New Insight into the “Fortuitous Error” that Led to the 2000 Nobel Prize in Chemistry

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Abstract. In 2000, the Nobel Prize in Chemistry was awarded to Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger "for the discovery and development of electrically conductive polymers." While this award was in reference to their collaborative efforts on conducting polyacetylene in the mid-to-late 1970s, the narrative leading up to these efforts began in 1967 with the production of polyacetylene plastic films via what has been called a "fortuitous error." At the heart of this discovery were Shirakawa and a visiting Korean scientist, Hyung Chick Pyun. The current report provides background on Pyun and, for the first time, presents his version of the events leading to the discovery of polyacetylene films in order to provide new insight into this important historical event.

Keywords: polyacetylene, plastic films, Nobel Prize 2000, polymerization conditions, Ziegler-Natta catalysis.

INTRODUCTION

In 2000, the Nobel Prize in Chemistry was awarded to Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger (Figure 1) “for the discovery and development of electrically conductive polymers,” which was in reference to collaborative efforts by these investigators on conducting polyacetylene in the mid-to-late 1970s.1-9 The narrative leading up to these collaborative efforts, however, began in 1967 with what Shirakawa has referred to as a "fortuitous error,” an event that resulted in the very first production of polyacetylene in the form of plastic films.10-13 According to Meriam-Webster, a legend is defined as “a story coming down from the past; especially: one popularly regarded as historical although not verifiable”. The story behind the critical discovery that polyacetylene could be synthesized as lustrous, silvery films has achieved such legendary status, with it having been told and retold by many different people over the years, with the story rarely told the same way twice.10-29

What is generally agreed upon is that this discovery was made in October of 1967,10-15 approximately a year and a half after Shirakawa had joined the group of Sakuji Ikeda (1920-1984) at the Tokyo Institute of Technology (Tokyo Tech).14 According to Shirakawa,10-15 another researcher under his supervision was preparing a sample of polyacetylene, but mistakenly used a
A thousand-fold excess of catalyst. The result of this error then caused the formation of “ragged pieces of a film” on the surface of the catalyst solution, rather than the typical black powder normally produced within the solution. Although interest in the electronic properties of polyacetylene date back to the 1958 report of Giulio Natta (1903-1979), studies prior to the discovery of polyacetylene films were limited to power samples, typically as pressed pellets.

At the same time, however, there are a number of variable aspects given in the many retellings of this event, including the identity and nature of the researcher who made the critical error. While the researcher's gender is generally viewed as male, he has been described by various sources as a "student," "Shirakawa's student," "foreign student," "graduate student," "Korean graduate student," "visiting Korean researcher," "Korean visitor," or "visiting scientist." Another variable point is the specific reason for the error itself. While most agree that it was the result of miscommunication, the nature of the miscommunication differs even within the accounts of the three Nobel laureates. For example, Shirakawa states “I might have missed the "m" for "mmol" in my experimental instructions, or the visitor might have misread it,” while MacDiarmid gives a different account, stating "I asked him how he [Shirakawa] had made this silver film of polyacetylene and he replied that this occurred because of a misunderstanding between the Japanese language and that of a foreign student". Although somewhat similar to that of MacDiarmid, Heeger gives still yet another version, stating “he [Shirakawa] had a Korean visitor who misunderstood what he said in Japanese.”

It is only in the acknowledgment of his Nobel lecture that Shirakawa finally reveals the name of the researcher at the center of this event to be Dr. Hyung Chick Pyun (Figure 2). Pyun was never included as a co-author on any of the papers on the synthesis of the polyacetylene films, although the initial 1971 report included an acknowledgment to "H. C. Pyun". Other than that, very little is known about Pyun and it is only recently that some biographical data has been reported. The goal here is to provide background on Pyun and, for the first time, present his version of the events leading to the discovery of polyacetylene films in order to provide new insight into this event.

