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## Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa

Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa at a reception during the International Conference on Synthetic Metals, organized in Gastein, Austria, in July 2000.

December 10, 2001, marked the 100th anniversary of the first award ceremony of Nobel Prizes. It was also the first anniversary of the award to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa of the Nobel Prize in Chemistry for their "discovery and development of conductive polymers". The path that brought together this trio of scientists born on three continents and comprised of a condensed-matter physicist, a polymer chemist, and an organometallic chemist tells a story on the importance of scientific curiosity, serendipity, interdisciplinary research, and the pursuit of beauty.

Alan Heeger was born in Sioux City, Iowa, in 1936, the son of a Jewish immigrant who had arrived with his parents from Russia in 1904. Alan and his brother were the first members of their family to receive a college education. After undergraduate studies at the University of Nebraska, he went to Berkeley where he worked in the group of Professor Alan Portis for his Ph.D. Immediately after completing his degree in 1962, he joined the Physics Department at the University of Pennsylvania, where he was to work for the following 20 years. In 1982, Alan Heeger was lured to the University of California at Santa Barbara where he established, together with Fred Wudl, the Institute for Polymers and Organic Solids. In 1990, he founded UNIAX Corporation with Paul Smith.

Alan MacDiarmid was born "down under" in Masterton, New Zealand, in 1927. After obtaining his M.Sc. degree at the University of New Zealand in 1950, he first came to the US, completing a Ph.D., at the University of Wisconsin in 1953, before embarking on a second Ph.D. that he completed in 1955, at Cambridge

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**Figure 1.** Picture of a *trans*-polyacetylene sample provided by Professor Alan Heeger, October 2001 (picture courtesy of Demetrio Filho).

University. He then crossed the Atlantic again to join the Faculty at the University of Pennsylvania where he is currently Blanchard Professor of Chemistry.

Hideki Shirakawa was born in Tokyo in 1936 and received all of his university education at the Tokyo Institute of Technology. After completing his Ph.D. in 1966, he joined the group of Professor Sakuji Ikeda at the same institution and began to investigate the polymerization of acetylene to elucidate the polymerization mechanism induced by Ziegler–Natta catalysts. In 1979, Hideki Shirakawa became Full Professor at the University of Tsukuba; he is now Emeritus Professor, having reached the mandatory retirement age last year. He has recently been asked to join the Council for Science and Technology Policy of Japan, a 15-member Council headed by the Japanese Prime Minister.

In 1967, Hideki Shirakawa made what turned out to be the key initial observation on the road to intrinsically conducting organic polymers. Thanks to a student inadvertently increasing the Ziegler–Natta catalyst concentration 1000 times more than what was called for the traditional polymerization recipe, the acetylene polymerization led, for the first time, to the formation of a beautiful silvery polyacetylene thin film (Figure 1), instead of the usual black powder.[1]

Meanwhile, at Penn, the Heeger–MacDiarmid collaboration started in 1975 when Alan Heeger, having studied metallic organic molecular crystals of the TTF-TCNQ type, became interested in the first metallic polymer, poly(sulfur nitride), $(SN)_x$. Having learned that Alan MacDiarmid had a background in sulfur nitride chemistry, Alan Heeger convinced to get him involved in the synthesis of the polymer. Soon, MacDiarmid succeeded in producing beautiful-looking, golden films of $(SN)_x$.[2]

Later that year, Alan MacDiarmid spent time in Japan as a Visiting Professor at Kyoto University and toured several other institutions. At the reception after a lecture he had given at Tokyo Institute of Technology, enthusiastic as always, he was showing around some of his golden $(SN)_x$ films, when one of the local professors (who it turns out had not attended his lecture) approached him with polymer films of his own: it was Hideki Shirakawa introducing him to polyacetylene, $(CH)_x$. Alan MacDiarmid was immediately attracted by the beauty of the silvery films and his instinct told him that there would be interesting things to come. Upon his return to Penn, he convinced Ken Wynne, the polymer program officer at the Office of Naval Research, to supplement his ONR grant to allow Hideki Shirakawa to come to Penn for an extended stay. Thus, when Hideki arrived at Penn in the late summer of 1976, the Heeger–MacDiarmid–Shirakawa trio was formed.

