BIOGRAPHICAL MEMOIRS

Alan G. MacDiarmid

April 14, 1927–February 7, 2007
Elected to the NAS, 2002

A Biographical Memoir by Richard B. Kaner and Andrew B. Holmes

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Alan G. MacDiarmid was a pioneer in the field of synthetic metals. His work on the first conducting polymer, polyacetylene, in collaboration with physicist Alan Heeger, showed that it was possible to combine three non-metallic elements—carbon, hydrogen, and iodine—to create a polymer that possessed an electrical conductivity comparable to that of metals. This opened a new area of research that has led to improved light-emitting diodes, colored screens for cell phones and television, and the promise of inexpensive solar cells and flexible electronics. In 2000, MacDiarmid and Heeger, along with Hideki Shirakawa, who made the first freestanding golden films of polyacetylene, shared the Nobel Prize in Chemistry.

Alan MacDiarmid was born in the small town of Masterton, New Zealand, (population 8,600) on April 14, 1927. He had four siblings and described his family as "warm, loving united and mutually supportive."[1] His father, Archibald, was an engineer who found himself unemployed during the Great Depression, so he moved the family nearer to the New Zealand capital of Wellington, where he found a job with a petroleum company. His family lived frugally, and Alan earned money by delivering milk and the local newspaper. He later recalled walking to school in bare feet, which was not that unusual in those days in New Zealand. Alan's family showed great hospitality to others less fortunate than themselves and had a tradition called "FHB," meaning "family hold back" to ensure that there was sufficient food to serve to guests. Alan's brother Roderick said that Lord Ernest Rutherford was a friend of his father and occasionally visited the family. MacDiarmid would join Lord Rutherford as the only other New Zealander to be awarded the Nobel Prize in Chemistry.[2]

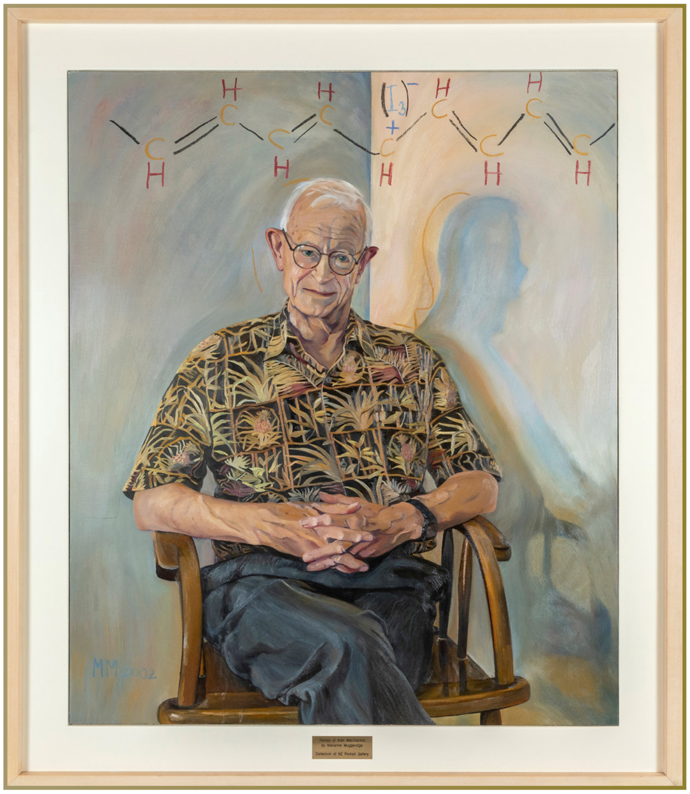

Figure 1 Portrait of Alan G. MacDiarmid. *Copyright Marianne Muggeridge, oil on linen, 2002. Courtesy of the artist and the New Zealand Portrait Gallery.*

Alan's interest in chemistry started at the age of ten when he found a book at the local library entitled *The Boy Chemist* (1924) by A. Frederick Collins, which he later noted would now be renamed to make it gender neutral. Alan checked this book out continually and completed most of the experiments in it within a year. He put his knowledge to use on Guy Fawkes Day with a homemade fireworks display. When his father retired on a low pension, Alan was forced to leave secondary school and get a job as a lab boy at Victoria University in Wellington.

