1

History of Conductive Polymers

J. Campbell Scott

IBM Almaden Research Center, San Jose CA

1.1 Introduction

It is generally recognized that the modern study of electric conduction in conjugated polymers began in 1977 with the publication by the group at the University of Pennsylvania [1] describing the doping of polyacetylene. Although there was some prior work dating back to World War II (see the review by Hush [2]) and even reports of electrochemical synthesis the nineteenth century [3], the Nobel Committee recognized the seminal contribution of Heeger [4], MacDiarmid [5] and Shirakawa [6] by awarding them the Nobel Prize for Chemistry in 2000. Shirakawa, who was based at the Tokyo Institute of Technology, had been visiting the lab of his collaborators at Pennsylvania at the time of the breakthrough research.

The story of polyacetylene is an example of a fortunate confluence of circumstances that is often under-appreciated in the history of scientific progress. In the 1970s, there was worldwide interest in the unique properties of materials with such a high degree of anisotropy that they can be considered one-dimensional (1D) systems. The Pennsylvania group, of which I was privileged to be a member until 1975, was jointly led by a chemist, Tony Garito, and a physicist, Alan Heeger, and was recognized worldwide as a primary center for that field. Early focus was on the study of charge-transfer salts, in which planar, conjugated, small molecules were stacked like poker chips. Experiments revealed a Peierls transition [7,8] and suggested the observation of Frölich superconductivity [9,10]. The emphasis then shifted to linear polymers as chemist, Alan MacDiarmid, entered into a

Nanostructured Conductive Polymers   Edited by Ali Eftekhari
© 2010 John Wiley & Sons, Ltd

collaboration with Heeger, to examine poly(sulfur-nitride), a crystalline solid, consisting of chains of alternating sulfur and nitrogen atoms, that exhibits metallic conduction [11] down to liquid helium temperatures, and has a superconducting transition at 0.26 K [12].

In the midst of this research, MacDiarmid was traveling in Japan and visited the laboratory of Hideki Shirakawa who was studying the Ziegler–Natta-catalyzed polymerization of acetylene. Standard practice was to use a concentration of the organometallic catalyst at the millimolar level. It is a catalyst after all. These low concentrations led to the infamous 'insoluble, intractable, black precipitate,' but Shirakawa had discovered that with concentrations closer to molar, he obtained a shiny 'metallic' film coating the wall of the reaction vessel. MacDiarmid returned to Pennsylvania, where he and Heeger quickly arranged to invite Shirakawa for a sabbatical visit.

The pieces were all in place. Scientifically, it was understood that pristine polyacetylene is a Peierls semiconductor, as evidenced by its bond-alternating structure; it was known that charge transfer to molecular donors or acceptors would result in partially filled bands and that the resulting incommensurability of the Fermi wave-vector would destabilize the Peierls phase. The interdisciplinary team had the ideal expertise: the chemists, led by Shirakawa and MacDiarmid, brought their synthetic expertise to the preparation of the polymer films; the physicists, led by Heeger and post-doc C. K. Chiang, brought physical measurement and interpretation of material properties, not just electrical conductivity, but also structural and spectroscopic. Together, they applied vapor-phase doping of molecular acceptors (halogens) and a donor (ammonia).

The publication by Chiang *et al*. [1] led to a huge surge in interest in 'synthetic metals.' In less than a decade, most of the monomer building blocks that we know today had been identified and many procedures for polymeric synthesis had been established. The chemical structures are illustrated in Figure 1.1. (In the nomenclature used in Figure 1.1, polyacetylene would be called polyvinylene. This is because some – 'common' – names derive from the compound that is polymerized, while others, more correctly according to IUPAC conventions, use the monomeric unit in the product polymer.)

An interesting sociological aspect of the research on conjugated polymers has been the evolving target for technological application, and hence emphasis on particular physical properties, that has motivated the research in the ensuing 30 years. Initially, and through the early 1980s, high electrical conductivity was the primary driving force. There were suggestions to replace (copper) electrical wiring in everything from printed circuit boards to home, and even grid, power distribution with inexpensive, light-weight polymeric conductors. As issues of processability, limits on conductivity, and environmental stability became more apparent these grand schemes fell by the wayside. Nevertheless, in certain niche applications, electrical conductivity is the primary attribute. For example, antistatic coatings are important in many textiles and in the roll-to-roll processing of polymer webs. Photographic film is a good example of the latter application and is the reason that Bayer initiated, in conjunction with Agfa, their development of the Baytron series of products based on poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulphonate) PSS. (PEDOT-PSS is currently marketed by H. C. Starck Corp. as their Clarion line of conductive coatings.)