HYUNG CHICK PYUN

Hyung Chick Pyun (Byun Hyung Jik; Byeonhyeongjik) was born December 23, 1926 in Bongsan county of Hwanghe province, now within North Korea. His family moved to Seoul in 1936, where he was educated at Kyungdong High School. In April of 1945, he entered the Sixth High school in Japan (which become part of Okayama University in 1949), before returning to Seoul in October 1945 to enter Kyungsung University’s preparatory school. Kyungsung University became part of Seoul National University in 1946, were Pyun completed a B.S. in Chemical Engineering in 1951. With the onset of the Korean War (1950-1953), he began working for the Science Research Institute of the Ministry of National Defense in December of 1950, while also completing his university studies. He continued there...
until 1960, when he moved to the newly established Korea Atomic Energy Research Institute (KAERI). Beginning in February of 1961, he spent a year at the University of Kansas, where he worked with William E. McEwen (1922-2002). He then published his first papers in 1964, the first of which was based on his work with McEwen. In 1967, he received support from the International Atomic Energy Agency (IAEA) to carry out research in Japan. Although it has been reported that Pyun had acquired his doctorate before working in Ikeda’s laboratory, this is incorrect and he received his Ph.D. in Nuclear Engineering from Seoul National University in 1970, based on work he had published in 1964. Although he expressed a desire to pursue polyacetylene research after his return from Japan, he was discouraged to do so by his superiors. As such, the only publication that appears related to his time in Tokyo was a 1969 report on the comparison of gamma irradiation vs. Ziegler-Natta catalyzed methods for the copolymerization of ethylene and tetrafluoroethylene (TFE) via the IR analysis of isotopically labeled species. The needed deuterated ethylene was to be prepared in Ikeda’s laboratory, which would then be copolymerized with TFE at the University of Tokyo. Pyun had successfully completed the work in Ikeda’s lab, but his work at the University of Tokyo was postponed as Tabata was visiting the United States and his return was delayed. During the month wait, Pyun became interested in the polyacetylene studies carried out by others in Ikeda’s lab and felt that its properties could be improved if larger polymer particles were generated. He proposed that this could be accomplished by decreasing the stir speed during polymerization and began investigating this. Pyun stated that:

One day...the stirring motor stopped during the experiment because the stirring speed had been excessively reduced. I was very embarrassed at first, but after a closer look, I found it surprisingly to see a silver film on the surface of the reaction solution. It was nothing more than a polyacetylene film... I realized that the scientists who were studying this field had not synthesized the acetylene in the film state because the polymerization reaction had proceeded with stirring. That is, if it is not stirred, it is allowed to polymerize in the film state. Stirring thereby was hindering film formation.

Pyun stated that he repeated the film production more than 10 times and thought that Ikeda would be very pleased, so he went to his office and gave a verbal report of his results. However, according to Pyun, Ikeda became upset and reminded him of the joint project with Prof. Tabata, who had now returned from the US. The following day, Pyun was then sent to Tokyo.

**PYUN’S ACCOUNT**

While previous efforts to obtain Pyun’s version of the events had been unsuccessful, the collaborative approach utilized here included a native researcher with access to Korean-language resources less available to western historians. Thus, it was confirmed that Pyun was still alive as of late 2017, although quite ill and had been in the hospital since the fall of 2016. While we were unable to talk to Pyun directly, his son Dr. Joongmoo Byun was quite helpful and provided us with a written account his father had prepared prior to his failing health. This document, roughly entitled “What is a Nobel Prize?” in English, was last revised in 2013 and detailed his memories and views on the discovery of polyacetylene films (see Supporting Information for the original Korean document and a working English translation). A previous version of this account had also appeared in a KAERI publication in 2002.

According to Pyun, he arrived at Tokyo Tech in 1967 to begin work on a collaborative project between Sakui Ikeda and Yoneho Tabata (University of Tokyo), with the goal of studying the copolymerization of ethylene and tetrafluoroethylene (TFE) via the IR analysis of isotopically labeled species. The needed deuterated ethylene was to be prepared in Ikeda’s laboratory, which would then be copolymerized with TFE at the University of Tokyo. Pyun had successfully completed the work in Ikeda’s lab, but his work at the University of Tokyo was postponed as Tabata was visiting the United States and his return was delayed. During the month wait, Pyun became interested in the polyacetylene studies carried out by others in Ikeda’s lab and felt that its properties could be improved if larger polymer particles were generated. He proposed that this could be accomplished by decreasing the stir speed during polymerization and began investigating this. Pyun stated that:.

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**Figure 2.** Hideki Shirakawa and Hyung Chick Pyun (1926-2018) at Tokyo Tech in 1967 [Courtesy of Joongmoo Byun].
University to finish his project there. Weeks later, Pyun returned to Ikeda's lab in order to collect a deuterated ethylene sample, at which point Shirakawa asked him to demonstrate how to make the film. According to Pyun, 47,48 he showed Shirakawa his method in detail, after which Shirakawa was able to reproduce his results. Meanwhile, the research in Tabata's lab was proceeding smoothly, but due to the initial delay, Pyun was short on time and decided to apply for an extension to the IAEA. This required a recommendation letter from Ikeda, however, which he refused to give, thus denying any extension. 47 Pyun then returned to Korea in March of 1968.

