

EARLY HISTORY OF POLYPYRROLE: THE FIRST CONDUCTING ORGANIC POLYMER

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Introduction

Conjugated organic polymers (Figure 1) have grown to receive considerable academic and technological interest due to their combination of the electronic and optical properties of traditional inorganic semiconductors with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs (1,2). In general, this class of polymers can be characterized as semiconducting materials that exhibit enhanced electronic conductivity (quasimetallic in some cases) in either their oxidized (p-doped) or reduced (n-doped) state (1,2). The resulting study of these materials has led to the current field of organic electronics, with considerable effort focused on the development of technological applications such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), field effect transistors (FETs), sensors, and electrochromic devices (1-4). In addition, the flexible, plastic nature of the conjugated organic materials used in these electronic devices has led to the realistic promise of flexible electronics in the near future (3,4).

Discussions of the history of this field generally begin in the mid-to-late 1970s with the collaborative

work of Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger on conducting polyacetylene (5-8). In 2000, these investigators were awarded the Nobel Prize in Chemistry for their early contributions to the field of conjugated organic polymers. The language of the award further reinforces the common view of the historical origins of these materials which states that

the award is “for the discovery and development of electrically conductive polymers” (9). It is only somewhat recently that reports have begun to present a more complete account of the early history of these materials, with particular attention given to highlighting the work that predates the commonly cited polyacetylene work of the 1970s (10-13). While this previous work may not have been as

dramatic or as fully realized as the later polyacetylene studies, many aspects and relationships attributed to the work recognized by the Nobel prize can be seen in these earlier contributions.

Within this body of earlier work, the first real successful production of an organic polymer with significant conductivity was reported in 1963 by Donald Weiss and coworkers in Australia on conducting polypyrrole (14-16). In contrast, the modern polypyrrole literature

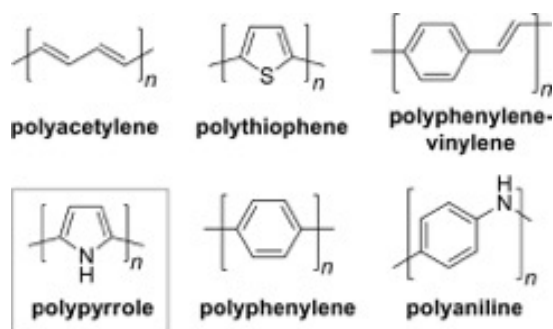


Figure 1. Common conjugated organic polymers.

typically points to the later work of Diaz and coworkers in 1979 (17) in presenting the early studies of the material (18-20), which further supports the view that the history of conducting polymers begins with polyacetylene and that other members of the family of conjugated polymers followed afterwards. Of course, the history of polypyrrole does not even really begin with the work of Weiss and dates even further back to 1915 with work on a black precipitate named “*pyrrole black*” by Angelo Angeli (21-28). This current report will attempt to present a more complete and detailed account of the early history of polypyrrole up through the commonly referenced work of Diaz and coworkers.

Angeli and Pyrrole Black

Angelo Angeli (Figure 2) was born August 20, 1864, in the town of Tarcento, located in the Udine province of

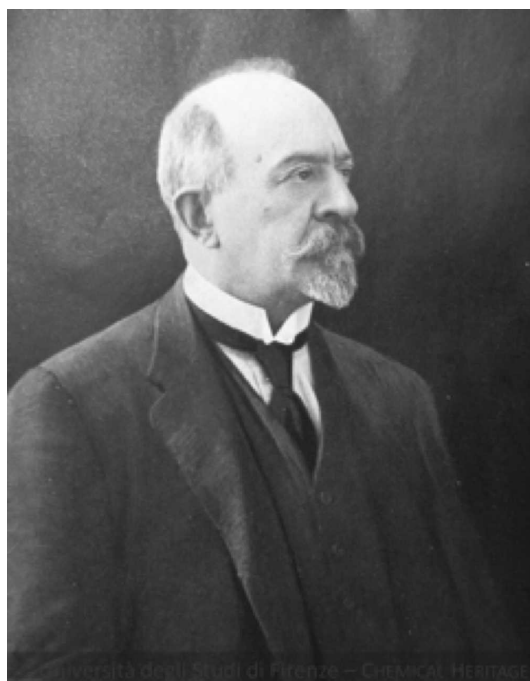


Figure 2. Angelo Angeli (1864-1931). Courtesy of the “Ugo Schiff” Chemistry Department, University of Florence, Italy.

