

THE PATH TO CONDUCTIVE POLYACETYLENE

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Introduction

In 2000, the Nobel Prize in Chemistry was awarded to Professors Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa “for the discovery and development of electrically conductive polymers” (1). This award was in acknowledgement of their early contributions to the field of conjugated organic polymers (Figure 1), particularly their collaborative work on conducting polyacetylene beginning in the mid-to-late 1970s (2). Conjugated organic polymers are a class of organic semiconducting materials that exhibit enhanced electronic conductivity (quasi-metallic in some cases) in their oxidized (*p*-doped) or reduced (*n*-doped) state (3). As such, these materials have been referred to as *synthetic metals* (4) and combine the conductivity of classical inorganic systems with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs. This combination of properties has led to the current field of organic electronics and the development of modern technological applications such as sensors, electrochromic devices, organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and field effect transistors (FETs) (3).

Needless to say, this class of materials has changed the way that the scientific community views plastics, as was outlined by the initial press release for the 2000 Nobel Prize in Chemistry (1):

We have been taught that plastics, unlike metals, do not conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year’s Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after certain modifications, be made electrically conductive.

In both quotes from the Nobel press release, however, credit for the discovery of conducting polymers via doping (i.e. oxidation or reduction) is specifically attributed to Heeger, MacDiarmid and Shirakawa, although investigations of electrically conductive conjugated polymers date back to the early 1960s, nearly 15 years before their

collaborative work on polyacetylene. That these previous studies are overlooked in most discussions of the history of conjugated polymers is unfortunate and I have attempted to rectify this in a recent publication that presents the prior contributions of Donald Weiss on conducting polypyrrole, as well as that of René Buvet and Marcel Jozefowicz on conducting polyaniline (5). In

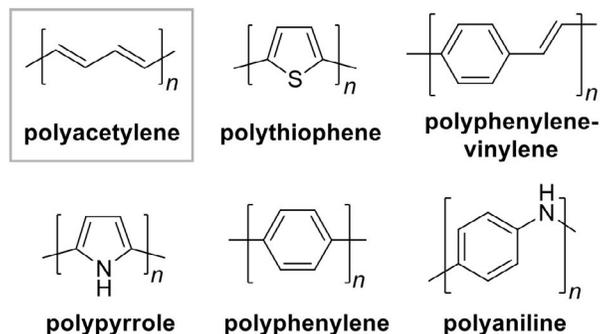


Figure 1. Common conjugated organic polymers.

addition, two other short historical accounts have also been recently published that have tried to shed light on some of these previous contributions (6). In continuing these collective efforts, the current manuscript aims to focus more deeply on the history of polyacetylene and will present a more complete picture of all those that contributed to the ultimate discovery of its highly conductive nature upon doping.

From Carbon Blacks to Conjugated Polymers

As early as the 1930s, scientists began to speculate about the possibility that electronic conduction might be observed in organic materials (7). However, it wasn't until the 1950s that significant experimental work began to appear on the subject. Of the various materials investigated, it was graphite and the carbon blacks (material from the partial burning or carbonizing of organic matter), that gave the most significant electrical conductivity (up to $50 \Omega^{-1} \text{ cm}^{-1}$) (7, 8).

Although the modern description of carbon blacks is a particulate, quasigraphitic material (8a), these materials were initially thought to be three-dimensional, cross-linked organic polymers with various structures and elemental constitutions depending on their origin (8b). As these "carbonaceous polymers" were considered to have chemical structures that were too complex and ill-defined, efforts turned to the production of related organic polymers as potential model systems with more defined and controllable compositions (8b).

The simplest of these model systems were *polyenes*, $(-\text{CH}=\text{CH}-)_n$ (9,10), sometimes referred to as *polyvinylenes*. Formal polyenes were often limited to shorter oligomers ($n = 2-10$) and were used to correlate physical and optical properties with conjugation length (9). The related polyvinylenes were polymeric analogues of the polyenes, with identical empirical formulas under ideal conditions. However, as these polymeric analogues were produced via the chemical elimination of poly(vinyl halide)s (11) or poly(vinyl alcohol) (12), they typically contained various defects from incomplete elimination. The first successful direct polymerization of acetylene was then accomplished by Giulio Natta and coworkers beginning in 1955 (13).

