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Historical Article

Path to the Synthesis of Polyacetylene Films with Metallic Luster: In Response to Rasmussen's Article

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Abstract. The 2000 Nobel Prize in Chemistry was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa "for the discovery and development of conductive polymers." Unlike metals, organic polymers or plastics do not conduct electricity. The three laureates found that polyacetylene can be doped on a film, which was initially synthesized by Shirakawa following a failed experimental trial by a Korean scientist, Hyung Chick Pyun. Later, Pyun insisted that he was the discoverer of polyacetylene films with silvery sheen. This note sheds light on the true history of the synthesis of polyacetylene films.

Keywords: polyacetylene film, Nobel Prize 2000, polymerization, Ziegler-Natta catalyst, fortuitous error, serendipity.

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INTRODUCTION

On October 10, 2000, the Royal Swedish Academy of Sciences announced that plastic can indeed, under certain circumstances, be made to behave like a metal – a discovery for which Professor Alan J. Heeger, Professor Alan G. MacDiarmid, and I, Hideki Shirakawa, received the Nobel Prize in Chemistry in 2000. This public announcement was followed by a story about the initial discovery of polyacetylene films: "once – by mistake – a thousand-fold too much catalyst was added."[1] Professor Bengt Nordén, chairman of the Nobel Committee for Chemistry, also used the term "mistake" in the prize announcement.[2] Commenting on a trigger of our achievements, he stated that the road to the discovery had started in 1967, when Shirakawa found that "by mistake" "a student [Pyun] had taken a thousand times too much catalyst" when polymerizing acetylene gas to make something called polyacetylene. At the beginning of my Nobel lecture entitled "The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers," given on December 8, 2000 at Aula Magna, Stockholm University, I acknowledged Dr. Hyung Chick Pyun (1926–2018), among other important contributors, for sharing a "fortuitous error" that motivated further work toward the discovery of polyacetylene films.[6]

In his recent article,[3] Professor Seth C. Rasmussen discussed the event leading to the discovery of polyacetylene films by fortuitous error, based mainly on a "working English translation" of Pyun's account written in Korean. Carefully reading Pyun's two original documents written in 2002 and 2013 (through Japanese translation), [4,5] I found numerous factual errors, distortions, and assumptions. In this note, I would like to correct them and present what happened regarding the synthesis of polyacetylene films with metallic luster, based on my memory and my laboratory notebooks.

PYUN'S EXPERIMENTAL TRIAL

In his article,[3] Rasmussen asserts that the core of the discovery of polyacetylene films resulted from the performance of both myself and Pyun, a scientist visiting Japan from South Korea, quoting the "fortuitous error" that I mentioned in the Nobel Prize lecture[6] and is described in the *Les Prix Nobel: The Nobel Prizes 2000* and its reprints.[7] This description is acceptable if the core of the discovery is interpreted as an important trigger for the synthesis of the metallic polyacetylene films. I repeat that the occurrence of the "fortuitous error" was a trigger for the subsequent synthesis of metallic polyacetylene films but not the successful synthesis itself.

However, Rasmussen does not present the discovery in this manner. Most descriptions in the article are based on Pyun's accounts[5] and third-party records, such as press reports by the Nobel Foundation and Royal Swedish Academy of Sciences at the time of the Nobel Prize announcement and award. The article lacks any of my own input, except for my printed Nobel Lecture and scientific papers. As a result, it depicts a biased account that contains serious errors.

In his document,[5] Pyun insists that he was an actual discoverer of polyacetylene films and not Shirakawa. He states, "A good result will be anticipated with the stirring speed reducing as much as possible during the polymerization process. One day, when I tried an experiment on acetylene polymerization with this idea, it happened that a stirring motor stopped suddenly, presumably due to setting the rotation speed too slow. I was very panicked at first, but with careful inspection of the reaction flask, I found that a silvery membrane had formed on a surface of the catalyst solution, to my surprise." He adds, "On this day, for some reason, the then assistant [Research Associate] Shirakawa was not in the laboratory."

These descriptions contain the two following factual errors: 1) "a silvery membrane had formed" and 2) "On this day, for some reason, the then assistant Shirakawa was not in the laboratory." The exact date of "this day" is not clear because the trial run was not recorded on my laboratory notebook as the trial run was not mine. According to my memory, what happened on "this day" is as follows. One of Pyun's two academic supervisors was Professor Yoneho Tabata (1928–2019) of Tokyo University, Faculty of Nuclear Engineering. Due to Tabata's prolonged trip to the United States, Pyun could not perform any primary research during the period, which he described as his free time. The "this day" that Pyun refers to likely occurred in August 1967 considering these circumstances. One day, Pyun came to my office and asked to try acetylene polymerization as he was interested in acetylene polymerization and polyacetylene. I provided an experimental protocol for performing acetylene polymerization as a trial experiment at my research laboratory (room number 404) at the Research Laboratory for Resources Utilization, Tokyo Institute of Technology.