northeastern Italy (29-31). The son of a modest merchant, he was forced to abandon his studies at the Technical School in Cividale del Friuli in order to help with the family business (29). His early passion for chemistry, however, was maintained by his close relationship with his uncles Giuseppe and Giovanni Carnelutti, who kept a small laboratory in their home and allowed him to participate in chemical experiments (29,30). At the

insistence of his mother (29), he ultimately returned to his studies, attending the Technical Institute of Udine (29-31). Following military service, he then enrolled at the University of Padua (29-31).

At Padua, Angeli began studying under the young Giacomo Ciamician (1857-1922), the new chair of general chemistry (29). Ciamician recognized his potential and asked Angeli to follow him to the University of Bologna in 1889 as his private assistant. Angeli then completed his studies at Bologna in 1891 (29-31), after which he obtained the *libera docenza* in 1893 (29,31). His growing body of published works permitted him to finish first in an academic competition for the chair in analytical chemistry in 1895 (29-31). Unfortunately, however, the competition was canceled without filling the chair (29,31).

While at Bologna, Angeli had also come to know Adolf von Baeyer (1835-1917). It has been said that von Baeyer recognized in Angeli a sure promise for Italian science and encouraged him to continue in his research (29-31). When Angeli won the chair of pharmaceutical chemistry at the University of Palermo in 1897 (29,31), he was initially unsure whether to accept the position (29). It was ultimately von Baeyer that persuaded him to accept the chair at Palermo (31) and Angeli then moved there in 1899 (29).

Angeli was called to Florence in 1905 to take up a vacant chair of chemistry at the Istituto di Studi Superiori (32), resulting from the death of Augusto Piccini (1854-1905) (29,30). He was reluctant to leave Palermo, but the poor health of his parents induced him to move back closer to family (29). He was asked to move to Rome in 1909 (29), but declined and remained at Florence where he took the chair of organic chemistry in 1916, a position specifically created for him by the University (30,31). In 1922, he was called back to Bologna to replace his former teacher, Giacomo Ciamician, but again he declined to leave the University of Florence and remained there until his death (29-31). He died from a fatal attack of pulmonary edema on Sunday, May 31, 1931, in his bedroom of a modest hotel where he had lived since his arrival in Florence in 1905 (30).

Angeli has been characterized as shy and introverted (29-31), finding it difficult to speak in public and limiting his participation in conferences or international meetings (30). Due to his nature, he never sought honors and awards. Still, his contributions were recognized, including being awarded the Military Cross for special services performed during World War I (31). In addition,

Angeli was repeatedly a candidate for the Nobel Prize in Chemistry from 1911 to his death (30).

As part of more general studies on the chemistry of pyrrole and indole, Angeli began studying the treatment of pyrrole with hydrogen peroxide/acetic acid mixtures as early as 1915 (22). Exposure of the heterocycle to these oxidizing conditions resulted in the formation of a black precipitate that he named “*nero di pirrolo*” or “*pyrrole black*” (21-23). Typically, one gram of pyrrole was dissolved in a sufficient amount of acetic acid, after which 2-3 grams of 50% H₂O₂ was added. After a short time, the solution became greenish brown, and over the space of a couple of days turned to black-brown. The product could be isolated as a thin black powder, either via spontaneous precipitation, dilution of the final solution with water, or addition of aqueous sodium sulfate (22,23). The product was insoluble in everything but basic solutions and purification methods included dissolution in base, followed by reprecipitation with either acetic acid or dilute sulfuric acid. The purified material was then filtered and dried at 120°C to give a fine powder of dark brown-to-black color (22,23).