Natta and the Polymerization of Acetylene

Giulio Natta was born February 26, 1903, in the small Italian city of Imperia, near the French border

(14). His father was a judge in Genoa (14be), where he attended school (14bd) before continuing on to the University of Genoa to study mathematics (14be). After two years, however, he moved to the Polytechnic of Milan in 1921 (14be) to study chemical engineering (14). In 1922, he began research at the Polytechnic's Institute of General Chemistry under Giuseppe Bruni and Giorgio Renato Levi (14e). Natta then received his *Dottore* degree in 1924 (14) and continued on as Bruni's assistant (14e). In 1927, he obtained the position of *Libero Docente* (14abc) which allowed him to teach (14a). After a period as assistant lecturer in chemistry at Milan (14b), he was made full professor and director of the Institute of General Chemistry at the University of Pavia in 1933 (14abcd). He then moved to occupy the chair of physical chemistry at the University of Rome in 1935 (14abcd), but left shortly thereafter to take the chair of industrial chemistry at the Polytechnic of Turin in either 1936 (14a) or 1937 (14bd). Finally, he was called back to his alma mater to take the chair of industrial chemistry of the Polytechnic of Milan in either 1938 (14abcd) or 1939 (14e), where he would remain until his retirement in 1973 (14).

Natta is best known for his work in high polymers, beginning with work on butadiene and synthetic rubber in 1938 (14abc). The same year he began work on olefin polymerization (14ab), which ultimately led to the extension of Karl Ziegler's work on metal-based polymerization catalysts and resulted in the discovery of new classes of polymers with a sterically-ordered structure (i.e. isotactic, syndiotactic and diisotactic polymers), as well as linear non-branched olefinic polymers and copolymers with an atactic structure (14). For these accomplishments, Natta shared the Nobel Prize in Chemistry with Ziegler in 1963 (14).

Following his successful catalytic polymerization of α -olefins and diolefins in the early 1950's, Natta then began investigating the application of the previously successful catalysts to the polymerization of the acetylenes (13). These efforts resulted in an initial Italian patent in 1955 (13a), followed by the publication in 1958 of the successful catalytic polymerization of acetylene via triethylaluminum (Et_3Al)/titanium alkoxide combinations (13b). As outlined in Figure 2, the best results were obtained using Et_3Al and titanium(IV) propoxide at 75°C , with a catalyst molar ratio (Al/Ti) of 2.5. These conditions resulted in 98.5% monomer conversion to give a dark, crystalline polymer that was completely insoluble in organic solvents (13b).

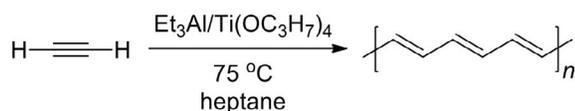


Figure 2. Catalytic polymerization of acetylene.

The polymers were characterized by X-ray diffraction of powder samples, which were found to be ~90-95% crystalline, with low amorphous content. The collected X-ray data were consistent with linear chains of polyacetylene in which the double bond configuration was thought to be predominantly *trans* (13b). The combination of the black color, the metallic luster, and the relatively low electrical resistivity ($\sim 10^{10} \Omega \text{ cm}$, compared to 10^{15} - $10^{18} \Omega \text{ cm}$ for typical polyhydrocarbons) led them to conclude that their polyacetylene was structurally identical to a very long conjugated polyene, although Shirakawa later stated that this conclusion was not accepted widely at the time (10).

It was also noted that the polyacetylene samples exhibited high reactivity, particularly with oxidants such as O_2 and Cl_2 (13b). Reaction with chlorine resulted in a white solid that was amorphous by X-ray characterization. Heating this product at 70-80 °C resulted in a rapid loss of HCl and darkening of the polymer. Alternately, nearly all of the chlorine could be removed by treatment of the polymer with potassium in hot ethanol, giving a black amorphous solid (13b).

Although Natta states in his 1958 paper that these results only represented an initial communication with additional reports planned (13b), no further work on polyacetylenes was ever published by Natta and his coworkers. Others, however, did not hesitate to continue this work (15) and as a result, *polyacetylene* gradually replaced the term *polyene* as more studies began to utilize Natta's polymerization methods (10). One of these research groups was that of Prof. Sakuji Ikeda at the Tokyo Institute of Technology, and it is with their work that we will continue our discussion.

Hideki Shirakawa and Polyacetylene Films

In the mid-1960s, Ikeda began studying the mechanism of acetylene polymerization by Ziegler-Natta catalysts (15cd), as well as developing new transition metal polymerization catalysts (16). In the process, it was found that in addition to polyacetylene, these methods also produced benzene and that the ratio of products varied with

the catalyst used (10,15cd). These ongoing mechanistic investigations were then continued by a new research associate, Hideki Shirakawa, who joined Ikeda's group in April of 1966 (10,17).