When the Holy Grail of copper replacement receded over the horizon, the emphasis in the late 1980s and early 1990s shifted to the optical properties. Since there is typically a large oscillator strength in the HOMO–LUMO transition of undoped conjugated polymers,
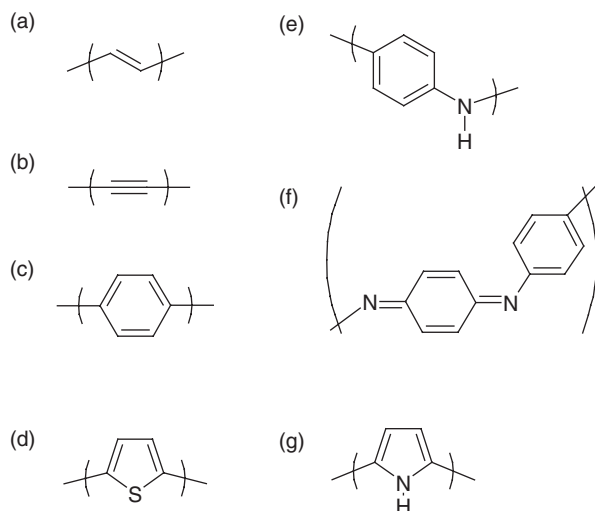
(a)

(e)

(b)

(f)

(c)

(d)

(g)

Figure 1.1 *Chemical structures for monomers of the conjugated polymers discussed in this chapter: (a) vinylene (the repeat unit of polyacetylene); (b) ethynylene (polydiacetylene is alternating vinylene-ethynylene); (c) phenylene; (d) thiophene; (e) leucoemeraldine form of polyaniline; (f) pernigraniline form of polyaniline (the number of protons can vary between the two limits); (g) pyrrole*

they are often highly colored and fluorescent. At that time there was great interest in nonlinear optics, as researchers were developing new materials, both organic and inorganic, for application in optical switches, modulators and the like. It was experimentally demonstrated [13] and theoretically understood [14,15] that many conjugated polymers also possess extremely high third-order optical nonlinearity. Although much interesting science emerged from this line of research, to my knowledge no technology is based on it.

Second-order nonlinearity and electro-optic response are much more amenable to device application. There are few conjugated polymers with intrinsic second-order nonlinearity, since homopolymers and alternating copolymers tend to have a center of symmetry. (This is not necessarily always so, since head-to-tail polymerization of an asymmetric monomer does not have mirror symmetry.) In 1990, the Cambridge group under the leadership of Richard Friend was investigating the electro-optic response of poly(phenylene vinylene). The story goes (I have heard several versions, probably with some embellishment) that graduate student Jeremy Burroughes had turned off the lab lights in order to minimize stray light, and applied a dc voltage to a sandwich-structured device – just the conditions required to observe the resulting electroluminescence. Of course, the publication of this observation [16] spawned an enormous worldwide research effort to optimize the materials and device structures (polymer light-emitting diodes or PLEDs) for use in flat-panel displays, signage and lighting.

The semiconductive properties of conjugated polymers are also exploited for application in thin-film organic field-effect transistors (OFETs). The earliest materials examined were polyacetylene [17], polythiophene [18], and an oligomer of thiophene [19]. In these

devices the polymer forms the channel between the source and drain electrodes of the device. The number of charge carriers in the channel is modulated by the voltage applied to the gate electrode. The conductance of the channel is proportional to the number of charge carriers and to their mobility. Hence, charge-carrier mobility is the primary metric in screening materials for use in OFETs. As several other chapters in this volume discuss in detail, polymer morphology at the nanoscale plays a crucial role in dictating the mobility. In any conductor a high degree of order is essential to achieve high mobility, since disorder leads to scattering, trapping at defects, and localization. However, as discussed by Kline *et al*. [20] among others, highly crystalline polymers are not necessarily ideal, because the crystallites are typically much smaller than the channel length, in which case the mobility is limited by transfer across grain boundaries. It seems preferable to have a high degree of polymer chain alignment, but with few grain boundaries and with many chains bridging between adjacent domains. Nano-morphology is key.

Another application which relies on the optical and semiconducting properties of conjugated polymers is solar-energy conversion. In this case, each photon of solar radiation is absorbed to generate an exciton – a bound electron–hole pair. The onset of absorption is below the HOMO–LUMO gap by an energy corresponding to the exciton binding energy. In contrast to many inorganic semiconductors used in solar cells, the exciton binding energy in conjugated polymers is several tenths of an electronvolt and therefore many times thermal energy (kT) at ambient temperature. Therefore excitons in conjugated polymers do not readily dissociate to create free electrons and holes. Excitonic solar cells rely on a hetero-junction to dissociate the excitons. In this device structure, an electron-transport material (n-type) is adjacent to a hole-transport material (p-type). If the energy level offsets (HOMO and LUMO of the n- and p-type materials) are sufficient compared to the binding energy, the exciton may dissociate at the interface. The exciton may be created in either the n- or p-type material or both, the difference being the absorption spectra and magnitudes of the binding energy.

Here again, nano-morphology plays a key role. The exciton has a characteristic lifetime, dictated by the sum of its radiative (re-emission) and non-radiative (heat-producing) decay rates. It is also mobile, diffusing through one of the polymeric semiconductors with a characteristic diffusivity. If the exciton lives long enough to diffuse to the n–p interface, high carrier-generation efficiency can be achieved. Since the exciton diffusion length in conjugated polymers is typically of the order of 5–10 nm, the n- and p-type materials must be blended at this length scale. Such 'bulk heterojunctions' were first demonstrated by the Santa Barbara [21] and Cambridge [22] groups.