Angeli went on to find that pyrrole blacks could be obtained using a variety of oxidizing agents (21), including nitrous acid (24), potassium dichromate (25) or chromic acid (27), lead oxide (25), oxygen and light (26), ethylmagnesium iodide and oxygen (26), potassium permanganate (26), and various quinones (27,28). Comparison of the results obtained from the different oxidants led Angeli to conclude (25):

Questi fatti presentano uno speciale interesse perchè dimostrano che la formazione dei neri di pirrolo molto probabilmente è preceduta da un processo di polimerizzazione della molecola del pirrolo, che si compie in modo più o meno rapido a seconda dei reattivi che si impiegano.

[These facts are of special interest because it shows that the formation of pyrrole blacks is most likely preceded by a process of polymerization of the pyrrole molecule, which takes place more or less rapidly depending on the reagents that are used.]

The isolated pyrrole black greatly resembled the natural pigment family of melanins (33) and chemical analysis revealed that pyrrole black contained N:H:C ratios similar to that of melanin (22,23). Further attempts to probe the structure of pyrrole black were limited by its insoluble nature, but included oxidative degradation to give cleavage products consistent with pyrrole and indole derivatives (22,23,25,26), leading to the conclusion that the pyrrole ring was retained in the structure of pyrrole

black. To further the scope of his study, Angeli found that the treatment of various functionalized pyrrole derivatives with oxidants could produce colored species, but did not result in the production of pyrrole black (24,25). Ultimately, his studies led Angeli to propose that the structure of pyrrole black contained units consisting of direct carbon-carbon bonds between pyrroles as shown in Figure 3a (25). It should be noted that this proposed structure is very similar to the currently accepted structure for oxidized portions of the polypyrrole backbone (Figure 3b).

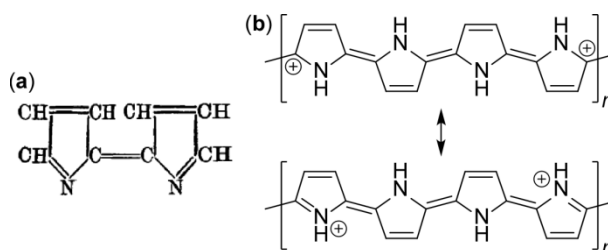


Figure 3. (a) Angeli's proposed basic unit for the structure of pyrrole black (reproduced from Ref. 25); (b) modern resonance structures describing oxidized polypyrrole.

Angeli ultimately concluded his work with pyrrole black in the early 1920s in order to move onto other research topics, although he did return to the subject with one final paper in 1930. At about that same time, however, another student of Ciamician, Riccardo Ciusa, began an independent investigation involving the polymerization of heterocycles in efforts to generate graphitic analogues from pyrrole, thiophene, and furan (34-36).

Ciusa and “Graphite” from Pyrrole

Riccardo Ciusa was born April 27, 1877, in Sassari, on the Italian island of Sardinia (37-39). He attended the Sassari Technical School before beginning studies at the University of Bologna in 1896 (37). In 1899, he then obtained a grant to attend the University of Torino, where he graduated *dottore* in chimica in 1902 (37,38).

After graduation, he returned to Sassari to become assistant of mineralogy for Prof. Boeris at the University of Sassari (37). In 1904, he obtained funding for specialized training abroad and traveled to Strasbourg to work in the laboratory of Prof. Johannes Thiele (37,38). He was then recommended to Prof. Ciamician by Prof. Gaetano Minunni of the University of Sassari, resulting in Ciusa's move to Bologna in 1906 (37).

After a brief time as assistant of agricultural chemistry, Ciusa became an assistant at the Istituto di Chimica

Generale in 1907, under the direction of Ciamician. The following year, he obtained the *libera docenza* in general chemistry, after which Ciusa taught the course on analytical chemistry at Bologna. He also went on to teach the chemistry of dyes and coloring at the newly founded Regia Scuola Superiore di Chimica Industriale di Bologna (37).