Shirakawa (Figure 3) was born August 20, 1936, in Tokyo (10a,17). Spending his childhood in the small city of Takayama, he entered Tokyo Institute of Technology in April of 1957 (17). For his undergraduate studies, he focused primarily on applied chemistry, although he did some work in polymer physics during his final year (17). He then changed his focus to polymer synthesis for his graduate studies (17), receiving a Doctor of Engineering degree in March of 1966 (17,18). In 1979, he moved to the University of Tsukuba, where he was appointed associate professor. He was later promoted to full professor in 1982 and formally retired from the University of Tsukuba as professor emeritus at the end of March 2000, shortly after being awarded the Nobel Prize in Chemistry with Heeger and MacDiarmid (17).



Figure 3. Hideki Shirakawa (1936-). Reproduced from Ref. 19a with permission of the Royal Society of Chemistry.

While working with Shirakawa in the fall of 1967 (10,17,19), a visiting Korean coworker (20) named Hyung Chick Pyun had attempted to make polyacetylene using conditions nearly identical to those reported by Natta (21), as shown in Figure 2 (13b). However, rather than generating polymer powder as expected, ragged pieces of a polymer film were produced instead (17,19ab). Upon reviewing the reaction conditions, Shirakawa found that the film formation was a result of the fact that the catalyst concentration used had been 1000 times higher than intended (10,17,19ab). Shirakawa explained the mistake as follows (17):

I might have missed the “m” for “mmol” in my experimental instructions, or the visitor might have misread it.

Curiously, MacDiarmid gives a quite different account, stating (19c):

...and he [Shirakawa] replied that this occurred because of a misunderstanding between the Japanese language and that of a foreign student who had just joined his group.

It has been pointed out, however, that Pyun spoke fluent Japanese (19d), which casts doubt on MacDiarmid's account. Regardless of what caused the error, the resulting highly concentrated catalyst solution accelerated the rate of polymerization to the point that the acetylene polymerized at the air-solvent interface, rather than in solution as was typical (17,21). As a result, Shirakawa was now able to reproducibly generate silvery plastic polyacetylene films via polymerization of acetylene on the surface of unstirred, concentrated catalyst solutions (21,22).

It was found that the backbone configurations of the resulting polyacetylene films were strongly temperature dependent (Figure 4) due to an irreversible isomerization of the *cis* to *trans* forms at temperatures above 145 °C (10a,21,22). The resulting copper-colored all-*cis* samples gave conductivities of 10^{-9} - 10^{-8} S cm^{-1} , while the silver-colored, all-*trans* samples gave higher values of 10^{-5} - 10^{-4} S cm^{-1} (22d). Surprisingly, the values of the all-*trans* samples are essentially the same as those previously reported for highly crystalline polyacetylene powders (15ab). As it had been previously shown the conductivity increased with polymer crystallinity (15a), one could expect the film to provide increased order and a corresponding rise in conductivity, but this did not seem to be the case (10a). Characterization of the films by X-ray diffraction (22b) gave data nearly identical to the previous studies of Natta (13b).

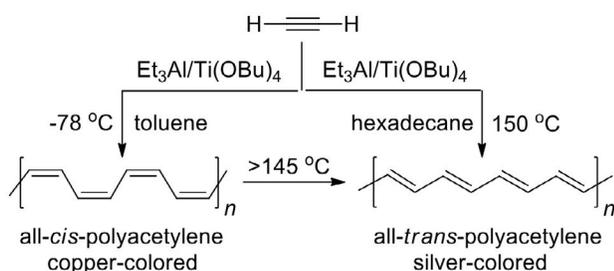


Figure 4. Temperature dependence of polymerization.

Attempts were then made to convert the polyacetylene to graphitic films. Initial attempts via pyrolysis failed and thus a chlorination/HCl elimination approach was then investigated (10). Treatment of polyacetylene with chlorine resulted in the formation of a white product (2a), similar to that previously reported by Natta (13b).

This product was then treated with base and heated at high temperature, but resulted in little graphitization of the material (10).