There is an additional constraint on the nature of the mixing, namely that the hole-transporting p-type phase be continuous to the cathode, while the electron-transporting n-type phase connect to the anode. Controlling the morphology of such bi-continuous networks is the goal of recent research on self-assembled block copolymers.

Most of this volume is devoted to the characterization and application of doped conjugated polymers, i.e. to their highly conducting 'metallic' state. I have touched upon some of the issues relating to the nano-morphology of undoped conjugated polymers, and to their application as semiconductors, because it is usually helpful to understand properties of the 'pristine' material prior to analyzing the effect of dopants. The remainder of this chapter is divided into sections devoted to, respectively, the work that preceded the Pennsylvania publication ('archeology and prehistory'), its immediate impact ('the dawn

of the modern era'), and the 'materials revolution,' which brought careful refinement of synthesis and processing, and thereby enables today's applications.

1.2 Archeology and Prehistory

Today's conductive polymer workhorses are primarily derivatives of polypyrrole, polyaniline and polythiophene. Each of these was known to the chemical community long before the work on doping of polyacetylene. The earliest publication that I am aware of concerns the oxidative polymerization of 'indigo' (i.e. aniline) by nitric acid [23]. This was soon, at the pace of ninteenth century science, followed by a paper 'On the production of a blue substance by the electrolysis of sulphate of aniline' [3]. The background was the industrial revolution, when chemists were exploring the usefulness of coal by-products and just post-Faraday, electrochemistry was in its infancy. Aniline was particularly interesting because it was a reagent in the synthesis of many of the dyes that we associate with the deep crimsons and purples of the Victorian era. Fritsche [23] and Letheby [3] had undoubtedly synthesized some form of polyaniline, long before the concept of linear polymerization [24,25], and long before the concept of frontier orbitals, which is so important in understanding organic chromophores, was developed by Fukui [26]. More on the early history of polyaniline can be found in the paper by Mohilner *et al.* [27] and in the review by MacDiarmid and Epstein [28]. By the 60s, it was recognized that the oxidation product of aniline was a linear oligomer or polymer [27], and the effect of acid on its conductivity had been discovered [29].

Likewise, chemical coupling to form oligomers and polymers of pyrrole, thiophene and many other heterocycles was begun in the nineteenth and early twentieth centuries (see citations in [30]). The resulting materials were poorly characterized, partly because of the rudimentary analytical techniques of the day, and partly because of their insolubility. In particular, it was rarely clear whether the products were branched or linear. Nevertheless, by the 60s [30], it became routine to measure the electrical conductivity of the product. The science learned was marginally useful, but a catalog of monomers was generated for future use.

An important development occurred in the late 60s in the studies by Wegner [31,32] of the polymerization of diacetylenes. He showed that single crystals of the monomer derivatives can be polymerized topotactically, essentially retaining the original crystal structure. For the first time, a class of conjugated polymers was amenable to crystallographic analysis: bond lengths and angles could be determined, and would serve as a reference for future structural studies of less well-ordered materials, and as input to *ab initio* molecular-orbital calculations. Initially, most interest on the physical properties of polydiacetylenes focused on their photoconductivity. We shall return to their dark conductivity below.

At the same time, in his lab in Tokyo, Hideki Shirakawa was applying Ziegler–Natta polymerization to the simplest conceivable monomer – acetylene, C_2H_2. By a 'fortuitous error' he discovered the effect of using $1000 \times$ the usual concentration of a particularly soluble organometallic catalyst. When he bubbled acetylene gas through the solution, a shiny, silvery film was deposited on the walls of the tube. The morphology of these films

consists of well-separated fibrils, leading to a high degree of porosity and large internal surface area, ideal for gas-phase doping. The visitor from Penn, MacDiarmid, was fascinated by what he saw in his lab.

While this work was being pursued in the chemical community, several groups of physicists, together with their chemist collaborators, were studying 'highly conducting one-dimensional solids' [33]. Many of the materials of interest were organic charge-transfer salts, of which TTF-TCNQ is probably the best-known example. The scientific interest lay in the intriguing phenomena associated with one-dimensional electronic structures. Peierls [7] had postulated that a 1D electronic system would spontaneously distort, and therefore could not be metallic at low temperature. This Peierls transition was observed in TTF-TCNQ at a temperature of about 40 K [8]. The low, and experimentally accessible, transition temperature is due to non-negligible interchain interactions and to the partial charge transfer from the TTF donor to the TCNQ acceptor. In contrast, in sp^2-conjugated polymers there is one π-electron per carbon atom. Thus a chain with equal bond lengths would result in a half-filled band. The Peierls distortion is then a simple dimerization of the chain, resulting in alternating long and short C—C bonds. The gain in electronic energy dominates the cost in lattice energy and results in a high transition temperature, well above the decomposition temperature of the organic polymers of interest.

