Chemical Education International, Vol. 3, Issue 1, AN-5, Published July 18, 2002

To the youth of the World who aspire to a career in chemistry

Message from Nobel Laureates to Young People (3)

Professor Hideki Shirakawa, 2000 Nobel Prize in Chemistry

This interview with Prof. Hideki Shirakawa (pictured left) by Prof Y. Takeuchi (right) and Prof. M.M. Ito was carried out at Prof. Shirakawa's office, in the General Council for Science and Technology in March, 2002.

The Committee on Chemistry Education (CCE) of IUPAC edits and issues an electronic journal, *Chemical Education International* (CEI). For the benefit of those who aspire to a career in chemistry, each issue contains a short interview with a Nobel Laureate in chemistry. In this way, we hope to provide a profile of those who are at the forefront of chemistry and give aspiring chemists role models for their future endeavors.

The intended readership of the interviews published in CEI are senior high school students who are at a point in their life where they must make decisions about their future career, or first year university students in science and technology who must begin to specialize in a chosen field of study.

We are extremely grateful to Prof. Shirakawa for his appreciation of the idea of this series of interviews and for kindly sparing us his precious time for the interview.

(S): Prof. Hideki Shirakawa
(CEI): Yoshito Takeuchi (Member, CCE), Masato M. Ito (Editor, CEI)

CEI: Professor Shirakawa, we would like to express our sincere thanks to you for sparing us your time for this interview. We understand that you are extremely busy.

The first thing we would like to ask you is how and when you became interested in science, and in chemistry in particular, and made up your mind to become a chemist.

S: I was asked much the same question several times when I received the Nobel Prize. In fact I have given several different replies, and now I feel that there is not a single definite answer. I have but a dim remembrance of those early days. When I was a junior high school student, I played outdoors most of the time; I collected insect specimens and gathered flowers and herbs. In a word, I was a boy who loved Nature. Perhaps, by having such a way of life, I gradually began to be impressed by the wonders of Nature. This feeling, to explore more deeply the wonders of Nature, must have been my motivation to become a scientist.

CEI: We learned from a newspaper article that you contributed an essay to a collection put together by students of your year in commemoration of your graduation from junior high school. In that essay you explained that your intention was to become a scientist, adding that your interest was in plastics. Does that mean that you were interested not only in Nature but also in technology?

S: Certainly, plastics are artificial and not a part of Nature. A combination of plastics and insects may seem a little unusual. However, plastic was a new invention which appeared when I was a child, and also it was very appealing. Most popular plastics at that time were polyvinyl chloride; nylon was also getting popular. My mother used to wrap my lunchbox with a Japanese wrapping cloth made of poly(vinyl chloride) (PVC) which was a popular item at that time. This Japanese wrapping cloth made of PVC was soft and flexible when warm, but it became stiff when the temperature dropped. When the lunchbox cooled down, the wrapping cloth tended to stiffen, keeping the shape of the lunch box. I thought it was rather clumsy and felt that there remained room for improvement of PVC.

CEI: Please tell us about the time when you were of senior high school age. Were you still able to indulge everyday in your love of Nature?

S: Well, there might have been some changes as compared with my junior high school days. I got involved in assembling a complete radio unit from its individual parts using just a soldering iron and a screw driver. It was a time when electronics engineering was developing rapidly, and the items I used underwent quantum changes; from the vacuum tube to the diode, and from there to the transistor. It was great fun. Throughout my junior and senior high school days, it can be said that I was interested in three fields: using today's vocabulary they were life sciences or biotechnology, polymer chemistry, and electronics. Perhaps I felt that I would be happy if I could major in one of these.

CEI: We wonder if, during your junior and senior high school days, there was a teacher who

influenced you in your choice of science for your future career.
S: Yes indeed; a female teacher. She taught science, though she was not in charge of our class. I was a member of my school's Science Club, which was an extracurricular activity in which we could participate. The school was kind enough to open the science laboratory for the Club so that we could do many interesting experiments which were beyond the boundaries of the curriculum. My teacher sometimes invited us to her house and gave us interesting talks. I can say that she fostered my interest in science and in chemistry in particular.

CEI: Had you already made up your mind to major in polymer chemistry when you entered the university?