As mentioned above, because this trial run was not my own research work, any relevant data, including the date and conditions for the polymerization, were not recorded in my laboratory notebook. I gave Pyun normal guidelines for the polymerization process, such as a solvent, species of the catalyst components, and their concentrations. I expected that the product would be in a powdered form as usual. After briefly instructing Pyun on the handling of lab wares and equipment, I returned to my office, a preparatory room next to the No. 404 lab.

The No. 404 lab, which I used as my own lab, was designed by Professor Sakuji Ikeda (1920–1984) as a tracer experiment for handling radioisotopes. When you enter the room from the passageway, you enter my office, a small preparatory room that students and I used as a study room. The No. 404 lab is accessible from the preparatory room. According to the lab rule, study desks were not placed in the No. 404 lab, so researchers and students spent their time in the preparatory room and only entered the lab to perform experimental work. At that time, the lab was freely open only to graduate and undergraduate students who were under my guidance. Therefore, Pyun could not carry out experiments for acetylene polymerization in my absence.

On that day, after some time, Pyun came to my office to say that the polymerization had stopped. As this experiment should have been easy to perform, I was puzzled by what could have gone wrong. I checked the apparatus carefully with him, the occurrence being inconceivable. I then found that the magnetic stirrer had stopped and, after watching for a while, the mercury manometer, which indicates the acetylene's pressure, did not decrease.

We confirmed that the acetylene monomer had not polymerized, meaning that the reaction had not taken place. The reaction flask was, therefore, detached from the vacuum line, and we looked carefully inside the flask. If the reaction had proceeded normally, we would have observed a powdery product, but instead, we found that a black flappy or spongy matter had formed on the surface of the catalyst solution. The product, which was extracted using a pair of tweezers, was like a black rag. It was not "the silvery membrane" that Pyun described. If the reaction had proceeded normally, the product would have been a powder. The trial was clearly a failure, and Pyun was in agreement. I remember the result of the run clearly, even now.

SUCCESSFUL SYNTHESIS OF POLYACETYLENE FILM WITH METALLIC LUSTER

I still do not fully understand why Pyun's trial run failed. However, because the product was not a powder but a quite different form, I thought that it might be possible to synthesize polyacetylene into a thin film by changing the polymerization conditions. I was also strongly motivated to clarify the cause of the failure. Immediately after Pyun's failure, I started a series of polymerization experiments with graduate students under my guidance by changing the concentration of the catalysts and other conditions. Pyun was not involved in this series of experiments.

Within one to two weeks, my students and I could successfully synthesize films of polyacetylene that were self-standing and could be easily handled by increasing the concentration of the catalysts by 1,000 or more times the normal condition. The self-standing film was such that it did not need lining. By improving the polymerization conditions and methods, we also found that a thin film with a silvery metallic sheen could be obtained by polymerizing acetylene on the glass surface of a reaction flask when a concentrated catalyst solution was applied to the glass surface of the flask. The side stuck to the glass surface of the reaction flask displayed a metallic luster, while the other side facing the acetylene gas took on a black color and a matted texture.

The difference in the appearance of the two sides was clarified by observations made through transmission and scanning electron microscopic observations. Scanning electron microscopic observations of a surface of the polyacetylene film revealed that the film was composed of entangled fiber-like long microcrystals (fibrils) with a diameter of ca. 200 Å. The morphology of an extremely thin film with several micrometers in thickness observed by a transmission electron microscope was also found to have the same microstructure. From these observations, it was clear that the whole film was composed of entangled fibrils.

Because these films are composed of loosely entangled fibrils and inevitably lead to low bulk density, the incident light on the surface of the fibrils scattered randomly. Consequently, both surfaces of these films appear matted black due to random reflections. The films formed on an interfacial surface of vapor/liquid (catalyst solution) reflect the trend strongly. Therefore, both sides of such films are the same matted black and show no metallic silverly luster. However, on the side of the film that touches the glass wall of the reaction flask applied by the catalyst layer, the growing fibrils are forced onto the glass wall during the polymerization reaction. Thus, the surface of the film facing the glass wall becomes flat with a higher density than the other surface. When incident light shines on this side of the film, the light reflects in the same direction, and the surface presents a silverly metallic sheen. Following this process, *cis*-polyacetylene synthesized at a very low temperature (as low as -78 degrees centigrade) has a copper-like reflection color. All double bonds in the *cis*-polyacetylene have a *cis* form of geometric isomeric double bonds through the conjugated molecular chain. The *cis* form of polyacetylene results in a reflection spectrum shift to higher energy than that of *trans* form, because the bandgap of the *cis* form is larger than the *trans* form, which has a silvery sheen.