Thus by the mid-70s, much of the preparative polymer chemistry and the physical understanding of conduction processes in 1D were well established.

1.3 The Dawn of the Modern Era [6]

Highly doped inorganic semiconductors are 'degenerate' because the donor (acceptor) impurity band overlaps the bottom of the conduction band (top of the valence band), leading to a nonzero density of states at the Fermi level. The result is a material with conductivity similar to that of a metal, and unlike the thermally activated response of the original semiconductor. This concept does not apply directly to doped conjugated polymers since energy of the dopant ion is typically not close in energy to the transport bands. The motivation to investigate the effects of doping on the conductivity of polyacetylene arose instead from experience with charge-transfer salts. The ground state of the system does not consist of neutral impurities that release mobile charge carriers as the temperature is raised, but rather of charged ions (anion or cation) with the counter-charge in the valence or conduction band of the polymer. The carriers are attracted to the opposite charge on the ions, but because of the relatively large molecular sizes and the screening effects of other carriers, the binding energy is low and at room temperature the carriers are quite mobile.

This concept – mobile charge carriers in the valence (HOMO) or conduction (LUMO) band of the polymer, with the counter-charges on ionic species – provides the fundamental framework for the subsequent development of polymeric conductors.

Following the 1977 publication by the Pennsylvania team, the field exploded. Dozens of research groups began programs to understand better the properties of polyacetylene and to search for new and better materials. There was considerable emphasis on determining the
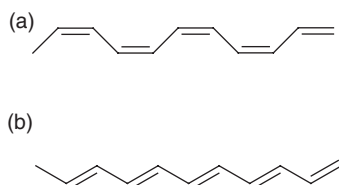
Figure 1.2 (a) cis *and (b)* trans *isomers of polyacetylene*

details of (what we would now call) its nanomorphology. There are two isomeric forms of polyacetylene $(CH)_x$: *cis* and *trans*, which can be readily distinguished by their vibrational (infrared and Raman) spectroscopy. The mechanism of Ziegler–Natta polymerization leads initially to the generation of the *cis* form, but this is metastable at room temperature and mild heating or exposure to vapor-phase dopants converts it to *trans*.

The fibrous morphology created during synthesis is highly crystalline. Since the fibrils are only about 200 nm in diameter, about 1 µm long and randomly oriented, the X-ray diffraction patterns yield only lattice spacings, not the full crystal structure. Ray Baughman and others members of the polymer chemistry group at Allied Chemical (as it then was) combined the X-ray diffraction results with molecular modeling to elucidate the crystal structure of the pristine isomers, and to determine the approximate location of the dopant ions [34]. Initially, iodine was of particular interest because it formed linear polyatomic ionic species (I_3^-, I_5^-, etc) residing in 'channels' between the polymer chains.

There was a great deal of debate about the homogeneity of doping, and its effect on the conductivity. There were those who argued that the doping was homogeneous and random, and that the concentration of charge carriers increases up to the point where their mutual screening induces a Mott insulator–metal transition. Others proposed highly inhomogeneous doping, essentially the growth of metallic 'islands' in an otherwise insulating polymer matrix. In this scenario, the macroscopically observed insulator–metal transition is due to the growth of the islands to the point where they coalescence into percolating conductive pathways. Although the controversy was never fully resolved to the satisfaction of all parties, it was nevertheless a great motivator, driving innovative research that ultimately contributed to a detailed understanding of the excitations of conjugated chains, their spectral and magnetic signatures, and their interactions.

A polymer chain of *trans*-$(CH)_x$ has the unusual property of geometric degeneracy – there are mirror-image distinct states, but possessing the same energy (see Figure 1.3).
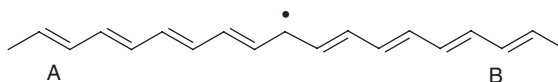

Figure 1.3 *Bonding structure of a soliton in polyacetylene. The configurations A, to the left, and B, to the right, are equivalent, but there is a defect where they meet. The central carbon atom shares electrons in three σ-bonds, but the fourth (π) electron is unpaired. The system is charge-neutral, but has spin ½*

Su, Schrieffer and Heeger (SSH) [35] addressed the nature of the topological defect that must be created at the junction between two mirror-image chains. The mathematical description of the defect belongs to a class of solution of nonlinear differential equations, and is known as a soliton. The solitons in *trans*-$(CH)_x$ exhibit reversed spin-charge relations: the neutral species has spin ½, while the addition or removal of an electron results in a nonmagnetic state. The soliton is not localized on a single carbon atom, as depicted in Figure 1.3, but is spread over roughly a dozen atoms, according to the parameters of the SSH Hamiltonian. Many of the theoretically predicted features of solitons were subsequently confirmed by experiment over the next few years: electron spin resonance was observed in undoped polyacetylene, and diminished at low dopant concentrations; measurements of the hyperfine coupling strength to the protons confirmed its delocalization; the presence of a mid-gap state was confirmed by photo-induced (pump-probe) absorption; and the symmetry changes induced by optical excitation or by doping were deduced from the infrared modes that appeared.

