the bromine doping of polyacetylene experiment [5]. Next, MacDiarmid discussed the chemistry of conducting polymers and recent development in plastic electronics [6]. Heeger discussed the physics of conducting polymers and the development of new industries [7].

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On November 23, 1976, Chwan-Kang Chiang and Hideki Shirakawa successfully performed the bromine doping of polyacetylene experiment in the physics laboratory located in the basement of the Laboratory for Research on the Structure of Matter (LRSM), University of Pennsylvania (Penn), Philadelphia, PA [8]. They discovered that a bromine-doped polyacetylene is a highly conducting polymer. This simple experiment impacted physics and chemistry through the discovery of metallic conducting synthetic organic polymers and the verification and demonstration of the doping concept in organic polymers. The significance of the bromine doping experiment is clear from the development of conducting polymers as a new branch of science.

The discovery of doped polyacetylene as an organic, electrically conductive material not only marked the birth of a new generation of polymeric materials, but also created a new frontier for 1-D physics. The discovery was widely recognized as a breakthrough in materials chemistry and an example of the potential for interdisciplinary research between physics and chemistry. To me, the discovery is an evolution of physical concepts through the material as a tangible realization of a physical concept. As a physicist, my interest and research are not limited to a single material, but rather on a specific phenomenon. In this paper, I attempt to tell a physicist's story of the historical bromine doping of polyacetylene experiment mentioned by Shirakawa at the conclusion of his Nobel lecture. I will retrace my efforts to search for high conducting organic materials in 1-D physics. My work in both physics and chemistry before the discovery was a prelude to this unique experiment. The collaboration between Shirakawa and me is an important example for all scientists.

My story began around the year of 1973, a few years before polyacetylene came to the research groups of Professors Heeger and MacDiarmid. My discussion will be limited to my research efforts on the electrical transport studies performed in the basement laboratory where I worked and where the discovery was made. I will first describe the background work that led to the adoption of a simple and novel measurement technique used to discover the doping effect on polyacetylene. Then, I will describe the planning and execution of the bromine doping experiment and our research efforts after the experiment. Finally, I conclude with a brief discussion of future directions.

2. Highly conducting one-dimensional single crystals

Physics theories of electronic conductors often start with a one-dimensional (1-D) system for simplicity. The connection between a 1-D and a 3-D conductor is not trivial. For electronic properties, traditional discussions of 1-D conductors use a linear hydrogen or sodium chain as an example even though these materials do not exist. A real linear carbon chain or polymer exists but was always an insulator. There had been many attempts to create linear atomic structures of various types. I had studied pure metals and three classes of highly conducting 1-D single crystal materials before I started work on polyacetylene (Fig. 1).

In the early 1970s, the unique structure of charge-transfer salts emerged as a new model material for 1-D conductors. 1-D physics based on organic single crystals soon became a focal point of solid state physics research. The electrical conduction property

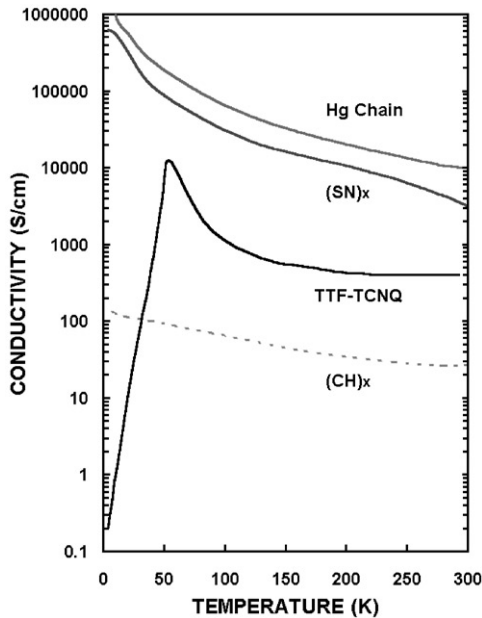


Fig. 1. Conductivities as a function of temperature for three types of 1-D synthetic metals and doped polyacetylene.

of 1-D system was an exceptionally exciting topic to me, because my research field was the electrical transport properties of pure metals and alloys. When I completed my Ph.D. under Frank Blatt and Peter Schroeder at Michigan State University, East Lansing, MI. Heeger's group at Penn was one of the leading research groups in the field. In 1974, I chose to join Heeger's group to do my postdoctoral research and hoped that I could contribute to 1-D physics. At the time, the most interesting subject was the electrical conductivity of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), a prototype 1-D highly conducting organic single crystal [9].