Smith and Doped Polyacetylene

About the same time that Shirakawa and Pyun accidentally produced the first polyacetylene films, Dorian S. Smith and Donald J. Berets at the American Cyanamid Company were investigating the effects of additives on the conductivity of polyacetylene powders (23). Dorian Sevcik Smith grew up in Winthrop Harbor, Michigan (24), before attending Illinois State Normal University (24,25). In addition to his coursework, he played football and was part of the University's sole undefeated football team in 1950 (24). For this distinction, the 1950 Redbirds team was inducted into the Illinois State Athletics Percy Hall of Fame in 1990 (26). After earning a B.S. in Education in 1953 (25), he was appointed by the Teachers College Board of the State of Illinois as a faculty assistant for the 1953-54 academic year (27). He then moved to the University of Illinois at Urbana-Champaign to continue his education with graduate studies in chemistry (24,25). There he studied the chemistry and electrochemistry of rare earth salts under the guidance of Prof. Therald Moeller (1913-1997). He received a M.S. in 1956, followed by a Ph.D. in 1958 (25).

Smith enjoyed a 10-year career as a chemist (24) at the American Cyanamid Company in Stamford, Connecticut, and the Enjay Chemical Company in New York (23), before becoming a financial analyst for various firms, including Donaldson, Lufkin and Jenrette, Chemical Bank and Yamaichi International, where he was Director of Research (24). After spending the majority of his working life in New York City, he retired to Wilmington, North Carolina, in 1996. He passed away peacefully at his home on December 4, 2010, at the age of 77 (24).

Initially, Smith and Berets were investigating the effect of oxygen impurities on the conductivity of pressed pellets of polyacetylene powder, finding that samples with lower oxygen content gave lower resistivity. In the process, however, they observed an interesting phenomenon (23):

On admission of 150 mm pressure of oxygen to the measuring apparatus (normally evacuated or under a few cm pressure of He gas), the resistivity of polyacetylene decreased by a factor of 10. If the oxygen was pumped off within a few minutes and evacuation continued at 10^{-4} mm pressure for several hours, the

original electrical properties of the specimen were restored.

They went on to conclude that oxygen is first adsorbed in a reversible manner, reducing the resistivity, but ultimately reacts with the polymer irreversibly resulting in the typically observed increase in resistivity.

The effects of various gases on the conductivity were then investigated to find that electron acceptors (BF_3 , BCl_3 , Cl_2 , SO_2 , NO_2 , O_2 , etc.) all resulted in a decrease in resistivity (i.e. an increase in conductivity), although oxidizing gases (O_2 , Cl_2 , and NO_2) ultimately resulted in chemical reaction with the polymer. In contrast, electron donors (NH_3 , CH_3NH_2 , H_2S , etc.) had the opposite effect on resistivity. The best results were obtained using BF_3 , which resulted in an increase in conductivity of three orders of magnitude (to $\sim 0.0013 \text{ S cm}^{-1}$). These results were explained as follows (23):

The effect on conductivity of the adsorbed electron-donating and electron-accepting gases is consistent with the p-type nature... If holes are the dominant carriers, electron donation would be expected to compensate them and reduce conductivity; electron acceptors would be expected to increase the concentration of holes and increase conductivity; this is observed.

Although they didn't completely understand the effect of the gaseous additions, they quite clearly state (23) that the *electrical conductivity depended on the extent of oxidation of the samples!* These results, however, did not seem to generate much interest and Berets and Smith never followed up this work with any additional studies. In fact, this work seems to be the only paper Smith ever published after completing his Ph.D. A few years later, however, two professors at the University of Pennsylvania began a related study with the addition of gaseous bromine to the inorganic polymer poly(sulfurnitride) (28).

MacDiarmid, Heeger, and Poly(sulfurnitride)

Alan Graham MacDiarmid (Figure 5) was born April 14, 1927, in Masterton, New Zealand (19c,29). Coming from a self-described "poor family," he was forced to leave high school at age 16 in order to take a part-time job after his father retired (19c,29). His job working as janitor and lab boy in the chemistry department at Victoria University College (19c), however, allowed him to apply himself as a part-time student and he was able to complete his B.Sc. in 1948 (29). After completing his B.Sc. at age 21, he was promoted to the position of demonstrator (19c) and he began studying the chemistry of S_4N_4 for

his M.Sc. thesis under Mr. A. D. Monro (19c,29). He published his first paper in 1949 (30) and completed his M.Sc. the following year (4,29).