The science of polyacetylene is fascinating, but as a polymeric conductor its material properties are not at all suited to technological application. It is insoluble in any common solvent; it has little mechanical strength, especially in its doped state, and cannot be molded nor effectively stretch-aligned; it is not stable in air. Immediately the effort began to find new polymers and better ways of processing. Exploration proceeded on many fronts, from the substitution of one or both hydrogen atoms in acetylene, to polymerization processes other than Ziegler–Natta catalysis, to the use of completely different monomers and to electrochemical oxidation.

An example of side-group substitution is poly(phenylacetylene). The phenyl group imparts considerably better stability. Due to steric packing constraints, it also changes the conformation of the backbone from planar zig-zag to helical. However, the crystallinity is considerably reduced, doping is not so effective and the conductivities obtained were lower than the unsubstituted polymer. The improvement in material properties was rather modest and not sufficiently encouraging to offset the loss in conductance, so PPA is one of many technological dead-ends encountered at that time.

Among the more successful synthetic procedures were those developed by Feast at Durham, [36] who developed a ring-opening synthesis procedure for polyacetylene derivatives. Meanwhile Naarmann at BASF showed the benefits of dissolving the Ziegler–Natta organometallic catalyst in a viscous solvent [37]. These routes permitted better morphological control and led to higher conductivity in the doped state, but still suffered from the inherent limitations of polyene chemistry.

Completely different monomers were called for. Before long, three of today's work-horses had been identified: pyrrole, aniline and thiophene. In Japan, Yamamoto [38] and in Germany, Kossmehl [39] synthesized polythiophene doped with pentafluoroarsenate. At the same time, the possibilities of electrochemical polymerization were recognized. At the IBM Lab in San Jose, Diaz used oxidative electrochemical polymerization to prepare polypyrrole [40] and polyaniline. [41] Electrochemical synthesis forms the polymer in its doped state, with the counter-ion (usually an anion) incorporated from the electrolyte. This mechanism permits the selection of a wider range of anions, including those which are not amenable to vapor-phase processes, such as perchlorate and tetrafluoroborate. Electrochemical doping also overcomes an issue associated with dopants

such as pentafluoroarsenate, neutral in the gas phase, but leading to hexafluoroarsenate anions in the doped compound, with the production of other species as by-products which are not easy to identify or trace. An additional advantage of synthesis in an electrochemical cell is that the dopants can also be removed by applying an appropriate reverse voltage. The polymer is neutralized ('dedoped'), while the new covalent bonds between monomers remain.

The polymers formed by electrochemical oxidation are also insoluble, and therefore still not generally useful as general-purpose electrical conductors. In addition, it was not always possible to control coupling sites between monomers. For example in polypyrrole, 2-5 coupling predominated, but reaction at the 3 or 4 sites could not be ruled out [42]. Oxidative coupling, for example with ferric chloride, was found to lead to similar poor control over the molecular structure and to insoluble polymeric adducts. The goal of high conductivity in a solution-processable polymer remained elusive. It would require a further decade of painstaking chemical research to develop procedures for the large-scale production of soluble metallic polymers.

Polyaniline is unique among the conducting polymers in its doping characteristics. Rather than changing its oxidation state (i.e. carrier density) by addition or removal of electrons, doping is accomplished by removal or addition of protons [28], using strong bases (e.g. ammonium hydroxide) or protonic acids (e.g. hydrochloric or sulfuric). The net effect is similar: electrons in partially filled frontier orbitals are responsible for carrying the current; overall charge neutrality is maintained by the protons bound to the backbone nitrogen atom and by the anion of the protonic acid.

In spite of the synthetic difficulties, the wide selection of new materials being provided by the chemists encouraged exploration of new physical phenomena among the physical chemists and physicists. Virtually none of these new polymers exhibits the topological degeneracy that is found in *trans*-$(CH)_x$. Therefore their charge species are not solitons, but rather polarons and, perhaps, bipolarons (see Figure 1.4). The question arose as to whether the cost in lattice energy to form two polarons would exceed Coulomb repulsion and lead to a net binding energy stabilizing the bipolaron. Magnetic and spectroscopic data [43,44] reveals that bipolarons were the dominant species in moderately doped polypyrrole. Many subsequent studies have shown that bipolarons are the species most frequently encountered when conjugated polymers are doped.
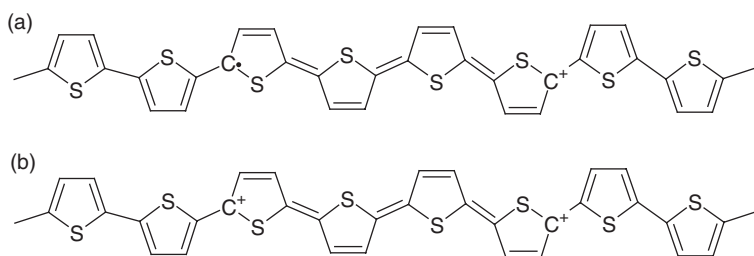