Research on $(SN)_x$ had shown earlier that treatment of crystalline films by halogens results in an increase in electrical conductivity by about 1 order of magnitude. The trio had therefore the idea of applying the same kind of redox chemistry (doping) to polyacetylene films. Two days before Thanksgiving 25 years ago, on November 23, 1976, C. K. Chiang, a postdoc with Alan Heeger, and Hideki Shirakawa performed the experiment in the basement of the Laboratory for the Structure of Matter at Penn. To their amazement, as soon as they deposited a drop of bromine on the polyacetylene film, the electrical conductivity jumped 10 000 000 times.[3] The era of organic conductive polymers had begun.[4]

Entirely new physical and chemical concepts evolved. After his return to Japan, Hideki Shirakawa devoted his time to perfecting the synthesis of polyacetylene and other conjugated polymers and to improving their mechanical properties, opening the way to intrinsically conducting plastics. In 1979, together with his friend Robert Schrieffer (the 1972 Nobel Laureate in Physics for his contributions to the microscopic theory of superconductivity) and Wu-Pei Su, Alan Heeger introduced the concept of solitons in degenerate ground-state structures such as *trans*-polyacetylene;[5] solitons were then followed by polarons and bipolarons. Even though it took some time for these models to be translated into chemical language, they are nowadays an integral part of the description of conjugated polymers and their evolution upon doping. Later that same year, Alan MacDiarmid, his postdoc Paul Nigrey, and Alan Heeger realized that polyacetylene can be repeatedly doped and dedoped electrochemically;[6] that discovery stimulated much work aimed at developing conducting polymer-based batteries and electrochromic displays. Alan MacDiarmid made another intriguing discovery when working on an old polymer, polyaniline, whose synthesis he had signifcantly refined. When exposed to a Brønsted acid such as HCl, the semioxidized form of polyaniline, emeraldine base, switches from electrical insulator to conductor. The protonation process in fact produces an increase in electrical conductivity by over 12 orders of magnitude, even though the number of electrons on the emeraldine chains remains constant.[7] This observation led to that concept of what is now often referred to in the literature as protonic acid doping.

These discoveries triggered the development a new, multidisciplinary field, the field of synthetic metals, at the crossroads of chemistry, physics, materials science, engineering, and, more recently, biology. A series of conferences were launched, now organized as the International Conferences on the science and technology of Synthetic Metals (ICSM); in parallel, the journal Synthetic Metals was born, with Alan Heeger serving as Editor-in-Chief for some 15 years until last year and with Alan MacDiarmid and Hideki Shirakawa on the board of Regional Editors.

By the early 1990s, the field had matured to the point that a Nobel Symposium was organized in Luleå, Sweden, near the Arctic Circle, in June 1991. At that occasion, Professor Bengt Rånby, a key figure of polymer science in Sweden, remarked that the discovery of conductive polymers by this trio, marked the advent of the "fourth generation of polymeric materials".[8,9] Other major discoveries that were made around the same time have now opened up the field of plastic electronics and photonics and promise a wide range of novel applications exploiting the electrical semiconductivity, the flexibility, and the simple deposition properties of conjugated polymers; for instance, the discovery by Professor Richard Friend and his group at Cambridge of electroluminescence in poly(*p*-phenylene vinylene), PPV,[10] and the discovery of ultrafast charge transfer in fullerene−PPV composites in Alan Heeger's group.[11]

Since 1976, Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa have continuously kept pushing the limits of the science and technology of synthetic metals. Their pioneering investigations and their never-failing enthusiasm have been a tremendous source of inspiration for all of us that work in this field and have stimulated many a young scientist to start studying the fascinating world of conjugated polymers. Their work is also a remarkable example of how science has evolved over the past decades, crossing over the barriers of disciplines and emphasizing the importance of collaborations among researchers with very different backgrounds. For all these accomplishments, we wish to congratulate them. We would also like to thank them for the pleasure it has been to collaborate with them for some 20 years.

## References and Notes


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(3) It is interesting to note that the effect of bromine was so dramatic that C. K. Chiang felt the need to take his apparatus apart to check for a short circuit and make sure nothing was broken (Chiang, C. K., personal communication).

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(9) Sadly enough, Professor Rånby passed away the very day of the announcement of the 2000 Nobel Prize in Chemistry on October 10, 2000.

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