Heeger's group was very successful, exciting and dynamic, because of the integration of strong organic chemistry efforts with a wide range of physical studies. The group had developed methods to purify organic charge-transfer salts and to grow high-purity single crystals. The purity and perfection of these crystals were essential to understanding the properties of organic salts. The metallic conductivity of TTF-TCNQ was due to its crystal structure. The linearly stacked large flat organic molecules forced electrons into a 1-D format, referred to as a quasi-1-D system. Not all quasi-1-D systems have very high conductivities. Some crystals are semiconducting rather than conducting because of their different structures. Also, impurities, defects, or disorder that alter the crystalline structure affect the 1-D conducting properties. The conductivity and the material structure issues were the focus of our studies at the time. The study of TTF-TCNQ was the precursor work to the doping concept for polyacetylene.

My research program on 1-D physics was heavily oriented towards chemistry through working with Anthony F. Garito, an excellent chemist in our group, while Heeger was

the director of the LRSM. My work, the electrical transport studies conducted in the basement laboratory was routinely applied to guide the synthetic chemistry in search of new materials. Garito and I focused our efforts on making new crystals that had similar or improved properties compared to TTF-TCNQ. The goal was to find a “true” organic metal or superconductor. We had some successes and discovered crystals with good conductivity such as 2,2',5,5'-tetraselenafulvalene-7,7,8,8-tetracyano-*p*-quinodimethane (TSeF-TCNQ). I studied many samples, either grown by us or brought to us by visitors. The charge-transfer salt crystals were very small and fragile. A four-probe conductivity measurement method for TTF-TCNQ developed by Larry Coleman and Marshall Cohen played a crucial role in our program [10]. I became an expert in the measurement technique and took charge of the basement laboratory. We were able to determine successfully the conductivity of very small crystals.

In addition to making new crystals, I also used physical methods to introduce disorder and impurities into, otherwise, perfect 1-D crystals. The study of radiation-induced defects in TTF-TCNQ was an attempt to control impurities in an organic material [11]. From handling the materials in these studies, I gained much experience in organic materials. I developed an in-depth understanding of organic crystals and some toward organic materials. The basement laboratory not only physically was distant from the rest of Heeger's laboratories on the fourth floor, but our research projects were also always a few steps ahead leading the rest of the group. We acted like the scout of the group, constantly searching for new materials. Although I published many papers, yet there was no exciting breakthrough that I originally came here for.

In 1975, two new novel inorganic 1-D material of interest reported in the literature. A new student, Richard Spal joined the basement laboratory. He and I studied the transport properties of the new inorganic 1-D material single crystal, $\text{Hg}_{3-\delta}\text{AsF}_6$, also called the mercury-chain compound. Another new student Yung-Woo Park joined Cohen and I studied on the transport properties of the inorganic polymeric single crystal, $(\text{SN})_x$. Because both of the materials were inorganic, the leading role in chemistry moved from Garito to MacDiarmid, who was an expert in inorganic materials. MacDiarmid's chemistry group made both materials for us. In the beginning, the crystals of the material were not perfect. Thus, most of my work focused on the development of these materials and synthesis of better crystals by working with chemistry students and postdoctoral fellows of MacDiarmid's group. Polyacetylene was a project, which grew from collaborative efforts.

