Chapter 8
Historical Background (Or: There Is Nothing New Under the Sun)

As we mentioned in Chap. 1, the 2000 Nobel Prize in Chemistry was awarded to Heeger, MacDiarmid, and Shirakawa “for the discovery and development of electrically conductive polymers”.

However, as is the case for many other scientific discoveries, there were actually several forerunners of Heeger, MacDiarmid, and Shirakawa. Indeed, in this context, it is worth considering another example from the field of electrochemistry: the renaissance of fuel cells, which were discovered independently by W.R. Grove and Ch.F. Schönbein in 1839.

Our case is also curious because the most important representatives of these materials, polyaniline and polypyrrole, were already being prepared by chemical or electrochemical oxidation in the nineteenth century. Of course, for a long time they were not called polymers, since the existence of macromolecules was not accepted until the 1920s, and it was decades before H. Staudinger, W. Carothers, P. Flory, and other eminent scientists could convince the community of chemists that these unusual molecules were real.

Therefore, it is somewhat interesting to review the story of polyaniline here, because it provides an insight into the nature of the development of science.

One may recall that aniline was prepared from the coal tar residues of the gas industry in the first half of the nineteenth century, and later played later a fundamental role in the development of organic chemistry and the chemical industry. First, aniline dyes replaced dyes from natural sources. Then coal tar dyes found use in medicine (to stain tissues), and P. Erlich discovered the selective toxicity of these compounds. This initiated the chemical production of medicines, and the establishment of the pharmaceutical industry.

Dr. Henry Letheby, who was a physician and a member of the Board of Health in London, was interested in aniline because it was poisoning workers. Letheby observed that a bluish-green precipitate was formed at the anode during electrolysis, which became colorless when it was reduced and regained its blue color when it was oxidized again [1].

It should be mentioned that Runge [2] and Fritzsche [3], who isolated aniline, also observed the appearance of a blue color during the oxidation of aniline in

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acidic media. Indeed, this was why Runge proposed the name kyanol (after the Greek word for blue) or Blauöl (blue oil in German). Eventually the name aniline, which was proposed by Fritzsche, came into general use. “Aniline” entered the English literature through the German word “Anilin,” from the French and Portuguese-Spanish “añil,” from the Arabic “an-nīl” (النيل), and ultimately from the Sanskrit word “nīlī” (नीली), for indigo.

Several researchers have investigated the oxidation of aniline in order to understand the mechanism of the reaction and also to prepare useful dyes for the textile industry. Fritzsche analyzed the material called “aniline black” [3]. Then, after Letheby’s experiment, Goppelsroeder [4], Szarvasy [5], and others repeated and verified Letheby’s findings. In the first decade of the twentieth century, a linear octameric structure was proposed and generally accepted. It was also recognized that this compound may exist in at least four different oxidation states (emeraldine series) [6, 7], as well as that “overoxidation” and hydrolysis lead to the formation of quinone. In 1935 Yasui [8] suggested a reaction scheme for the electrooxidation of aniline at a carbon electrode. Khomutov and Gorbachev made the next step in 1950 [9]. They discovered the autocatalytic nature of the electrooxidation of aniline. In 1962 Mohilner, Adams, and Argersinger reinvestigated the mechanism of the electrooxidation of aniline in aqueous sulfuric acid solution at a platinum electrode [10]. They proposed a free radical mechanism and wrote that “the final product of this electrode reaction is primarily the octamer emeraldine, or a very similar compound” [10].

The first real breakthrough came in 1967, when Buvet delivered a lecture at the 18th meeting of CITCE (later ISE), and this presentation appeared a year later in *Electrochimica Acta* [11]. Here we cite the first sentence of this paper, which speaks for itself: “Polyanilines are particularly representative materials in the field of organic protolytic polyconjugated macromolecular semiconductors, because of their constitution and chemical properties.” They also established that polyanilines “also have redox properties,” and that “the conductivity appears to be electronic.” It was also shown that “polyanilines are also ion-exchangers.” Finally they proposed that “polyanilines… can be utilized for making accumulators with organic compounds”.

At the conference there were two questions: “What is the magnitude of the activation energy of the electronic conduction process in your polymer?” (from M.Peover), and “Did you observe a relationship between ionic transport and chemical changes in the composition of the material (oxidation and reduction products)?” (M. Pourbaix). Although both questions are related to important properties, one may conclude that the discovery did not give rise to great excitement at the time.

While Josefowicz et al. [11] used chemically prepared PANI pellets as an electrode and for conductivity measurements, investigations of the mechanism of electrochemical oxidation also continued [12, 13], and the name polyaniline was generally accepted [13]. The paper of Diaz and Logan that appeared in 1980 [14] initiated research into polymer film electrodes based on polyaniline, which continues even today.

It should be mentioned that the “discovery of conducting polymers” in connection with polyacetylene is an exaggeration not only because of the example of polyaniline described above since polypyrrole was prepared even earlier. Australian researchers have published a series of papers entitled “Electronic conduction in polymers” in 1963 [15–17]. They prepared iodine-doped polypyrrole by pyrolysis of tetraiodopyrrole, which showed rather good conductivity. They cited the paper by Szent-Györgyi and Isenberg, who had prepared a charge-transfer complex of pyrrole and iodine even earlier [18]. Very deep is the well of the past.

We could compile the whole stories of polypyrrole and other conducting polymers in a similar way, but the polyaniline saga alone provides an excellent illustration of the development of science. In fact, the discovery in the 1970s of polyacetylene—which had no practical importance but helped to arouse the interest of researchers and public alike—was another episode in the history of conducting polymers. Thus, these materials have a long history and—perhaps without any exaggeration—a bright future.

References

1. Letheby H (1862) J Chem Soc 15:161
2. Runge F (1834) Pogg Ann 31:63, 32:331
3. Fritzsche J (1840) J Prakt Chem 20:453
4. Goppelsroeder F (1876) CR Acad Sci Paris 82:331
5. Szarvasy E (1900) J Chem Soc 77:207
6. Willstätter R, Dorogi S (1909) Berichte 42:4118
7. Green AG, Woodhead AE (1910) J Chem Soc 97:2388
8. Yasui T (1935) Bull Chem Soc Jpn 10:306
9. Khomutov NE, Gorbachev SV (1950) Zh Fiz Khim 24:1101
10. Mohilner DM, Adams RN, Argersinger WJ (1962) J Electrochem Soc 84:3618
11. de Surville R, Josefowicz M, Yu LT, Perichon J, Buvet R (1968) Electrochim Acta 13:1451
12. Dunsch L (1975) J Prakt Chem 317:409
13. Breitenbach M, Heckner KH (1973) Electroanal Chem Interf Chem 43:267
14. Diaz AF, Logan JA (1980) J Electroanal Chem 111:111
15. McNeill R, Siudak R, Wardlaw JH, Weiss DE (1963) Aust J Chem 16:1056
16. Bolto BA, Weiss DE (1963) Aust J Chem 16:1076
17. Bolto BA, McNeill R, Weiss DE (1963) Aust J Chem 16:1090
18. Szent-Györgyi A, Isenberg I (1960) Proc Acad Sci St Louis 46:1334