MacDiarmid then received a Fulbright fellowship to attend the University of Wisconsin, where he studied inorganic chemistry under Prof. Norris F. Hall (19c,29). There he earned a M.S. in 1952 and a Ph.D. in 1953 (4,29,31). While still at Wisconsin, he obtained a New Zealand Shell graduate scholarship to study silicon hydrides under Prof. Harry J. Emeléus at Cambridge University (19c,29). He completed his second Ph.D. in 1955 (4,29) and held a brief appointment as assistant lecturer at the University of St. Andrews in Scotland before joining the Department of Chemistry at the University of Pennsylvania (29). MacDiarmid maintained his position at Penn until the end of his career, but also held positions at the University of Texas at Dallas, becoming the James Von Ehr Chair of Science and Technology and professor of chemistry and physics there in 2002, and at Jilin University in China, becoming professor of chemistry there in 2004 (29). MacDiarmid continued to work until his death on February 7, 2007 (29,32).

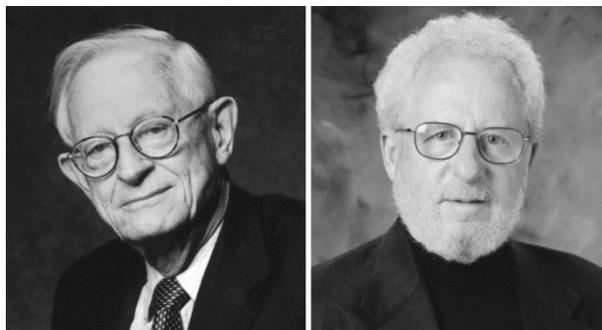


Figure 5. Alan G. MacDiarmid (1927-2007) and Alan J. Heeger (1936-). Reproduced from Ref. 19a with permission of the Royal Society of Chemistry.

Alan Jay Heeger (Figure 5) was born January 22, 1936, in Sioux City, Iowa (33). His family moved to Omaha when he was nine and later attended the University of Nebraska with the initial goal of becoming an engineer (33). However, that changed after his first semester and he pursued dual studies in physics and mathematics (33). After completing his B.S. in 1957, he began graduate studies in physics at Berkeley, ultimately joining the research group of Alan Portis (33). After completing his Ph.D. in 1961 (34), he went directly to join the Physics Department at the University of Pennsylvania in 1962 (33a), working initially on the metal physics of tetrathiafulvalene-tetracyanoquinodimethane

(TTF-TCNQ) (33). In 1982, Heeger moved to the University of California, Santa Barbara (UCSB), where he still actively pursues research in conjugated materials. In addition to his faculty position as professor of physics, he also served as the director and co-founder of UCSB's Center for Polymers and Organic Solids.

The collaboration between the two Penn colleagues began in 1975, after Heeger became intrigued by re-ports of the metallic polymer poly(sulfurnitride), $(\text{SN})_x$ (19a,33). Learning that MacDiarmid had some experience with sulfurnitride chemistry, he approached him about working together on a study of this new polymer (19a,33). Their collaboration then began with development of the first reproducible preparation of analytically pure $(\text{SN})_x$ via the solid-state polymerization of S_2N_2 to give a lustrous golden material (28ab). The following year they reported the characterization of its electronic properties, giving conductivities of $1.2\text{--}3.7 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ (28c). Finally, following up on previous reports that $(\text{SN})_x$ reacted with halides, they treated the polymer with bromine vapor to produce the derivative $(\text{SNBr}_y)_x$ that resulted in a 10-fold increase in conductivity in comparison to $(\text{SN})_x$ (19a,28c).

Doped Polyacetylene Films

Shortly after the beginning of the collaboration with Heeger (33), MacDiarmid spent three quarters of a year as a visiting professor at Kyoto University (19c,29). During his visit, he was asked to give a lecture at the Tokyo Institute of Technology and met Shirakawa over tea after his lecture (19a,29). After seeing MacDiarmid's golden $(\text{SN})_x$ film, Shirakawa said that he had a similar material and returned to his lab to retrieve a sample of his silver-colored polyacetylene film to show MacDiarmid (29). The film captured MacDiarmid's interest and after returning to the states, he inquired into the possibility of supplemental funding in order to bring Shirakawa to Penn to work on polyacetylene (19c,29). ONR Program Officer Kenneth Wynne agreed to support Shirakawa's visit (19a) and thus he began working with MacDiarmid and Heeger as a visiting scientist in September of 1976 (10a,17).

Upon arriving at Penn, Shirakawa and MacDiarmid first worked to improve the purity of the polyacetylene films in order to increase its conductivity (19c). As discussed above, previous studies by Smith and Berets (23) had shown that conductivity did increase with decreased oxygen content and thus limiting other impurities could possibly further increase the film's conductivity.