The mercury-chain compound is a remarkable 1-D material and a very interesting physics subject itself [12,13]. The compound contains novel orthogonal interpenetrating 1-D mercury atom chains. The 1-D mercury chain was evidenced by a very large linear specific heat [14]. It was a beautiful, shiny, golden single crystal. Unfortunately, the compound was extremely air sensitive and studying it was very difficult. Even non-contact studies, such as optical properties, were difficult. Much effort was focused on designing an apparatus for transport measurements. We gained much experience in handling and measuring air sensitive samples inside a dry box. As a result, working with the air sensitive polyacetylene material was an easy task. In addition, we learned to use an uncommon gas, AsF_5 , which eventually became an important dopant for polyacetylene (Table 1).

Table 1
Electrical conductivity of some 1-D crystals and undoped polyacetylene

Materials	Conductivity (S/cm)	Remark
TTF-TCNQ	300	Quasi 1-D, single crystal
(SN) _x	3000	Fibrous, single crystal
Hg _{2.86} AsF ₆	10000	Atom chain, single crystal
(C ₂ H ₂) _n	0.00001	Complicated

Sulfur nitride polymer, (SN)_x, was actually the first metallic and superconducting polymer [15,16]. It is a novel inorganic polymeric single crystal with a lustrous golden color. MacDiarmid's group was able to grow large golden crystals. Despite the success of the chemistry program, which improved purity and grew the largest crystals in the world, the crystals were still less than 4 mm in length! The (SN)_x crystal was a highly oriented bundle of fibers, which presented a problem for DC transport measurements. The samples showed anisotropic conduction properties, but these properties may not be intrinsic to the polymer. It was difficult to determine the precise dimensions of the sample cross-section. Hence, we used smaller cross-sectional bundles for DC conductivity measurements, hoping that the conductivity would increase. Since the samples were soft and easy to bend, they could have had many defects that reduced the conductivity. This led me to studying their mechanical properties with Norman Brown using compression method [17]. In an attempt to increase the conductivity, I began to stretch (SN)_x along the fiber direction and measured the conductivity. The results were difficult to interpret because of large experimental uncertainties. The major source of the uncertainties was the dimension of the fibrous sample. To overcome these uncertainties, I designed a unique mechanical deformation and in situ four-probe DC conductivity measurement experiment for the (SN)_x fibers less than 4 mm long [18]. I had just written a paper and was enjoying my personal success with the in situ experiment when I paid attention to the more complicated polyacetylene polymer. Later, the measurement was redesigned for the doping of polyacetylene. The (SN)_x work brought us one step closer to the discovery of organic conducting polymers.

Polyacetylene came to us, with its silvery color, at the time when we were studying two golden crystals, (SN)_x and the mercury-chain compound [19,20]. Polyacetylene is one of the simplest conjugated polymers known. Initially, all of us naively described the polyacetylene polymer like (SN)_x. We changed the formula of polyacetylene from (C₂H₂)_n to (CH)_x in analogy to (SN)_x. However, the silvery film had a low conductivity and a sponge-like fibrous microstructure, which was immensely different from the beautiful 1-D single crystal materials we were studying at the time. These properties of organic polymers could never be a subject of interest for physicists with our project!

I was asked only to measure the conductivity of polyacetylene to satisfy our chemistry collaborators. It was hoped that the four-probe technique would help to show a little higher conductivity than what Shirakawa had reported [21]. Unfortunately, I found the conductivity of polyacetylene was very low, consistent with the reported values. However, the synthesis of polyacetylene by the Shirakawa method used very

high concentrations of catalyst. Although the films were washed many times, it was felt that the impurity level in the films might remain very high. Therefore, based on the experiences in preparing $(\text{SN})_x$, chemists hoped to improve significantly the synthetic method and make highly conducting polyacetylene.

In the preceding 2 years, I had studied many different materials. All of the high conducting materials were well-defined single crystals. No physicist would believe that an organic polymer could have some electrical conductivity, let alone high conductivity. I had got to be mad to continue on this research. Undoubtedly, it would be considered a mad thing to do, then!