DISCUSSION

In his written account, 47 Pyun highlighted a number of issues he had with the accepted version of the accidental discovery. This included statements that described him as only a graduate student, that said he that did not know Japanese well, and that said he did not follow directions, specifically that he had used a thousand times too much catalyst. The first two of these were indeed incorrect, as has been previously pointed out by select historical studies of these events. 24,26,28 As given above, although he did not yet have his Ph.D. during his time in Ikeda's lab, the research that became his dissertation had already been completed and Pyun was already 17 years into his professional career at the time. In a similar vein, the issue of language had already been disproven by Hargittai, 24 who had confirmed with Shirakawa that Pyun had grown up in Korea during the years that the country was under Japanese occupation and thus spoke fluent Japanese. To be fair, however, Shirakawa had never described him as a student, nor had he ever said that Pyun's Japanese was a limitation and both of these points had been introduced by others during the many retellings of these events.

The final point, however, is more problematic. According to Pyun, he did not make any errors in the experimental conditions, did not use excess catalyst, and had purposely reduced the stirring rate, which resulted in the formation of the polyacetylene films. 47,48 As such, he felt that he had been unfairly denied the credit for the discovery, which in his view was not an accident. The view that this innovation was solely the result of reduced stir rate, however, is not consistent with the wealth of evidence to the contrary. The production of linear, conjugated polyacetylene dates back to the 1955 work of Giulio Natta (1903-1979), who had used very similar conditions to that of Ikeda's group. 30-32 More critically, Natta's original polymerizations were performed both with and without stirring, but always giving a crystalline powder, not a film. Furthermore, the critical requirement of catalyst concentration for film formation was independently confirmed by multiple groups after Shirakawa and Ikeda finally reported the detailed experimental procedure in 1974. 28,51 Finally, in 1987, Herbert Naarmann at BASF, along with coworkers from the University of Montpellier, published a paper that probed in great detail the effect of polymerization conditions on the properties of the resulting polyacetylene. 52 This study too was done without stirring and concluded that the film density was directly related to the catalyst concentration, with true films only formed via the application of high catalyst concentrations. As such, there is no experimental or literature support for Pyun's belief that he did not use a thousand-fold excess of catalyst in the original experiments. At the same time, it should be pointed out that his insistence that the reaction not be stirred does play a role in this process. As the film is formed at the gas-solvent interface, an unstirred solution provides a calm, undisturbed surface optimal for the production of smooth, uniform films, and it is perhaps not coincidence that Pyun did not observe film formation until the stirrer failed.

While there has never been any doubt that Pyun was the first one to prepare polyacetylene films, the addition of his version to the previously available accounts now allows some additional insight into these events. From Pyun's own accounts, he began performing acetylene polymerizations, but seemingly with limited knowledge of the existing polyacetylene literature at the time, 28 or even the wealth of such work carried out at Tokyo Tech. 33-41 Furthermore, based on Ikeda's reaction when Pyun reported his results and Pyun's own insistence that Shirakawa did not supervise his polymerizations, it appears that he did not have permission to carry out these experiments. After Pyun had been expelled from the lab, Shirakawa was then tasked with figuring out what Pyun had done, but could not reproduce his results. While it is not currently possible to confirm this, it appears that Pyun's notebook did not indicate the atypical catalyst concentration and it was only after witnessing Pyun perform the experiment that the unusual amount of catalyst came to light, after which Shirakawa was then able to reproduce the results. Shirakawa was then the one that studied the process in detail, after which he able to provide an accurate account of how the polyacetylene films were being produced, as well as detailed studies of the polymer structure, film morphology, and resulting electronic and optical properties. While it is very unfortunate that Pyun felt he was denied fair credit, this new insight does allow us to finally
understand Pyun’s role in these events. His actions did result in the first formation of polyacetylene films, but the lack of understanding of what he did makes it difficult to give him sole credit for discovery as he desired. Still, many researchers would have probably made him a coauthor on the first paper reporting the film formation, rather than just an acknowledgement. Of course, the specific criteria for determining authorship can vary by both discipline and research group, and deciding what merits authorship is not always a straightforward process. Furthermore, it is important to remember that while Shirakawa is always the focus when discussing this work, he was only a research associate at the time and would not have been the one to determine authorship. Rather, it was Ikeda who was the principle investigator and the decision concerning authorship would have ultimately been his to make.

Finally, some may feel that Shirakawa’s version of the discovery was an attempt to distort the facts or cover up what happened. Here it is essential to separate the legend from verifiable statements, recognizing that while many have attributed comments to him, the truth is Shirakawa has actually said very little on the subject and what has been said is somewhat vague. Unfortunately, this has led others to fill in the details based on their own preconceptions, thus leading to the multiple and erroneous versions of this important event.

ASSOCIATED CONTENT

Supporting Information: Pyun’s original account in Korean, as well as a working English translation.

ACKNOWLEDGMENT

I would like to thank Joongmoo Byun for providing significant material on his father, as well as Choon H. Do, whose collaboration made this project possible.

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