Alan graduated from cleaning duties and washing glassware to providing classroom demonstrations for A. D. Monro, one of only two academic staff at Victoria University. Alan then embarked on a four-year part-time bachelor of science degree, followed by a master of science degree. During this time, he developed an interest in tetrasulfur nitride (S_4N_4), which produces bright orange crystals. This experience would lead to his subsequent collaboration with Alan Heeger at the University of Pennsylvania.

There were no doctoral programs in the southern hemisphere at that time, so Alan was keen to move to the United Kingdom to continue studying in an advanced research program. Although his bid for an 1851 Exhibition Research Fellowship did not succeed, a friend mentioned the newly created Fulbright Scholarship for study in the United States. He was awarded a Fulbright and steered by the U.S. Consul to the University of Wisconsin for its excellent reputation for inorganic chemistry. Alan thought he would only be there for two semesters, but with further financial support from the Wisconsin Alumni Research Foundation, he spent three years working with Norris Hall to earn a Ph.D. studying exchange kinetics in ^{14}C and ^{15}N-labeled hexa-cyano-complexes of transition metals.[3]

Alan was still interested in visiting the United Kingdom and on the advice of a friend applied for a Shell New Zealand Fellowship. This enabled him to go to the University of Cambridge and work with Harry J. Emeléus on silicon hydrides, for which he was awarded a second Ph.D. in 1955.[4] While at Wisconsin, Alan had met Marian Mathieu, and they were married in Cambridge on July 10, 1954. They had four children: Heather, Dawn, Duncan, and Gail, and were together for thirty-six years until Marian's untimely passing in 1990.

After teaching for six months at Queen's College at the University of St. Andrews in Scotland, Alan was recruited to the University of Pennsylvania (Penn) in Philadelphia as an instructor in chemistry. His initial research continued on silicon hydrides with funding from the Air Force Office of Scientific Research, as these materials were of interest as potential rocket fuels. His research on derivatives of S_4N_4 attracted support from Ken Wynne at the Office of Naval Research (ONR). With his coworkers, Alan published more than ninety papers on these two topics over the next twenty years, leading to his receiving the American Chemical Society's (ACS) prestigious Frederic Stanley Kipping Award in Silicon Chemistry in 1971. Alan moved through the academic ranks from assistant to associate to full professor at Penn, culminating in an appointment as the Blanchard Professor of Chemistry in 1988.

In response to the launch of Sputnik, the U.S. Department of Defense, through the Defense Advanced Research Projects Agency, funded the creation of the Laboratory for Research on the Structure of Matter (LRSM) to carry out interdisciplinary materials research at Penn. LRSM broke ground in 1962 and was completed two years later, with both MacDiarmid and Heeger as founding members.

At a meeting in MacDiarmid's office, Heeger mentioned the work of Mortimer Labes at Temple University in Philadelphia in which he reported that polysulfur nitride, $(SN)_x$, was an electrical conductor. Because MacDiarmid had worked on S_4N_4, a precursor to $(SN)_x$, it made sense for him to investigate its synthesis. In fact, research conducted with Anthony F. Garito showed that pure $(SN)_x$ could be prepared by slowly and carefully growing explosive crystals of S_2N_2 from the vapor phase at 0 °C (over forty-eight hours) followed by solid-state polymerization at room temperature over three days, resulting in beautiful golden crystals.[5] The conductivity was metal-like, and doping with bromine led to shiny black crystals with a conductivity of 3.8×10^4 S cm^{-1}. These crystals were subsequently shown to be superconducting below 0.26 K.[6]

In 1975, while MacDiarmid was a visiting professor at Kyoto University, he was invited to give a lecture on $(SN)_x$ at the Tokyo Institute of Technology. After displaying his golden crystals, Alan was told there was a researcher there, Hideki Shirakawa, who made golden films. He had missed the lecture and was invited to meet Alan over tea. On seeing the golden films of polyacetylene, Alan enquired about their conductivity, which was 10^{-5} S cm^{-1}, making this material a semiconductor with an electrical conductivity comparable to silicon. Alan immediately invited Shirakawa to visit his lab at Penn so they could dope the polymer in hopes of increasing its conductivity as with doping $(SN)_x$.