3. Experimental design concept^{1,2}

Around June 1975, before Shirakawa came to Penn, I had read his preprint from MacDiarmid [21]. Later, after listening to his seminar to our group, I began a quick initial study. It became clear that the visually shining polyacetylene was completely different from $(\text{SN})_x$ and all other 1-D materials. The conductivity of $(\text{CH})_x$ was almost one billion times smaller than $(\text{SN})_x$. Besides, the microstructure of $(\text{CH})_x$ was so complicated that it could not be a subject of our interest for 1-D physics.

At the time, 1-D physics required materials with perfect crystal structures. I did not believe that an organic polymer could have a high conductivity. On the other hand, having been deeply involved in chemistry, I fully understood the importance of the studying of the conductivity of polyacetylene. I felt the urge to further pursuit with an exploring concept and idea as a physicist. Rather than simply rejecting polyacetylene, as I did with many earlier samples, I read in greater depth about the chemistry of polyacetylene. After months of hearing no progress in chemistry group, I decided to modify and prepare my own samples guided by my own conductivity experiment. Rather than focusing on impurities as the cause of low conductivity, I considered whether it was possible to improve the conductivity by modifying the polymer. I hoped to produce a material like simple organic salt TTF-I with an action like the intercalation of graphite.

As mentioned earlier, all charge transfer complexes, organic and inorganic crystals studied had 1-D structures. At the time, I was also working on a number of charge-transfer salts including TTF-Cl, TTF-I, TTF-Br, TCNQ-Li, TCNQ-K, TCNQ-Na, and TCNQ-Cs for applications as electrode materials. All these materials have good 1-D structures, yet only moderate conductivity. I also noticed that *cis*- $(\text{CH})_x$ resembled half of a benzene ring or part of a graphite sheet. For a while, I continued thinking about the possibility of making a simple polymer-salt complex that contained a structure of half of benzene rings.

¹The knowledge we have today about this field certainly is different from the time that I did the work. My limited knowledge of $(\text{CH})_x$ was learned from Shirakawa's preprint, his seminar, and many private discussions. I am responsible for all statement here.

²The experimental work described in this paper was done while the author was at the University of Pennsylvania. NIST is not liable for the uncertainty of the experimental data presented here.

Finally, I decided to make an imaginary complex salt, “(CH)-I” I proceeded to discuss the idea of polyacetylene and iodine reaction with Shirakawa. Our discussion led me to another aspect of Shirakawa’s research. Before coming to Penn, Shirakawa had started a new research project in which he utilized the high carbon content of $(\text{CH})_x$ to make graphite or carbon black. He used chlorine to remove the hydrogen from the CH chains. When reacting with chlorine, the polymeric $(\text{CH})_x$ lost its silvery shiny color and changed to pale white. The resulting white film had no conductivity. After hearing the chlorine story, my plan was almost cancelled because it indicated that the reaction would not produce a higher conductivity material. However, Shirakawa also mentioned a novel observation that the infrared spectra disappeared for a brief period of time when the $(\text{CH})_x$ film was first exposed to chlorine. After learning of this observation, I decided to continue my experiment to possibly find an intermediate state or to determine how the small conductivity was lost. For this purpose, a new experimental approach was required. I thought if I used the same design as the experiment of stretching $(\text{SN})_x$, then I might be able to stretch the polymer again.

As I described earlier, the electrical conductivity, mechanical strain and stress were measured simultaneously when I studied $(\text{SN})_x$ [22]. With the successes from the simple epoxy-string measurement technique, I continued to plan on applying the same measurement technique and hoped to determine the value of n in a $(\text{CH})_n$ -I complex if it could be formed. Shirakawa pointed out that iodine would be too weak to remove hydrogen from polyacetylene. We concluded that we needed to work with chlorine gas for conductivity measurement. However, I did not have chlorine in the lab. Rather than wait for the supply of chlorine gas, we decided to use liquid bromine.