During World War I, Ciusa served as an infantry officer in the Italian Army. Upon his return to Bologna, he was named *aiuto* in 1919, a promotion granted to a limited number of the best assistants which included a small increase in salary (37,38). He then continued as assistant to Ciamician until the professor's death in 1922. After Angeli declined to return to fill Ciamician's position, Ciusa was appointed provisional director of the Istituto di Chimica Generale and was charged with taking over the teaching of general chemistry (37).

Ciusa was appointed professor of pharmaceutical chemistry at the University of Cagliari in November of 1922, but he elected to stay at Bologna instead. Then, in November 1924, he was appointed professor of pharmaceutical chemistry for the newly established University of Bari, where he remained until his retirement in 1960 (37-39). His research at Bari focused on pyrrole and its derivatives, including natural pyrrole-based species such as chlorophyll. He later became interested in plant chemistry and photochemistry, and served as Dean of Faculty from 1932-1952 (40).

At the end of his time as Ciamician's assistant, Ciusa began investigating the thermal polymerization of tetraiodopyrrole as a potential route to a material that could be considered a type of graphite generated from pyrrole (34-36). By heating tetraiodopyrrole in vacuum at 150-200°C, he produced a black material with a graphitic appearance. Analysis of this material gave an elemental composition corresponding to $[C_4NHI]_n$ (Figure 4), which Ciusa considered to be an intermediate in the formation of graphite (34-36). He later proposed the two structures given in Figure 5 as possible representations of this intermediate (36).

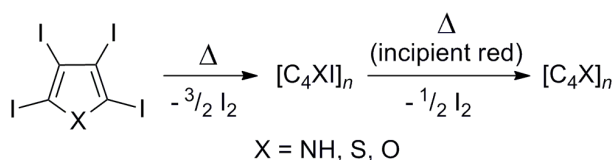


Figure 4. Thermal polymerization of tetraiodoheterocycles

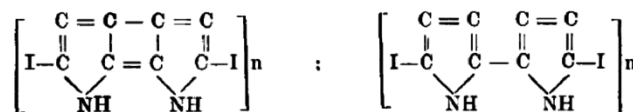


Figure 5. Ciusa's proposed structures for $[C_4NHI]_n$ (reproduced from Ref. 36).

Reheating this material at higher temperature (incipient red) liberated the final iodine atom to give a black material with similar appearance to graphite flakes and an elemental composition of $[C_4NH]_n$ (35). Ciusa went on to repeat this process with both thiophene and furan (Figure 3) to get similar results (35,36). He summarized the results of these efforts as follows (35):

È notevole il fatto che nei tre casi studiati sinora, tre atomi di iodio si eliminano a temperatura relativamente bassa e contemporaneamente, mentre il quarto atomo si elimina in una fase successiva della reazione ed a temperatura più elevata.

[It is remarkable that in the three cases studied so far, three atoms of iodine are eliminated at relatively low temperature and at the same time, while the fourth atom is eliminated in a later stage of the reaction and at a higher temperature.]

Finally, he applied this approach to the thermal polymerization of hexaiodobenzene to produce a graphitic material that he described as similar to ordinary graphite. Measurement of the resistivity of the synthesized material showed the low resistivity expected of graphite, although it was approximately six times more resistive than an authentic sample of graphite (37).

Unfortunately, Ciusa did not attempt to measure the resistivity of the heterocyclic graphites. In addition, he never reported any further characterization of these materials other than their graphite-like appearances and elemental compositions. It is also interesting to note that he never seemed to make any connection between the materials he was producing and the previous reports of pyrrole black by Angeli. Ciusa's work, however, did not go completely unnoticed. Nearly 40 years later, his thermal polymerization studies became the foundation of efforts by Donald Weiss and coworkers to produce conductive organic polymers (14-16).