S: Not necessarily. I entered Tokyo Institute of Technology (TIT), which at that time had only one faculty, the Faculty of Science and Engineering. We did not belong to any single department when we entered the university. The rule was that, on entering third year, we were to choose a department that specialized in the research area we wished to study. There was no possibility left for me to be a biologist, so I had to choose from one of two remaining options: polymer science or electronics. Eventually I chose polymer science.

CEI: Prof. Shirakawa, would you tell us a little about your college life, including how you came to make the choice of doing research on polymer science?

S: Well, I was very happy when I entered the University now that I could study my favorite chemistry as much as I liked. At the same time my love of Nature, which stemmed back to my childhood, was growing, and in making up my mind to pursue mountaineering in earnest, I joined the University Mountaineering Club. This cost me a lot of money in travel expenses etc, so I did some tutoring to earn some money. The trouble was that this took up much of my time. Then, a friend of mine brought some good news. According to him, one of the professors who studied the physical properties of polymers was recruiting a laboratory assistant. I jumped at this possibility. I really needed the money, but this was not the only positive; even if I was only a mere assistant, it was really interesting for me to be able to do experiments at a research level.

CEI: What kind of experiments did you do as an assistant?

S: My employer was Dr. Ichitaro Uematsu who was at the time an instructor who belonged to the laboratory of Prof. Kisou Kanamaru, a physical chemist specializing in polymers. Dr. Uematsu was involved in measuring the physical properties of a solid material which was prepared from stereoregular polypropylene, which was newly prepared on trial by high temperature/high pressure molding. My job was to prepare specimens whose physical properties were to be measured.

CEI: How did you like the job?

S: The procedure itself was simple. I just measured out a certain amount of powdered polypropylene, put this into a medal molder, heated it up to a predetermined temperature and molded it by applying high pressure. It was stimulating, however, to be surrounded by many sophisticated pieces of apparatus in the laboratory. I liked the atmosphere of a research laboratory, which was something that could not be experienced in the undergraduate student laboratories.

CEI: That experience was before you started your experiments for the graduation thesis?

S: Yes, indeed. At the latter stage of the 3rd year, the largest concern for students was the choice of the professor who would supervise their studies for the graduation thesis. Soon after I entered TIT, I became interested in studying the synthesis of polymers, and I wanted to be supervised by a particular professor in this field, namely by Professor Shu Kambara. At that time there was a regulation that the maximum number of students that could be supervised in the graduation work by one professor should be six. Unfortunately more than six students applied for Prof. Kambara's laboratory. We students discussed, and decided that the selection should be made by tossing a coin. Regrettably enough, I was one who lost the contest.

CEI: Life is hard, indeed! How did you get over the problem?

S: Other laboratories specicalizing the synthesis of polymers had already filled their student quotas, and the only remaining possibility was to belong to Prof. Kanamaru's laboratory. Prof. Kanamaru was a physical chemist of polymers, and was well known as the most severe professor in the Department. There was no room for choice, and I became a member of the Kanamaru laboratory. By coincidence, Dr. Uematsu directly supervised me during the graduation study. At the beginning of my graduation study, it was difficult for me to get used to studying the physical properties of polymers, and sometimes I failed to find the motivation to study hard. But gradually I became interested in the physical chemistry of polymers and perhaps even began to appreciate it, at least to some extent.

CEI: So you completed your graduation study and then entered into the Graduate School. In Japan it is usual for a graduate student to be in the same laboratory where one completes the graduation study.

S: This was not the case with me. Although I did not realize the situation when I started my graduation study, Prof. Kanamaru was leaving TIT because of age limit regulations at the same time as I completed my graduation study. So if I wanted to enroll as a graduate student, I had to find another supervisor. Prof. Kanamaru seemed to understand the situation, and he also knew that I wanted to be a synthetic polymer chemist. One day Prof. Kanamaru advised me to call on Prof. Kambara to pay my respects, and I did so. Later it turned out that that visit was nothing but an interview as a part of the entrance examination for the Graduate School. So, from the following April I became a member of the Kambara Laboratory, and I was very happy to finally become a synthetic polymer chemist. One year in the physical chemistry laboratory may be regarded as a kind of diversion; however that single year studying the physical chemistry of polymers seemed to widen my scope in research. Success in the synthesis of a compound is not the end of the research. The structural study of synthesized polymers, for instance the relation between the structure of the polymer and its physical properties, would become a new target. Thus, this experience in physical chemistry would prove to be very useful later in my career, particularly when I was studying polyacetylene.