Figure 1.4 *Bonding structure of (a) a polaron and (b) a bipolaron in polythiophene*

1.4   The Materials Revolution

By the mid-80s it was clear to most researchers that success on the conductivity side had taken its toll on polymer processability. Attention turned back to restoring the solubility and mechanical properties of the polymer. Polyaniline received the most attention initially. The nonconductive emeraldine base form is soluble in *N*-methylpyrrolidone [28] and films can be cast. Subsequent doping with a protonic acid from aqueous solution, or *in situ* with a photo-acid generator [45], is necessary to achieve conductivity. Polyaniline is also soluble in sulfuric acid, not the most convenient of solvents. Nevertheless it proved possible to spin fibers [46], cast films and extrude sheets of conductive polyaniline sulfate, but the laboratory experiments did not make the transition into large-scale manufacturing.

A major advance in the solubilization of polyaniline was 'self-doping' by the attachment of a sulfonic acid side group to the backbone ring [47,48]. The resulting material is essentially a 'polyzwitterion' with the acid proton transferring to the basic amine backbone. The polymer is then soluble in mildly basic aqueous solutions and can be coated over large areas.

Almost simultaneously, another breakthrough occurred when it was realized that the protonic acid dopant could be selected or modified to act as a surfactant. Homologs of toluene sulfonic acid were the first examples examined [49], and camphor sulphonic acid proved to be one of the most interesting and promising acid surfactants [50], solubilizing polyaniline in *m*-creosol.

During the same period, the German chemical company, Bayer AG, was developing a soluble polythiophene derivative (PEDOT-PSS), motivated primarily by the need for electrostatic dissipation during the coating of photographic film. At the time, Bayer owned the photography company Agfa. Web-coating of the polymer substrate ('celluloid') leads to significant static charge build-up, and uncontrolled discharge amid the vapors of organic solvents was a major concern. The early phases of this research began in the late 80s, but the company considered it highly proprietary, applying for patents in Germany in 1988. The US patent was issued in 1991 [51]. There are no publications in the scientific literature until the company began to consider offering evaluation quantities for other applications [52]. Then, some of the details of the chemistry [53] and physical properties [54] began to appear.

Thus, by the mid-90s, the scientific foundations were well established, and methods had been developed to overcome the difficulties of achieving both conduction and processability in the same material. Many potential applications had already been identified and patents filed. New companies were started and more established companies initiated new business units, both on the supply side as vendors of the materials and on the demand side as developers of technological applications. Naturally, most of this work was hidden behind closed doors and presentations were aimed more at venture capitalists than at the scientific community. Publicity was generated, not by talks at scientific conferences, but rather by carefully managed press releases. The subsequent history is probably better documented by a business analyst than by a scientist.

The scientific story, however, does not end there. The identification of new potential applications demanded modifications and improvements in the materials, which in turn revealed more interesting and possibly useful properties. In 1993, Joel Miller, who had

recently moved to the University of Utah after working at Xerox and then DuPont, published a pair of articles listing, first, the attributes and potential applications [55] and then the existing commercially available products [56] based on conducting polymers. The latter list is dominated by applications dependent on electrochemical properties: batteries, electrolytic capacitors and electrodes for plating baths. Antistatic coatings, usually as blends in other polymers, for textiles and in electronic packaging are also prevalent. The list of potential applications spans the gamut from biochemical sensors to protection against lightning strikes in aircraft. One barely anticipated application now represents a major part of polymer production is in anticorrosive coatings [57]. In retrospect, it is not surprising that these electrochemically active materials might provide some benefit, but the detailed mechanism(s) of the protection are still an active area of research. A second unanticipated use is for electrodes in flat-panel displays, particularly polymer light-emitting diodes. The original motivation was to find a flexible replacement for indium tin oxide (ITO)-coated glass, but the conductivity of polymers was insufficient to carry the necessary current. However, it was found that a layer of various polyanilines or PEDOT [58,59] on top of ITO led to improved device performance and greatly enhanced lifetime. This 'hole-injection layer' is now one of the primary uses of PEDOT-PSS.

Intrinsic, i.e. undoped, conjugated polymers are now of great interest for their semiconducting properties. Research, development and commercialization have continued as applications for light-emitting diodes, field-effect transistors, photo-detectors, solar cells and chemical sensors were identified. For these technologies exquisite control over the chemistry is required in order to minimize defects which may limit performance and lifetime. Attention must also be paid to termination of the polymer chains, and to the elimination and/or removal of the trace amounts of polymerization catalysts. The methods of polymer chemistry, developed originally for careful control of the molecular structure of commodity polymers, were applied and adapted. Precise coupling and condensation reactions, using functionalized monomers as precursors, ensure that the resulting polymer has the desired linear structure. The range of chemical methods (Knoevenagel, Heck, Suzuki, Yamamoto and others) is described in the excellent review by Kraft *et al.* [60], who were primarily interested in luminescent polymers at the time.