Fortunately, Ken Wynne at ONR came up with the $21,650 needed to sponsor Hideki Shirakawa's six-month visit to Penn. Ken has noted that these were the most productive funds he provided as a program manager, because they led directly to the Nobel Prize-winning work. Once at Penn, Shirakawa demonstrated how golden films of polyacetylene could be grown on the surface of a Ziegler-Natta catalyst when using a one-thousandfold higher than usual concentration of a titanium tetrabutoxide-triethyl aluminum catalyst.[7] Years earlier, Giulio Natta, had tried to polymerize acetylene, but only produced a black precipitate. He later would share the 1956 Nobel Prize in Chemistry with Karl Ziegler for their development of the catalysts that would open up the field of inexpensive ways to make the polymers that we use every day, such as polyethylene and polypropylene. Because no one else had studied this polymerization in any detail, Shirakawa thought this might be a useful area for research and discovered how to make films. The story of this fortuitous discovery is well documented in a retrospective on this field of science.[8] Once at Penn, MacDiarmid's team

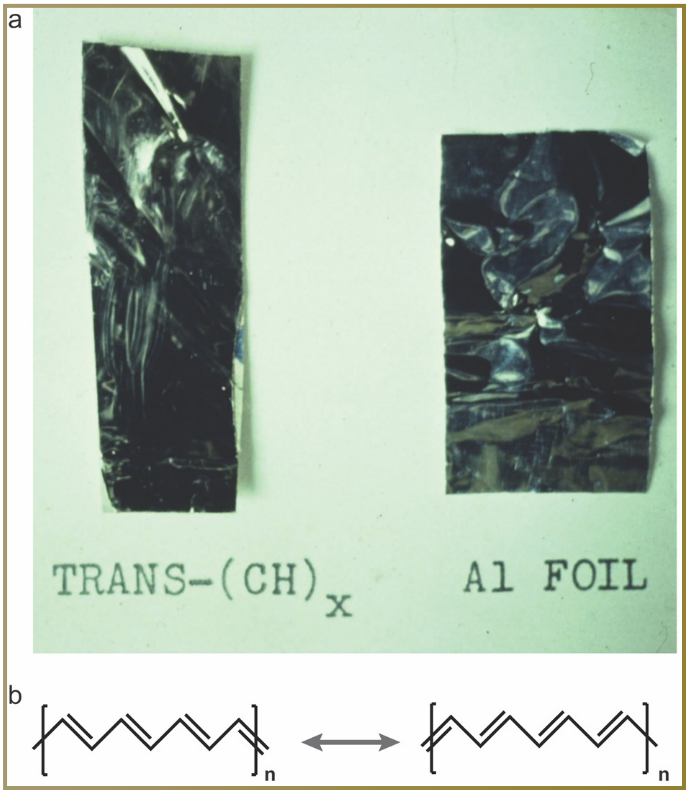

Figure 2 a. A photo of trans-polyacetylene, $(CH)_x$, taken alongside aluminum foil. b. The degenerate (equal in energy) ground state structure of trans-polyacetylene.

originally tried doping the polyacetylene films with bromine. This worked initially but then led to overoxidization as bromine starts to add across the double bonds within hours, thus lowering the conjugation and diminishing the conductivity. By using the milder oxidizing agent iodine, they were able to make metallic polyacetylene films that were stable in an inert atmosphere and could even be handled in air. The doped films produced in MacDiarmid's lab with Shirakawa's help were then taken to Heeger's lab across the street, where they measured a conductivity in excess of 1,000 S cm^{-1}.[9,10] Because this conductivity is comparable to metallic mercury, the first flexible metallic polymer had been created![11]