Weiss and Conducting Polypyrrole

Donald Eric Weiss (Figure 6) was born October 4, 1924 (11,41-44) in the Melbourne suburb of St. Kilda, in Victoria, Australia (11,41,43). He was the only child of H. Vernon Weiss and Lillian née Le Lievre (11,41, 43), who separated when he was only 3 years old (41). Weiss

and his mother then moved to Adelaide (41), where he attended Mitcham Primary School and Scotch College (11,41-43,45). In 1942, he enrolled in the Industrial Chemistry degree program at the South Australia School of Mines (now part of the University of South Australia) (11,41-43). During his first two years, he did most of the courses at the adjacent University of Adelaide, finally transferring there in 1944 (41,43,45). In his third year, he failed Electrical Engineering I and had to repeat it by correspondence from Burnie, Tasmania (41), where he had found employment as a shift chemist for APPM (Australian Pulp and Paper Manufacturers) (41-46). He was ultimately awarded his BSc in 1945 (11,41,42,44).

Wanting to be involved in research, Weiss took a position in 1947 as a development chemist at Commonwealth Serum Laboratories (CSL, Melbourne), where he attempted to improve their new penicillin process (11,41-45). Early in 1947, he attended a meeting of the Royal Australian Chemical Institute (41) where he met Dick Thomas, who was the leader of the Minerals Utilization Section of the CSIR (Council for Scientific and Industrial Research) Division of Industrial Chemistry at Fishermen's Bend (another Melbourne suburb) (11,41,43,45). As a result, Weiss moved to CSIR (now CSIRO) on January 2, 1948 (41,42), to work under Dirk Zeidler in the Chemical Engineering Section, Division of Industrial Chemistry (11,41-45). In October of 1958, Weiss submitted a collection of his CSIR research to the University of Adelaide in support of his candidature for the degree of Doctor of Science (D.Sc.) (11,47). He was awarded the D.Sc. in 1960 (11,41,42,44).



Figure 6. Donald E. Weiss (1924-2008), courtesy of Robert Weiss.

About this same time, Weiss began research on semiconducting organic polymers as potential electrically-activated and easily regenerated adsorbents for a proposed electrical process for water desalination (11,48). These efforts began in 1959 with the preparation of xanthene polymers (48,49). While these organic materials exhibited p-type semiconductor behavior, the measured resistivity was still quite high ($R_{\min} = 7\text{-}20 \times 10^3 \Omega \text{ cm}$) (49).

Weiss then came across the papers of Ciusa (34-36), which suggested that Ciusa's pyrrole "graphite" might provide a new approach for their efforts (11,48). As Ciusa had not reported the electrical properties of his pyrrole materials, Weiss and coworkers set out to reproduce the production of the previously reported pyrrole materials in order to characterize the resulting structure and potential conductivity. Weiss did not follow the exact methods of Ciusa (34-36), but used modified conditions in which a series of polymers was prepared by heating tetraiodopyrrole at temperatures as low as 120°C in a rotating flask under a flow of nitrogen. The nitrogen was used to both maintain an inert atmosphere and to transfer iodine vapor away from the reaction (14). The products of these reactions were reported to be insoluble, black powders, which were described as "polypyrroles" consisting of (14):

...a three-dimensional network of pyrrole rings cross-linked in a nonplanar fashion by direct carbon to carbon bonds.

Analysis of the products revealed that the determined composition did not agree with those reported by Ciusa and considerable amounts of oxygen were also found. It must be noted that Ciusa prepared his material in vacuum, while Weiss prepared his material under a nitrogen flow, which could at least partially account for the differences. Weiss, however, concluded that the oxygen arose from the adsorption of water and oxygen during the isolation and grinding of the product. This was then at least partially verified by finding that the oxygen could be driven off with heat, with the polymer then reabsorbing oxygen upon standing (14). In addition, it was found that the materials contained both "adsorbed molecular iodine" and nonreactive iodine which was concluded to be "iodine of substitution" (11,14). Based on the various descriptions given by Weiss and coworkers, a hypothetical structure for the polymeric material is given in Figure 7.