CEI: Please proceed then to the crucial part; your progress starting from the beginning of your career to your ultimate success in being awarded the Nobel Prize.

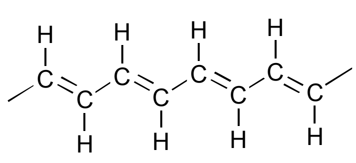
S: The theme of my research was to clarify the mechanism of the reaction of polymerization of acetylene to polyacetylene. The polymerization reactions are sometimes tricky. A minor difference in reaction conditions sometimes produces a considerably different product. The reaction requires the use of a catalyst, and so we employed a catalyst called a Ziegler-Natta catalyst, $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$.

CEI: It was said that you employed too much catalyst. Was this the case? This episode is rather popular and has been quoted in many articles.

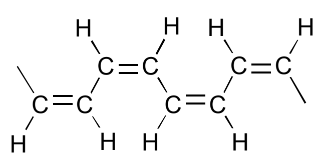
S: This actually happened to one of my research associates who wanted to gain some experience in the synthesis of polyacetylene. I taught him the procedure, but by mistake he used too much catalyst. The required concentration of the catalyst is normally in the order of mmol/liter, but he used the catalyst in a concentration as high as mol/liter; 1000 times more concentrated! Previously we obtained only a pulverulent body. That time we obtained a film. We guessed that the reaction took place too rapidly and made a film on the surface of the catalyst solution because the quantity of the catalyst was excessive. Anyway, a black film was obtained.

CEI: Serendipity has often been referred to in connection with your discovery. When you saw the film for the first time, did some anticipation of a great discovery flash through your mind?

S: No, not at all. At least not at that time. I vividly remember, however, that obtaining the film pleased me very much because I realized that now I could determine the infrared spectra of the polymer. At that time we were investigating the mechanism of the polymerization reaction of acetylene, and I wanted to examine the structure of the double bond in the polymer. In polyacetylenes, the single bond and the double bond (note: originally triple bond) are linked alternatively in the polyacetylene. There are two ways of linking two double bonds: as the s-*trans* conformation and in the s-*cis* confirmation. In order to know which form is involved, determination can be made of the infrared spectrum of the polymer as a thin film. So far, we had failed to obtain a good film. So we shouted with excitement at this breakthrough in our research. We were a bit worried because the film was too black. We laminated the film and determined its infrared spectrum. There was no problem and we could measure the spectrum. Since the spectrum looked rather simple, I intended to make a full theoretical interpretation of all absorptions.



s-*trans* form 1



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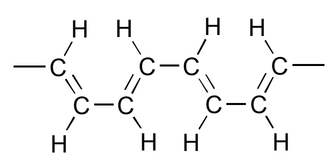

s-*cis* form

CEI: It is rather surprising to hear the story. To a polymer chemist such a theoretical problem of physical chemistry must have been rather tough.

S: Perhaps I am the kind of person who would never be satisfied unless I tried something thoroughly by myself. In addition, I had some previous experience. During the preparation of the thesis for my Ph. D., it became necessary to analyze the infrared spectra of compounds I had prepared in order to elucidate their structure. Accompanied by Dr. Noboru Yamazaki, an instructor at that time (now he is Professor Emeritus, Tokyo Institute of Technology), I visited Prof. Takehiko Shimanouchi at the Department of Chemistry, Faculty of Science, the University of Tokyo, a leading scientist in the field of infrared spectroscopy. Prof. Shimanouchi kindly taught me the technique of vibration spectroscopy and I could see for myself how interesting this methodology would be to use.

I thought I should try by myself to carry out a full theoretical interpretation of all absorptions, given that I did have some experience in the area. I had to write a computer program necessary for the calculations. It took many, many days. It seems that in those days I had more time for research as I was an instructor and had fewer responsibilities in relation to teaching and administration. Thankfully, I was successful in being able to interpret theoretically all the absorptions. Later, Prof. Mitsuo Tasumi, Prof. Shimanouchi's successor and a leading scientist in infrared spectroscopy, praised me, saying "you have done a good job!"

CEI: How does the story go after that?

S: Now that it was a much easier task to prepare a thin film and determine its infrared spectrum, we polymerized acetylenes in which deuterium or C-13 isotope were incorporated. By repeating measurements and analyses, we found that in this polymerization reaction, the triple bond in acetylene was cleaved to form a *cis*-double bond in the polymer.