Two of the earliest conjugated polymers are no longer the subject of active research as conducting materials. Polydiacetylene is the most highly crystalline polymer, and therefore the one with the highest potential carrier mobility. However, it has proved impossible to dope to any significant degree. It is being developed for sensor applications because of its optical properties and biocompatibility. Polyacetylene is chemically the simplest conjugated polymer, and although it provided a great deal of interesting science and proved to be a model for many other materials, it is not itself technologically useful.

1.5   Concluding Remarks

The history of research on conjugated polymers reveals its highly interdisciplinary nature and the importance of collaboration. Prior to the 70s, there was much in the chemical literature about the synthesis of many of the materials that form the basis for today's inventory, but the synthetic chemists were generally not experienced in the preparation of

samples suitable for detailed physical characterization. Similarly, although physicists had begun to study the organic solid state, the research was mainly on small molecules which chemical supply companies could provide. The major breakthroughs began when chemists and physicists began to work together to design and synthesize specific molecular structures to achieve the desired physical properties.

Such 'structure–function' relationships form the paradigm of modern materials science, and in the 80s and 90s many academic materials/chemical/polymer engineering departments were rebuilding to include a greater emphasis on soft-matter and electronic properties. They recruited young faculty members with degrees in chemistry or physics, with the result that the boundaries between these various departments has become blurred.

From the very beginning of the modern era, there was strong involvement of theorists. Theoretical physicists were particularly interested in the topological defects inherent in 1D systems, and the reversed spin-charge relationships of solitons and polarons. Quantum chemists focused on the molecular-orbital theory of extended structures. Both disciplines struggled with the relative importance of electron correlations and electron–phonon interactions.

As potential applications were identified, researchers from other engineering fields became involved. Electrical engineers brought their expertise in electronics, optoelectronics and display technology. Materials engineers joined with electrochemists to study anticorrosion coatings. Bioengineers recognized the potential for sensors and bioanalytical assays. The list of author affiliations of this volume testifies to the success of this interdisciplinary approach.

A historical review such as this is not only about the science and the published literature. It is also about the people involved and their interactions. The scientific progress which is summarized in this chapter is the result of collective endeavor, with a large number of scientists making contributions with various levels of impact. They came together at several exciting international topical conferences, particularly during the 80s. The 'Conference on Organic Conductors and Semiconductors' was first held in Siofok, Hungary in 1976, and took place annually until 1982. It acquired the name 'International Conference on Synthetic Metals' (ICSM) in Helsingor, Denmark in 1980. Since 1982, ICSM has been held every two years, most recently in Porto de Galinhas, Brazil, in 2008. There had been several other *ad hoc* conferences and workshops during the prior decade, notably in Saarbrucken, Germany in 1974, and at Lake Arrowhead, California in the same year, where many of the researchers cited among the references came to know each other, exchanged ideas and frequently engaged in heated discussions. The journal, *Synthetic Metals*, was initiated in 1979 expressly to serve this subfield of the scientific community, and continues to this day with editors, contributors and referees from around the world. *Organic Electronics* began publication in 2000, and organic electronics as a topic comprises a major fraction of the articles in *Advanced Materials*, and *Advanced Functional Materials*.

Advances in science do not occur in a vacuum. They are based on prior research, which in many cases may not have seemed relevant at the time. Progress is punctuated, with periods of great activity interspersed with times of relative quiet. Breakthroughs occur due to the development of new instrumentation, the discovery of a new material, and/or because of the efforts of particularly passionate and skilled scientists. In many cases, the subjects of the initial scientific excitement turn out not to be the leading candidates for

technological application. Their usefulness lies in the science lessons that they teach us, and conjugated polymers from aniline and pyrrole blacks in Victorian times, to polydiacetylene and polyacetylene in the 70s, to today's poly(phenylene vinylene)s and poly(spiro-bifluorene)s, have taught us many interesting lessons.

Acknowledgments

References

[1] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. McDiarmid, Electrical conductivity in doped polyacetylene, *Phys. Rev. Lett.*, **39**, 1098–1101 (1977).

[2] N. S. Hush, An overview of the first half-century of molecular electronics, *Ann. N. Y. Acad. Sci.*, **1006**, 1–20 (2003).

[3] H. Letheby, On the production of a blue substance by the electrolysis of sulphate of aniline, *J. Chem. Soc.*, 161–163 (1862).

[4] A. J. Heeger, Semiconducting and metallic polymers: the fourth generation of polymeric materials, *Curr. Appl. Phys.*, **1**, 247–267 (2001).

[5] A. G. Macdiarmid, 'Synthetic metals': a novel role for organic polymers, *Curr. Appl. Phys.*, **1**, 269–279 (2001).

[6] H. Shirakawa, The discovery of polyacetylene film – the dawning of an era of conducting polymers, *Curr. Appl. Phys.*, **1**, 281–286 (2001).

[7] R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London, 1955.

[8] F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, X-ray-diffuse-scattering evidence for a phase transition in tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ), *Phys. Rev. Lett.*, **35**, 445–449 (1975).