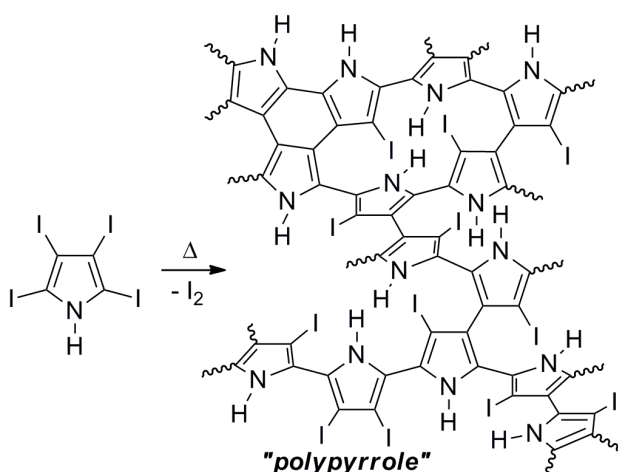


Figure 7. Hypothetical structure of Weiss's polypyrrole.

Electronic characterization of the polypyrrole powders were then carried out by measuring the resistivity (R) of pressed pellets under a stream of nitrogen to give values of 11-200 Ω cm at 25°C (16,50). In addition, a temperature-dependent study of the resistivity provided a temperature profile consistent with a standard semiconductor (16). These values correspond to conductivities ($1/R$) of 0.005-0.09 Ω^{-1} cm $^{-1}$ and while they are still below that of carbon black, they are drastically better than the previous xanthene polymers and represented the highest reported conductivities for a non-pyrolyzed organic polymer. Weiss described the nature of this conductivity as follows (16):

However it is apparent that the polymers are relatively good conductors of electricity. Since no polarization was observed during the measurement of the electrical resistance, even over substantial periods of time, it is assumed that the conductivity is of electronic origin.

Of significant interest was the discovery that the removal of adsorbed molecular iodine by either solvent extraction (16), chemical or electrochemical reduction (14,15), or thermal vacuum treatment (16) resulted in a significant increase in resistance. Electron spin resonance (ESR) studies then provided evidence for the formation of a strong charge-transfer complex between the polymer and iodine (15). This led to the following conclusion (16):

Charge-transfer complexes of strength sufficient to cause partial ionization induce extrinsic [semiconductor] behaviour by changing the ratio of the number of electrons to the number of holes.

Thus, they understood that (14):

The presence of the oxidant iodine, and in its absence oxygen, facilitates oxidation of the polymer.

Of course, this oxidative process (Figure 8) describes what would later be called p-doping of the polymer, which was ultimately determined to be the key to produce highly conductive organic polymers (1,6-9,13). Weiss, however, admitted that the full role of the iodine oxidation to conductivity was not realized at the time (48).

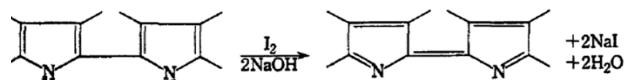


Figure 8. Iodine oxidation of polypyrrole under basic conditions (reproduced from Ref. 15 with permission of CSIRO Publishing).

Weiss and coworkers went on to study a few more related polymers (51-53), but ultimately determined that the use of these organic polymers for an electrical desalination process was impractical and thus moved on to other projects by 1967 (11,48). In February 1974, he became the Chief of CSIRO's newly formed Division of Chemical Technology (41) and it was during these years that he made his most well-known contributions. Most notable of these were the development of magnetic ion-exchange resins and SIROFLOC, a large-scale continuous water treatment process (43,45,48). During his career, Weiss earned a number of prestigious awards, including his being made an Officer (OBE) of the Most Excellent Order of the British Empire in 1976 for his contribution to science (11,42,43). After 36 years at CSIRO, Weiss retired in October of 1984 (11,41-43,48). He then passed away on July 30, 2008, in the eastern suburb of Blackburn (41) due to pneumonia brought on by a battle with lung cancer (43,54).

Pyrrole Black at the University of Parma

About the time that Weiss and coworkers were wrapping up their work with the polypyrrole-iodine materials, resurgence in the study of pyrrole black was occurring in Italy at the University of Parma. This was primarily due to the research of Luigi Chierici (d. 1967), Gian Piero Gardini (d. 2001), and Vittorio Bocchi (55-61). While the specifics of their collaborations are not clear, it appears that Chierici was the guiding force behind these efforts as he was already studying pyrrole black as early as 1953, before either of the others had come to Parma. Of the three, it is Gardini of whom we have the most knowledge. After receiving a degree in Industrial Chemistry from the University of Bologna in 1961, he moved to the University of Parma in 1962 and joined Chierici as a professor in the Institute of Pharmaceutical

Chemistry (62). The final member, Bocchi, then joined them about 1966. The three did not work together for long, however, as Chierici died on March 3, 1967 (58,61), leaving Gardini and Bocchi to carry the research forward.