MacDiarmid and Heeger continued to study polyacetylene for the next several years. They showed that the doping mechanism involved delocalized electrons that were free to move along the conjugated backbone of trans-polyacetylene [Figure 2]. Because trans-polyacetylene has a degenerate conjugated backbone (in other words, the alternating single and double bonds are equal in energy in either direction), solitons (solitary waves that hardly dissipate) were shown to be the main mechanism behind the electrical conductivity.[12] This led to the concept of spinless conductivity as the p-type dopants created empty bands of spinless mobile solitons. MacDiarmid and Heeger then demonstrated n-type doping of polyacetylene using alkali metals.[13] Although these materials would ignite in air, they were quite stable in an inert atmosphere or under vacuum. The n-doped polyacetylene films also exhibited spinless conductivity, this time as a result of n-solitons, in other words, a band of mobile states filled with paired electrons. Once the doping level of either p-type or n-type doped polyacetylene exceeded a few percent, the material exhibited the classical properties of metals, including Pauli-type paramagnetism and reflectivity.

Although the early promise of metal-like doped polyacetylene excited people's imagination for creative uses, such as rechargeable batteries for electric vehicles,[14] the fact that doped polyacetylene lacked air stability meant that it was not suitable for most applications. Therefore, researchers began exploring other conjugated polymers, including polythiophenes, polypyrroles, and polyanilines and their derivatives. In fact, not long after his discovery of doped polyacetylene, MacDiarmid started searching for a more processable and stable conducting polymer. He decided that polyaniline was most promising because the starting monomer, aniline, is one of the world's most-used chemicals. In fact, almost all of the blue, green, and black colors in the clothes we wear stem from aniline derivatives.

Although polyaniline had initially been explored in the early 1900s, Alan was able to advance the field by exploring its ability to be doped by essentially any strong acid.[15,16] After Heeger moved to the University of California, Santa Barbara in 1982, MacDiarmid began a very fruitful collaboration on polyaniline with the physicist Arthur Epstein at the Ohio State University. They confirmed that polyaniline could be made in different oxidation states, including the fully reduced leuco-emeraldine form, the half oxidized emeraldine form, and the fully oxidized pernigraniline form. Note that these forms are named after their colors: white, green, and black, respectively. After studying the interconversion of the different forms of polyaniline, they found that only the doped emeraldine oxidation state gave high electrical conductivity [Figure 3].[17] MacDiarmid and Epstein then discovered that doping polyaniline with strong acids in the solvent m-cresol produced highly conducting polyaniline because it created a more ordered form of the polymer. They called this effect secondary doping, noting, "A secondary dopant differs fundamentally from a primary dopant in that the new properties it imparts may persist, albeit to a reduced extent, even after its complete removal."[18]

MacDiarmid's pioneering research into conducting polymers would eventually lead to their application in many commercial products. But because most of these uses involve such things as antistatic coatings and electromagnetic shielding, we don't normally think about the conducting polymers inside the products that make this possible. The most widely

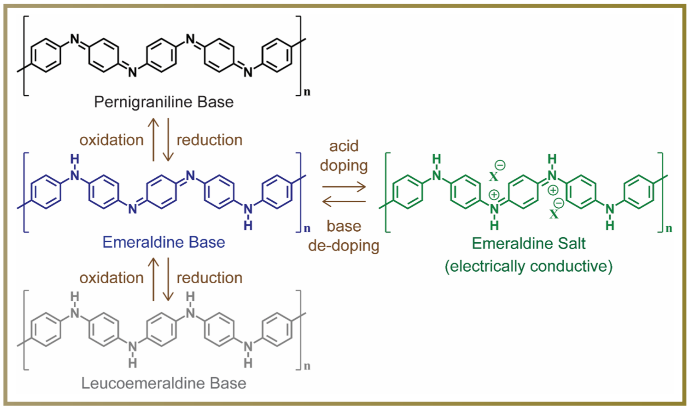

Figure 3 Molecular structures of polyaniline in its pernigraniline (oxidized), emeraldine (middle oxidation), and leuco-emeraldine (reduced) forms. The emeraldine salt becomes electrically conductive after acid doping.