The liquid bromine vaporizes in air and could react with the polyacetylene sample. Bromine, iodine and alkaline metals were being used daily in my projects of TTF and TCNQ systems. So for experimental convenience, the bromine-doping concept was established. Later, I learned from experts of BASF that the halogen reactions were well-known facts in the field and they would never dream to apply in this way.

4. Bromine doping experiment

The bromine doping of polyacetylene experiment was an in situ measurement, that is, “measurements” were made while the chemical reaction was in progress. The “experiment” was designed to carry out a controlled chemical reaction and an electrical conductivity measurement simultaneously. We planned to observe changes in the electrical conductivity of polyacetylene as electrons were removed from the polymer during a chemical reaction.

Fig. 2 shows the experimental setup of the bromine doping experiment performed by Chiang and Shirakawa in 1976 [23]. The four-probe electrical conductivity measurement setup was enclosed inside a glass flask. The electrical contacts were made through sealed electrical wires. The flask had an additional arm that allowed the injection of liquid bromine by a hypodermic needle through a rubber seal.

While the polymer was exposed to the vapor from one small drop of bromine, the conductivity of polyacetylene increased dramatically! The current increase in the first

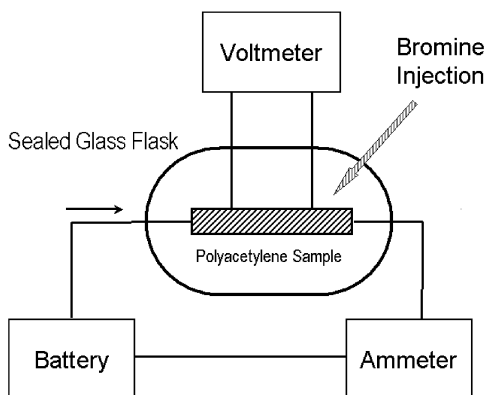


Fig. 2. The schematic of the first doping experiment of polyacetylene.

minute was so drastic that it burned out the current scale of a model K160 Keithley digital meter.³ This happened because I had expected the conductivity to remain low throughout the reaction. My reasoning was based on the polycrystalline nature of polyacetylene. If some small, higher conducting crystals were produced during the reaction; they would be imbedded in the complicated microstructure of the polymer. I would need the highest sensitivity of the instrument to detect changes in the sample resistance. Therefore, I had set the measurement meters at the most sensitive conditions. Furthermore, in order to apply a higher voltage from the battery, I had removed the protecting resistor in the system. I had not expected the conductivity to increase so rapidly that I would not have time to readjust the detection system [24].

As shown in Fig. 3, we observed the increase in conductivity of polyacetylene by over six orders in magnitude within minutes, followed by a slower rate of increase to a maximum. At the end, the conductivity actually began to decrease as I had anticipated [23]. The decrease is an important indicator for the onset of chemical reaction. To make even higher conducting sample, we planned to use less reactive iodine and prepared samples in chemistry laboratory.

We had produced a bromine-doped polyacetylene polymer, the world's first conducting synthetic organic polymer. By adding a small amount of bromine to an organic polymer, the polymer was transformed from an insulator to a metallic conductor. Amazingly, the sample survived after carrying a current that burned out the scale of a digital ammeter. A synthetic metal was discovered [25]. Conducting polymer was born!

The use of bromine was a wonderful and fortuitous choice. The reactivity of bromine and my available experimental design allowed the chemical reaction to proceed very slowly. The bromine reaction effect on the conductivity of $(\text{CH})_x$ could be clearly observed. In addition, the reaction was able to proceed to a maximum, which indicated the chemical bonding had begun. Thus, the results of my experimental attempt to

³ Certain materials and equipment identified in this manuscript are solely for specifying the experimental procedures and do not imply endorsement by NIST or that they are necessarily the best for these purposes.