THE FORTUITOUS ERROR

I referred to Pyun's trial run as a "fortuitous error" because, as a result of that failure, a black flappy or spongy matter was formed instead of the powdery product that should have formed under normal conditions. This accident became a trigger for the successful synthesis of films with a metallic sheen. Immediately after Pyun's trial run, while continuing experimental trials to clarify the reason for the failure, we found that films formed on the surface of a much more concentrated catalyst solution – a thousand times more – instead of the traditional mmol/liter order of concentration. Using these films as a specimen for infrared spectroscopy, Raman scattering spectroscopy, X-ray diffraction, and normal vibrational analysis, among other tests, our primary intention to clarify the mechanism of acetylene polymerization reactions with Ziegler-Natta catalysts was accomplished within an unexpectedly short period (just less than two years). Because the unforeseen failure of Pyun's test run had triggered the successful syn-

theses of polyacetylene films, and I thought of this fortuitous error as a result of "serendipity," I introduced this occurrence as a typical example of fortuitous error at domestic academic meetings and workshops, as well as international conferences and institutions. However, our polyacetylene study, published in academic journals internationally or domestically received little attention at the time.[8]

As context, it may be pointed out that research activities on organic and polymeric semiconductors declined globally after the 1960s, after being very active from the early 1950s to the 1960s. In particular, Natta et al. succeeded in synthesizing polyacetylene by the polymerization of acetylene using so-called Ziegler-Natta catalysts in 1958.[9] The product was an intractable black powder used for the elucidation of various chemical and physical properties of polyacetylene.

Several years after our successful synthesis of polyacetylene films, I was invited to conduct collaborative research with MacDiarmid, Department of Chemistry, University of Pennsylvania. MacDiarmid had been intrigued by the silvery metallic luster of the polyacetylene film (with a silvery sheen) when he visited and gave a seminar at the Tokyo Institute of Technology in 1975. In September 1976, we began joint research on the chemical and physical properties of polyacetylene with Heeger, a solid-state physicist of the Physics Department at the University of Pennsylvania. On November 23, 1976, when we tried to add a small amount of bromine to a piece of polyacetylene film, we found, to our surprise, that the electrical conductivity of the polyacetylene film increased a hundred thousand times. This epoch-making result was reported at an international conference held in New York City in May 1977, and we followed up with two consecutive communications.[11] The result initiated considerable interest among many researchers around the world. The newborn field was named conductive (conducting) polymers and synthetic metals, and a new journal entitled *Synthetic Metals* was born in October 1979. With increasing research activity in this field, the episode of the successful synthesis of the silvery films of polyacetylene was shared widely among researchers.

When I delivered talks at academic meetings and lectures at universities and institutions, I referred to the episode as a typical serendipitous event. As Pyun's trial run was unsuccessful, I did not mention his name in view of his honor. To avoid embarrassing him, I referred to him in evasive terms, such as "a foreign researcher," "a visiting researcher," and sometimes simply "a researcher," "a student," or "a graduate student." I now regret not mentioning his name. The episode resulted in gossip among researchers about how this "foreign researcher" did not understand Japanese and could not follow directions. I am very sorry that Pyun had to endure this.

PYUN'S RESEARCH SUBJECT

I do not remember the exact date of Pyun's visit as a foreign researcher to the lab of Ikeda, Division of Macromolecular Materials, Research Laboratories for Resources Utilization, Tokyo Institute of Technology, as I have no written record of his visit. However, his visit occurred one year after I started my post as a research associate in the division in April 1966.

According to Pyun's document,[5] he visited Japan in May 1967 and returned to Korea in March 1968. I am unsure when I first met Pyun in person or at laboratory meeting. However, I have a vivid memory of how he first introduced himself as he told me that his family name was "HEN 邊" – that is, the side (hen) of a triangle. I knew that he grew up in the era of Japanese colonization, and he was forced to be educated in Japanese. Later, he struggled through the Korean War (1950–1953). However, he never communicated about his difficult life in Korea. He was always easy to work with and he never expressed any inability to understand Japanese.