used conducting polymer is a derivative of polythiophene called PEDOT:PSS, which stands for poly(3,4-ethylenedioxythiophene) polystyrene sulfonate.[19] The polystyrene sulfonate dopant acts as a surfactant and makes this polymer processable in water. Conducting polymers have helped improve capacitors, light-emitting diodes, and colored screens for cell phones and televisions.[20,21] They have even been used in oil and water separation membranes.[22,23] Conducting polymers hold great promise for inexpensive solar cells and flexible electronics. Many researchers are now studying artificial muscles, wearable electronics, and even bionic parts made using these materials.

Alan MacDiarmid had an outsized personality that left a lasting impression on those who were fortunate enough to meet him at scientific conferences or other venues. He said that the most important thing to do when listening to a lecture is to formulate a question, whether you ask it or not. The more far-afield the lecture is from your area of expertise, the more difficult this becomes, but it will focus your attention on the speaker. Alan made great efforts to attend student poster sessions and ask questions of the students. Alan was well known for several of his favorite sayings, including “science is people” and “the harder I work the luckier I get.”

Alan invited his research group each summer to a cabin he owned in the Pocono Mountains of Pennsylvania, a couple of hours by car from Philadelphia. Alan had a boat that he drove and taught his students how to water ski.

Alan MacDiarmid received recognition for his extraordinary work on conducting polymers. The ACS honored Alan with the Award in the Chemistry of Materials in 1999. The next year, he received the Rutherford Medal from the Royal Society of New Zealand and the shared Nobel Prize in Chemistry. In 2002, Alan was elected as member of both the National Academy of Sciences and the National Academy of Engineering. That year he also received the ACS William H. Nichols Medal for materials chemistry and was presented with the Order of New Zealand. In 2003, he become a Fellow of the Royal Society and in 2004 was presented with the Friendship Award from the People’s Republic of China. There are now several institutes around the world honoring the legacy of Alan MacDiarmid. They include the Alan G. MacDiarmid Institute at the University of Texas at Dallas, where Alan held a joint appointment starting in 2002; the MacDiarmid Institute for Advanced Materials and Nanotechnology, headquartered at the University of Auckland in New Zealand; and the MacDiarmid Institute of Organic Nanomaterials at Jilin University, in Changchun, China. Other MacDiarmid Institutes have been established in Brazil, India, and South Korea. Alan MacDiarmid made many visits to Australia, where he chaired the International Advisory Committee for the University of Wollongong’s ARC Centre of Excellence for Electromaterial Science.

Alan was very generous with his time. After he gave the plenary lecture at the International Conference on the Science and Technology of Synthetic Metals in Ireland at Trinity College Dublin, he asked one of us (RBK) to meet with him to discuss the latest research on nano-polyaniline.[24] During the discussion, he was handed two fountain pens, one green containing doped polyaniline in the emeraldine oxidation state and the other blue containing polyaniline in its de-doped state. Alan was very excited to see that polyaniline, simply by making it nanostructured, became processible in water. Alan carried these fountain pens containing polyaniline ink around with him for the last few years of his life, showing them to anyone interested in conducting polymers. Alan MacDiarmid passed away on February 7, 2007, in Philadelphia.

Note

This memoir is adapted from a corresponding Royal Society Biographical Memoir: Alan Graham MacDiarmid, Holmes, A. B.; Klein, M. L.; Baughman, R.H. *Biogr. Mems. Fell. R. Soc.*, 2023, 74, 259-282, https://doi.org/10.1098/rsbm.2022.0045.

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