CEI: Could you feel something that would foretell your subsequent great discovery?

S: Well, at that time I rather simply thought that I could finish that research successfully now that the structure of the polymers was elucidated. If I think back to those days, I could say that my goal was to attempt to expand the scope of the research.

CEI: What did these attempts include?

S: These were not necessarily unusual in their approach. It seemed interesting to me, and probably to other chemists, to attempt to add chlorine and bromine to the double bond of the polymers. We thought that if we could eliminate the hydrogen halide by heating, we would be able to obtain graphite since the remaining structure should be carbon only. Regrettably, that attempt was not successful.

We measured infrared spectra of the reaction product between the polymer and the halogen. To our surprise, no signal was observed because there was very intense absorption in all the regions measured. (note : Virtually no infrared light transmitted through the film. It should be pointed out that infrared light does not transmit through a metallic film.) Anticipating that the film might have some electric conductivity, we checked this property with the aid of a small hand-held voltmeter to measure resistance. The needle did not move at all. With the benefit of hindsight, I should have used a much more sensitive instrument capable of measuring electric resistance in the order of a gigaohm.

There was another problem. Three absorption signals could not be interpreted properly when we measured the infrared spectrum of the product. Later we learned about the effect of doping, and it became possible to interpret the three signals; which were due to the carbocation (positive ion of carbon generated from polyacetylene by removal of an electron) formed by the addition of bromine. It was possible to clarify the origin of the electrical conductivity in this way.

CEI: Did you go to United States around that time?

S: Yes, it was at that time that I went to the United States I thought at that time that we had come to the end of the investigation, and so it would be timely and stimulating to go, when I received an invitation from there. When I arrived at the University of Pennsylvania, I explained to Professors MacDiarmid and Heeger the story to that point in time. They suggested we should try to measure the electric resistance of the film while exposing it to a halogen vapor. Upon attempting this, to our surprise, the needle underwent a large deflection.
Why was I able to obtain a very good result in the long run? Perhaps it is because I always try keeping to and concentrating on the one thing. The basis of my research has always been the elucidation of the reaction mechanism of polymerization. The discovery of conducting polyacetylene may be regarded as a logical outcome of long-term perseverance with this research.

CEI: Thank you very much for your very interesting and stimulating talk.

Finally, may we ask you to offer a word or two to young people all over the world who are interested in chemistry?

S: I simply hope that they will hold communion with Nature, and will love Nature. Everything will begin from this love of Nature. Recently, “virtual” things have become very popular. I believe, however, that opportunities to touch real materials for yourself are very important. These objects should not necessarily be limited to specific materials. Living things, as well as machines and electronic circuitry, all of these, are things to be touched by your own hands.

CEI: Thank you very much indeed.

Information:
Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa were awarded the Nobel Prize in Chemistry in 2000 for showing how plastic can be made to conduct electric current. This surprising discovery has radically altered our view of plastic as a material. Conductive polymers today constitute a growing research field of great significance to chemists and physicists alike.

Professor Shirakawa was a faculty member of Institute of Materials Science, University of Tsukuba for more than 20 years. He explored an unprecedented new area of polymer science by transforming an insulating polyacetylene to an electrically conducting one. This achievement was often said to be triggered by a mistake when he was a research associate in the Chemical

Resources Laboratory at Tokyo Institute of Technology—a thousandfold too much catalyst was added during the synthesis of a polymer, resulting in a beautiful silvery film that possessed many properties superior to metals

When Professor Alan MacDiarmid heard about the film synthesized by Dr. Shirakawa, he invited him to become a post-doctoral fellow the University of Pennsylvania in Philadelphia, USA. They worked together with Dr. Alan Heeger in order to understand the mechanisms of the appearance of conductivity in insulating polymers. They finally came to the conclusion that it is possible to introduce carriers in polymers by doping: modifying polyacetylene by oxidation with halogen vapor.

In 1977, Shirakawa, Heeger, MacDiarmid, and others published their discoveries in "Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene $(CH)_n$" in the scientific journals. The discovery was considered a major breakthrough in the field of polymer science. Since then, the field has grown greatly and has also led to many new present-day applications.

For more info, visit the Nobel website
<http://www.nobel.se/chemistry/laureates/2000/>