As I had only recently joined the lab, I was not informed about how and why Pyun had joined the Ikeda lab as a foreign associate. However, I knew vaguely that his research purpose was the clarification of certain polymerization mechanisms using isotopes as one of his supervisors was Tabata, Department of Atomic Engineering, University of Tokyo. I found out only recently that, as mentioned above, Pyun's research in Tabata's lab was interrupted for some time because Tabata's return from his visit to the United States was delayed. During this period, Pyun visited my lab to conduct the trial run on the polymerization of acetylene, feeling that he had free time to work on subjects outside his main focus during Tabata's absence.

According to Rasmussen's article and Pyun's documents, Pyun's research subject was the copolymerization of ethylene and tetrafluoroethylene and the analysis of its molecular structure by infrared spectroscopy. There was no discussion at the lab meeting that Pyun had joined the research group to study acetylene polymerization. At that time, I was unaware of whether Ikeda was unwilling for Pyun to deviate from his primary subject of interest, and I did not know that Tabata's return had been delayed. However, I accepted his offer to perform a trial run without hesitation. It was very clear that the

trial run was an experience test for him, and he did not undertake it as a research collaborator in the ongoing work in Ikeda's lab.

It turns out that, as described below, Pyun conducted two or more related tests after this initial test. However, I am sure that his additional experiments were performed after our group's establishment of the synthesis of self-standing polyacetylene films with a silvery luster. I was hired as a research associate in the Division of Macromolecular Materials, Research Laboratory for Resources Utilization, Tokyo Institute of Technology, on April 1, 1966, and I continued my research work in the same lab for five years during my graduate student days. At that time, Dr. Shu Kambara (1906-1999) was the professor, and Ikeda was the associate professor of the division. Soon after, Kambara retired on March 31, 1967, and subsequently, Ikeda was promoted to the position of professor on August 1, 1967.

Ikeda had been engaged in research on the vulcanizing mechanism of natural and synthetic rubber using radio isotopes from his associate professor days. After becoming professor of the division, he then continued to work on the mechanism of ethylene and acetylene polymerization with Ziegler-Natta catalysts using tracer techniques. When I became a research associate, Ikeda was very close to his work on ethylene polymerization and had just started research on acetylene polymerization, and I participated in this work.

When Pyun came to my lab to request permission to perform a trial run on acetylene polymerization, his intention, I later realized, was quite different from what he originally stated. When I was a graduate student, Dr. Masahiro Hatano (1930–, who later moved to the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University) was a research associate under Kambara and undertook research on the polymerization of compounds with carbon-carbon and carbon-nitrogen triple bonds for the synthesis of polymer semiconductors. The Kambara and Ikeda Lab has a long history of research on acetylene polymerization and polyacetylene, and Hatano developed acetylene polymerization for many years and accumulated relevant techniques.

Pyun was interested in related research work on semiconducting polymers, which he sought to learn more about by joining Ikeda's group. In fact, he wrote in his document[5] that "I thought of spending my unexpected free time carrying out acetylene polymerization as I learned from various reports in the lab that this lab [the Kambara and Ikeda Lab] had conducted related studies for nearly ten years, and I was much interested in such work." Regarding his research purpose, he also writes, "I thought that even if acetylene polymers are powder, if the polymerization can be controlled to produce particles larger in size, various properties [of acetylene polymers], such as conductivity, would be closer to true values." As mentioned above, he writes that it would be better to decrease the stirring speeds as much as possible during the polymerization reaction to increase the size of the particles. I never heard such a clear idea from him at that time and only learned of it after reading his document. It is worth noting that while he writes that it would be better to increase the size of particles, he provides no idea of how to produce polyacetylene in film form.

As mentioned above, Pyun's trial run was not recorded in my laboratory notebook. While it would be best to check Pyun's notebook regarding the trial run, I learned from reading his documents that he was unable to bring the notebook home following Ikeda's instructions. His laboratory notebook went missing after that.

His document[5] include many inconsistent descriptions of his stay in Japan. The following is one example: "About two weeks after starting my work at Professor's Tabata lab at the University of Tokyo, I went to the Tokyo Institute of Technology to take the deuterated stocked ethylene in the Ikeda lab. There I encountered Professor Kambara's retirement memorial lecture, which had started just then in the auditorium." He continued with the following observations: "The audience was full in the auditorium, and the title was 'A History of the Development of Polymer Science and Engineering in Japan.' I was staggered on hearing Professor Kambara's words in the last part of his lecture in front of such a large audience. He disclosed 'a long-awaited method of producing polyacetylene in the form of polyacetylene film had been attained in Japan, and the inventor is the assistant [Research Associate] Shirakawa of the Ikeda lab.'"