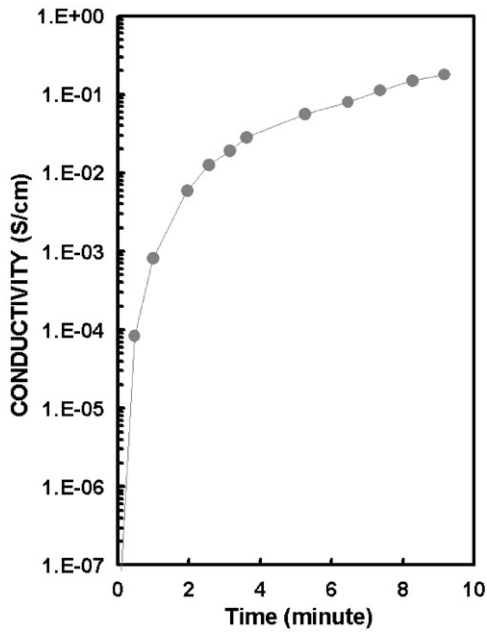


Fig. 3. First 10 min conductivity data after polyacetylene was exposed to bromine. The line is for the guide of reader's eyes.

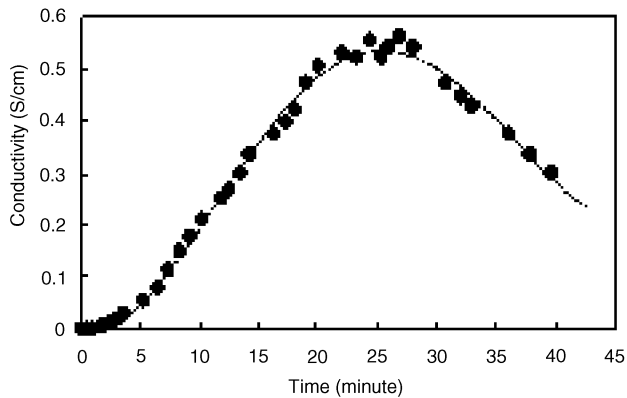


Fig. 4. The experimental data of the first doping experiment of polyacetylene. The line is for the guide of reader's eyes.

modify polyacetylene chemically turned out to be a beautiful doping experiment. The method was simple, yet vividly demonstrated amazing results in the first experiment (Fig. 4).

5. Development of polymeric semiconductor concept

The successful bromine doping of polyacetylene experiment was followed immediately by an active search for more dopants and related polymers. The less reactive halogens were the best candidates. Chemists tried to prepare doped polyacetylene with dopants such as iodine and AsF_5 . Others tried to extend the observations to other polymers, such as adding bromine to $(\text{SN})_x$. In fact, doping could be done simply during sample preparation [26]. Park took the responsibility of performing conductivity measurements to help chemists. He also started the first systematic study of the transport properties of doped polyacetylene.

The most important issue to me, then, was determining the physical origin of the phenomenon. There was much speculation about what had happened to the polymer. Our conductivity data strongly suggested that the effect could be related to the doping phenomena in semiconductors. The idea of doping organic semiconductors was well known and had been discussed in literature [27]. The other possible working model was the intercalation of graphite. To pursue the concept of doping, we needed additional evidence to show that polyacetylene is a semiconductor. Curtis R. Fincher was seeking proof from optical properties [2]. My priority was to find an n-type dopant [28]. Shek-Chung Gau and I tried to use sodium and lithium as n-type dopants. Gau successfully did the first n-type doping of polyacetylene with sodium ions deposited electrochemically. We also demonstrated that n- and p-type dopants could compensate for each other. A primitive P–N junction was constructed to demonstrate these semiconductor concepts. In addition, we showed that impurities in a polymer could also be compensated for by n-type dopants. Using the Mott model and far infrared spectra data, we were able to estimate a critical doping level on the order of 1%, which is much higher than that in conventional semiconductors. At this point, we had both optical data and electrical data to firmly support the concept of a polymeric semiconductor. We proposed a polymeric semiconductor model [2]. From that point on, polymers had a better physical basis to be considered as electronic materials. Recently, electronic industries have used the semiconductor concepts to make field effect devices, polymer chips and other molecular level electronics [29–31].