Parma founded the Institute of Organic Chemistry in 1968, which included both Gardini and Bocchi as faculty. Within this new organizational structure, both men worked under the Director of the Institute, Prof. Giuseppe Casnati (63). Gardini was then appointed to the chair of organic chemistry in 1980 (62,64). In 1984, he succeeded Prof. Casnati as Director of the Institute, which then became the Department of Organic and Industrial Chemistry in 1992, with Gardini remaining as Director (62,63). He continued as Director of the Department until 1998 (62,63), before dying in 2001 (64).

These efforts were a fairly direct extension of the previous work of Angeli. Most of their efforts focused on identifying the intermediates and byproducts formed during the oxidative polymerization of pyrrole with H_2O_2 (55-58), with Gardini concluding in 1973 that the mechanism needed much more research to be well defined (18). However, the most significant results came via collaboration with Parma's Institute of Physics, which focused on ESR studies of pyrrole black (59,60). The first of these studies utilized pyrrole blacks produced via Angeli's initial H_2O_2 /acetic acid conditions (59). In the second study, however, the polymeric material was obtained via electrolysis (60), thus representing the first example of an electropolymerized polypyrrole (18,19). The polymer was obtained by applying a constant current of 100 mA to a platinum electrode in a solution of pyrrole in H_2SO_4 . Over a period of two hours, a laminar film formed on the electrode, which was then rinsed with distilled water and dried under vacuum (60). X-ray analysis of the film indicated that the material was essentially amorphous and conductivity measurements gave a room temperature value of $7.54 \Omega^{-1} \text{cm}^{-1}$, considerably higher than that reported by Weiss and coworkers for the thermally-produced polypyrrole-iodine materials (16). It should be pointed out that these results were not compared to the previous work of Weiss and coworkers, nor is there any evidence that the Parma researchers were even aware of previous reports of conducting polypyrrole materials. Lastly, the ESR studies indicated the presence of antiferromagnetic interactions, strongly interacting polymer chains, and highly mobile electrons, although the spin density was found to not be very high (60).

In an additional study, Chierici and Bocchi then analyzed the electropolymerized material via oxidative degradation (61). While additional degradation products

of unknown composition were detected in comparison to the traditional pyrrole blacks produced via H_2O_2 oxidation, the major product for all materials was pyrrole-2,5-dicarboxylic acid. This led to the conclusion that all of the pyrrole blacks studied consisted of chains of α,α' -linked pyrroles (Figure 1) (61).

In 1975, Gardini spent time as a visiting scientist at the IBM Research Laboratory in San Jose, California (62). This initial visit was repeated with additional stays in 1978 and 1981 (62). It was during these visits that Gardini began working with Arthur Diaz.

Diaz and Electropolymerized Polypyrrole Films

Arthur F. Diaz was born in 1938 in southern California (65). After high school, he attended San Diego State University, receiving a B.S. in Chemistry in 1960 (66,67). He then pursued graduate studies at UCLA under Dr. Saul Winstein (1912-1969), earning his Ph.D. in 1965 (65-67). He stayed on at UCLA, first as a post-doctoral researcher and then a research associate, before eventually being hired by TRW Systems (66). He then joined the Department of Chemistry at the University of California, San Diego, as an Assistant Professor in 1969 (66,67). In 1974, he spent one year as a Program Officer for the Educational Division of the National Science Foundation, before returning to California to join the IBM Almaden Research Laboratory in San Jose, where he became manager of the Advanced Materials group (66,67). After 20 years at IBM, he retired in 1995 and joined the Department of Chemical and Materials Engineering at San Jose State University (66,67).