Kambara's retirement date was March 31, 1967, and by custom, lectures by retiring professors were held just before their retirement. If the date of Pyun's visit to Japan was May 1967, as noted in Rasmussen's article, it would be impossible for him to attend Kambara's final lecture as it was before his visit to Japan. Therefore, this must be a continuity error.

Pyun further infers that the abovementioned audiences provided information to the mass media in Japan and that the media caused a media circus immediately after the announcement of Shirakawa's Nobel Prize in Chemistry. Soon after the announcement by the Nobel Committee on October 10, 2000, three young journalists visited my home and questioned me closely as to why Pyun was not a joint prize winner, which left me with an unpleasant memory. The journalists were from one of three big presses in Korea; if my memory is correct, the press was *The Dong-a Ilbo*. From this, I learned for

the first time that Pyun was known as a leading scientist in the synthesis of polyacetylene in Korea, and thus he missed receiving what would have been Korea's first Nobel Prize in Chemistry.

I have no memory of any discussion with Pyun regarding research, especially on acetylene polymerization and the properties of polyacetylene during his one-year stay at the Tokyo Institute of Technology and the University of Tokyo. However, I realized that Pyun was highly interested in polyacetylene as an important candidate in semiconducting polymer by reading related articles before visiting Japan. In his document, he describes that while in Japan "my study of polyacetylene study was stopped after all…," calling up for me his strong emotion toward polyacetylene study.

RECORD OF PYUN'S WORK IN MY LABORATORY NOTEBOOKS

To refresh my memory to write this note, I checked my 15 laboratory notebooks used during my period at the Tokyo Institute of Technology and more than 20 notebooks related to my research works. These showed me that Pyun conducted several experiments on acetylene polymerization. The date of these experiments cannot be specified, but presumably, it was in mid-September 1967, after we established the synthetic method of self-standing polyacetylene films with a silvery sheen.

The first assumable description was a series of runs in which Pyun carried out three polymerizations of deuterated acetylene by changing the polymerization temperature. The results of the elemental analyses of the deuterated polyacetylenes are recorded in my notebook No. 3, page 442, as Pe-1 polymerization temperature 60 degrees centigrade, Pe-2 polymerization temperature 20 degrees centigrade, and Pe-3 polymerization temperature -78 degrees centigrade, respectively. The code "Pe" can be understood as Pyun's initial. He synthesized deuterated acetylene by himself as precursors for the synthesis of deuterated ethylene, such as $C_2H_2D_2$ and C_2D_4, as monomers for deuterated polyethylene. It was my assumption that he tried to polymerize the deuterated acetylene prior to his primary purpose.

The next record was on the mass-spectroscopy analysis of ethylene-d_4, synthesized by Pyun. The result is described in my notebook No. 3, page 444, October 13, 1967. The ethylene-d_4 was synthesized by an additional reaction of deuteron to acetylene-d_2 for the copolymerization of ethylene and tetrafluoroethylene. For his primary purpose, Pyun synthesized acetylene-d_2 himself as an intermediate for the synthesis of ethylene-d_4. Presumably, he attempted to polymerize the acetylene-d_2 as a monomer.

His experimental results, mentioned above, were recorded twice in my notebook because I was familiar with the application procedures for elemental analysis and mass-spectroscopy. Thus, his products, acetylene-d_2 and ethylene-d_4, were passed to each analytical lab via me, and the data were, necessarily, recorded in my notebook.

The first appearance of the term "polyacetylene film" is recorded clearly in my notebook No. 3, page 452, on November 8, 1967, as X-ray scattering analysis was carried out in the X-ray analysis room of the Department of Textile Engineering. The measurements were performed at two different temperatures – 21 and 80 degrees centigrade – to measure the estimated thermal expansion coefficient of polyacetylene films. It should be noted that these analyses were carried out for a series of measurements of the various physical properties of polyacetylene films, and there was no relation to Pyun's research.

CLOSING REMARKS

The Nobel Committee announced that our Nobel Prize in Chemistry in 2000 was awarded "for the discovery and development of conductive polymers" based on the doping of polyacetylene attained by the three laureates. It should be noted that it was not for the synthesis of polyacetylene films. However, there is no doubt that the synthesis of polyacetylene films was a key factor in the discovery of conducting polymers. In this account, I have presented the truth to the best of my ability, based upon my memories and my notebooks. I further want to stress that Pyun's contribution was minimal and that his claims that he was the discoverer of the synthesis of polyacetylene were his strong belief, but they were not supported by the truth of what happened. However, his one-year stay in Japan was not satisfactory, and as one of the concerned personnel, I regret that his research work was not attained fully due to several unfavorable events during his stay in Japan.

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