Since the method of doping had been demonstrated in this first experiment, the verification of the concept of doping became very clear and very easy to repeat. It has been applied toward finding other conducting polymers. In 1980, Baughman discovered a second metallic organic polymer [32]. And since, more conducting polymers have been identified. The novelty in the properties of polyacetylene soon became a new branch of organic polymer science. It was labeled as the fourth generation of polymer materials in the Nobel Symposium of 1993 [33,34].

6. Conducting polymers as models for quantum theories

Since the beginning, the complexity and the potential of polyacetylene had been repeatedly underestimated. While the molecular formula may be very simple,

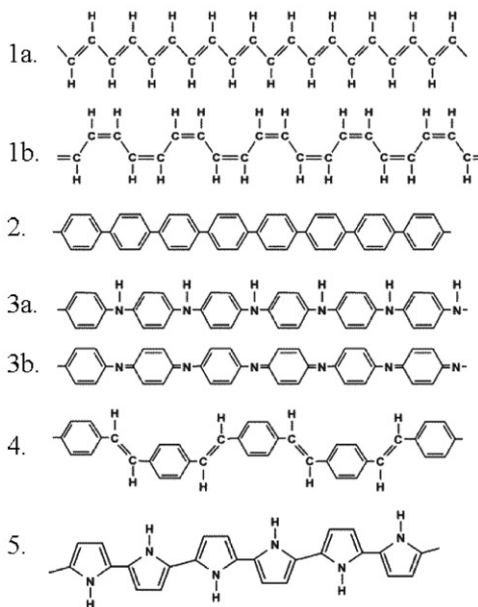


Fig. 5. Some conducting polymers: (1) polyacetylene, (2) poly-*p*-phenylene, (3) polyaniline, (4) polyphenylene vinylene, (5) polypyrrole.

polyacetylene provides sufficient complexity to be a model system, not only for polymer science, but also for quantum phenomena.

While the concept of a semiconductor was being developed for doped bulk polyacetylene, the fundamentals of the 1-D polymer nature were not clearly explored. Electrical transport along a molecular-chain is a fundamental conceptual problem. In 1979, Wu et al. (SSH model) used a soliton concept to explain the charge movements in the backbone of polyacetylene chain [35]. Solitons in polyacetylene are more complicated and interesting when the model includes additional properties of electrons such as spin. Since then, there has been much theoretical interest in solitons in polyacetylene. I believe that both quantum physics and quantum chemistry will continue to use polyacetylene as a model system to develop new concepts.

On the other hand, conducting polymers have developed from polyacetylene into a new generation of polymers (Fig. 5). The strong coupling between electrons and the molecular lattice provided many opportunities to develop new ideas for quantum theories. Theoretical predictions based on these theories can be tested not only in simple linear polyacetylene, but also in more complicated conducting polymers. Computer modeling has also been helpful. Computers have been used to simulate solitons in polyacetylene and also to visualize other quantum behavior in conducting polymers. Since there are already many conducting polymers and many chemical variations of a given polymer system, these conducting polymers provide vast test beds for quantum theoretical experiments. It was indeed unexpected that a simple conductivity experiment would have such a substantial impact on science.

7. Conclusion

The importance of the bromine doping of polyacetylene experiment is not only the discovery of the first conducting synthetic organic polymer, but also a verification of the doping concept for organic polymers. Doping was the key to studying the physics and chemistry of conducting polymers. Since the seminal doping of polyacetylene experiment, we have integrated the electronic physics into organic polymer chemistry and opened the door to a new generation of polymer science with the establishment of new industries. The effort to understand how electrons move in polyacetylenes continues. Polyacetylene remains a unique model polymer system for quantum physics, quantum polymer and organic polymer chemistry. However, there are many other new conducting polymers and, among those, many have better long-term stability and stronger potential for electronic applications. Due to the complexity of these polymer systems, new theoretical approaches with computational assistance will be needed. The understanding of these model polymer systems is not only of fundamental interest but also of great importance to industrial applications in the 21st century.

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