Upon arriving at IBM, Diaz was charged with developing a new project of significant impact, preferably in the area of electrochemistry, as IBM was interested in building capabilities in this area (66). This led to an interest in modifying the surfaces of electrodes, resulting in some time studying monolayers and thin films. Conducting polymers were becoming a current hot topic, and he considered the use of such materials for modified electrodes, but was unsure as to how to make this work with polyacetylene (66). It was at this point, during one of Gardini's visits to IBM, that Gardini mentioned to Diaz about the pyrrole black work being done at Parma, particularly the most recent success in electropolymerization (66).

The combination of the material's intractability and conductivity intrigued Diaz and thus he began investi-

gating the generation of electropolymerized films (66). After a matter of time, Diaz was able to perform the electropolymerization of pyrrole under controlled conditions, allowing the generation of strongly adhered films onto electrode surfaces in a reasonable and repeatable manner (17,66). Diaz found that the use of deoxygenated aprotic solvents resulted in better material properties (17,68) than the previous aqueous conditions utilized in the Parma work (60). Under optimum conditions, the polypyrrole films were synthesized galvanostatically on a platinum surface from pyrrole in a 99:1 acetonitrile-water mixture with tetraethylammonium tetrafluoroborate as a supporting electrolyte (17,19,68). It was found that the water content of the solution could be used to control the adherence of the film to the substrate. Absence of water produced poorly adhering, non-uniform films, while adherence improved with increasing amounts of water (68).

Elemental analysis of the material indicated that it was primarily coupled pyrrole units, plus BF_4^- anions, in the ratio of ca. 4:1 (17,68). It was concluded that the pyrrole units of the polymer backbone carried a partial positive charge balanced by the BF_4^- ions (69,70). The pyrrole-linked structure was confirmed by Raman and reflective IR analysis showing bands characteristic of pyrroles (69). Consistent with the previous Parma study, electron diffraction indicated that the films were not very crystalline, showing only diffuse rings corresponding to a lattice spacing of 3.4 Å (69).

The electrical conductivity of thicker free-standing films (5-50 mm) were examined via four-point probe to give room temperature conductivities of $10\text{-}100\ \Omega^{-1}\ \text{cm}^{-1}$ (17,18,68-70). Diaz thought that the drastically improved conductivity in comparison to the Parma results was at least partially due to higher quality films resulting from the fact that he grew his films slowly and very thin (70). In comparison, his impression was that the Parma films were quite thick (66). It is now fairly well understood that the structural order of the film decreases with the corresponding film thickness, which also results in a decrease in film conductivity. As with the previous materials reported by Weiss and coworkers (16), temperature-dependent conductivity measurements of the electropolymerized films revealed a temperature profile consistent with a classical semiconductor (69,70).

Conclusions

The above discussion has hopefully illustrated the extensive work reported on polypyrrole dating back to the earliest work of Angeli in 1915, nearly 65 years

before the seminal work of Diaz in 1979. While most of these reports used the earlier term of *pyrrole black* to refer to these materials, it is quite clear from their discussions and analysis that these materials in question were polypyrrole. In addition, the electrically conductive nature of this material has been known since the work of Weiss and coworkers in 1963, with the magnitude of its conductivity significantly increasing with each sequential improvement in the polymer's production. It is also important to note that with the exception of the work of Diaz, all of the research presented above occurred before the collaborative polyacetylene work of Heeger, MacDiarmid, and Shirakawa (10-13). As such, it is hard to support the statement quoted in the introduction that these three gentlemen discovered electrically conductive polymers, although their early contributions definitely sparked the broad interest in the field.

It should also be pointed out that the work of Diaz and coworkers discussed herein has significance beyond the simple fact that it represented the highest conductivity of polypyrrole in the early years of the growing field of conjugated organic polymers. While he was not the very first to report the electropolymerization of a conjugated polymer, Diaz was the one that not only optimized this process in terms of quality and reproducibility, but then demonstrated that this could be broadened to a wide family of conjugated systems. As a result, electropolymerization quickly became the most common method for the generation of conjugated polymeric films, until it was ultimately supplanted by the current focus on soluble, processible materials.

Acknowledgements

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