Eventually, they were able to make films with purities as high as ca. 98.6% (29), but found that conductivity actually decreased as the film purity was enhanced (38,55). Temperature-dependent conductivity measurements were also made to determine whether polyacetylene had the temperature profile of a metal or semiconductor (55). As Hatano had previously reported such measurements for polyacetylene powders in 1961 (28), resulting in a temperature profile consistent with that of a semiconductor, it is unclear if it was thought that the film might have a different response in comparison to the pressed pellets, or if they were just unaware of Hatano's work at the time.

Based on the observed relationship between purity and the resulting conductivity, it was proposed that perhaps the impurities in the film were acting as dopants which thus increased the conductivity of the polyacetylene (19c,29), as Heeger and MacDiarmid had previously seen in the addition of Br_2 to $(\text{SN})_x$ (19c,28d). This reasoning was also supported by previous in situ IR measurements by Shirakawa and Ikeda during the treatment of polyacetylene films with halide vapors, which revealed a dramatic decrease in IR transmission (10). This change in transmission suggested that the initial halogen-treated material might have unusual electronic properties (19a) and thus it was decided to study the conductivity of the films upon bromine addition.

The critical measurements were then carried out on November 23, 1976 (10,17), by Shirakawa and Dr. Chwan K. Chiang, a postdoctoral fellow of Heeger (17). The conductivity of a *trans*-polyacetylene film was measured by four-point probe while being exposed to bromine vapor (2a,17,19a). The conductivity rapidly increased with the addition of 1 Torr of bromine, resulting in a change of approximately four orders of magnitude (from 10^{-5} to 0.5 S cm^{-1}) within only 10 minutes (2a). These measurements were then repeated using iodine in place of bromine to give an even greater increase in conductivity (up to 38 S cm^{-1}) (2a).

Later that same year it was demonstrated that higher conductivities of 160 S cm^{-1} could be obtained with further optimization of the iodine treatment, although the substitution of AsF_5 for iodine could produce even higher conductivities (2bc). Thus the treatment of polyacetylene films with AsF_5 gave conductivities of 220 S cm^{-1} for the *trans* isomer, with even higher values (560 S cm^{-1}) for the *cis* isomer (2b). The very high values for the AsF_5 -doped *cis*-polyacetylene films then led them to repeat the iodine treatments using *cis*-polyacetylene in 1978, resulting in conductivity values above 500 S cm^{-1} (2d). That same year, it was also demonstrated that

polyacetylene could be doped with electron-donating species such as sodium to give conductivities of 8 S cm^{-1} (2c). Heeger and MacDiarmid then reported maximum values of 200 S cm^{-1} for electron-donor treated films in a final 1978 paper (35).

Conclusions

Beginning with the work of Hatano in 1961 (15a), these collective studies demonstrated that the conductivity of polyacetylene was electronic in nature and not consistent with an ionic mechanism. Also demonstrated was the fact that these organic could be chemically doped with electron-acceptors (*p*-doping) or electron-donors (*n*-doping) in a manner analogous to classical inorganic semiconductors such as silicon. Lastly, it was shown that polyacetylene could be transformed from an insulator to a semiconductor or even quasi-metal, depending on the extent of chemical doping. As such, it represented the first example of an organic material capable of undergoing a metal–insulator transition.

While all of these discoveries are typically credited to Heeger, MacDiarmid, and Shirakawa, the above discussion has hopefully illustrated that their seminal work was built upon previous studies, some of which had already shown aspects of these properties. In particular, while the work of Smith and Berets (23) was less developed and they never described their studies as “doping,” it is quite clear that they were showing the same effects that later resulted in the more dramatic conductivity increases reported nearly a decade later. As such, it is curious to imagine how much their previous work influenced the doping studies in the late 1970s. At least Shirakawa was familiar with the work, as he repeatedly referenced Smith and Berets as early as 1973 (22ab). In terms of the collaborative papers with Heeger and MacDiarmid, however, Smith and Berets are not mentioned until the third paper, where it is acknowledged that polyacetylene powder had been previously treated with electron-withdrawing species, but state that the conductivities were still very small (2c). In the following paper, they also refer to the oxygen content study of Smith and Berets (2d). Curiously, however, they do not mention this previous work when reporting in 1977 that treatment of *trans*-polyacetylene films with NH_3 vapor results in a decrease in conductivity by four orders of magnitude (2bc), the same result previously reported by Smith and Berets in 1968 on pressed pellets (23).

Acknowledgements

The author would like to thank Prof. John Reynolds (Georgia Tech) for bringing the work of Smith and Berets to his attention. Thanks are also given to North Dakota State University for financial support.

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