[9] H. Frohlich, On the theory of superconductivity: the one-dimensional case, *Proc. Roy. Soc. A*, **223**, 296–305 (1954).

[10] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Superconducting fluctuations and the Peierls instability in an organic solid, *Solid State Commun.*, **12**, 1125–1132 (1973).

[11] V. V. Walatka, M. M. Labes, and J. H. Perlstein, Polysulfur Nitride—char22a One-Dimensional Chain with a Metallic Ground State, *Phys. Rev. Lett.*, **31**, 1139–1142 (1973).

[12] R. L. Greene, G. B. Street, and L. J. Suter, Superconductivity in polysulfur nitride (SN)x, *Phys. Rev. Lett.*, **34**, 577–579 (1975).

[13] F. Kajzar, S. Etemad, G. L. Baker, and J. Messier, $X^{(3)}$ of trans-(CH)$_x$: Experimental observation of ^2A_g excited state, *Synth. Metals*, **17**, 563–567 (1987).

[14] Z. G. Soos and S. Ramasesha, Valence bond approach to exact nonlinear optical properties of conjugated systems, *J. Chem. Phys.*, **90**, 1067–1076 (1989).

[15] S. N. Dixit, D. Guo, and S. Mazumdar, Essential-states mechanism of optical nonlinearity in π-conjugated polymers, *Phys. Rev. B*, **43**, 6781–6784 (1991).

[16] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns, and A. B. Holmes, Light-emitting diodes based on conjugated polymers, *Nature*, **347**, 539–541 (1990).

[17] F. Ebisawa, T. Kurokawa, and S. Nara, Electrical properties of polyacetylene/polysiloxane interface, *J. Appl. Phys.*, **54**, 3255–3259 (1983).

[18] H. Koezuka, A. Tsumura, and T. Ando, Field-effect transistor with polythiophene thin film, *Synth. Metals*, **18**, 699–704 (1987).

[19] G. Horowitz, D. Fichou, X. Peng, Z. Xu, and F. Garnier, A field-effect transistor based on conjugated alpha-sexithienyl, *Solid State Commun.*, **72**, 381–384 (1989).

[20] R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. S. Liu, J. M. J. Frechet, and M. F. Toney, Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight, *Macromol.*, **38**, 2219–3312 (2005).

[21] C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, Sensitization of the photoconductivity of conducting polymers by C_{60}: Photoinduced electron transfer, *Phys. Rev. B*, **48**, 15425–15433 (1993).

[22] J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti, and A. B. Holmes, Exciton diffusion and dissociation in a poly(p-phenylenevinylene)/C_{60} heterojunction photovoltaic cell, *Appl. Phys. Lett.*, **68**, 3120–3122 (1996).

[23] J. Fritsche, Vorläufige notiz über ein neues zersetzungsproduct des indigo durch salpetersäure, *J. Prakt. Chem.*, **16**, 507–508 (1839).

[24] H. Staudinger, Über polymerisation, *Ber. Chem.*, **53**, 1073–1085 (1920).

[25] W. H. Carothers, Polymers and polyfunctionality, *Trans. Faraday Soc.*, **32**, 39–49 (1936).

[26] K. Fukui, T. Yonezawa, and H. Shingu, A molecular orbital theory of reactivity in aromatic hydrocarbons, *J. Chem. Phys.*, **20**, 722–725 (1952).

[27] D. M. Mohilner, R. N. Adams, and W. J. Argersinger, Investigation of the kinetics and mechanism of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode, *J. Am. Chem. Soc.*, **84**, 3618–3622 (1962).

[28] A. G. MacDiarmid and A. J. Epstein, Polyanilines: a novel class of conducting polymers, *Faraday Discuss.*, **88**, 317–332 (1989).

[29] L. T. Yu, M. S. Borredon, M. Jozefowicz, G. Belorgey, and R. Buvet, Experimental Study of direct current conductivity of macromolecular compounds, *J. Polym. Sci. Part C-Polym. Symp.*, **16**, 2931 (1967).

[30] M. Armour, A. G. Davies, J. Upadhyay, and A. Wasserman, Colored electrically conducting polymers from furan, pyrrole and thiophene, *J. Polym. Sci. A*, **1**, 1527–1538 (1967).

[31] G. Wegner, Topochemical reactions of monomers with conjugated triple bonds I. polymerization of 2.4-hexadiyn-1.6-diols derivatives in crystalline state, *Z. Naturf.*, **24b**, 824 (1969).

[32] G. Wegner, Topochemical polymerization of monomers with conjugated triple bonds, *Makromol. Chem.*, **154**, 35–48 (1972).

[33] J. T. Devreese, R. P. Evrard, and V. E. van Doren, (Eds), *Highly Conducting One-Dimensional Solids*, Plenum, New York and London, 1979.

[34] R. H. Baughman, S. L. Hsu, G. P. Pez, and A. J. Signorelli, The structures of *cis*-polyacetylene and highly conducting derivatives, *J. Chem. Phys.*, **68**, 5405–5409 (1978).

[35] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Solitons in polyacetylene, *Phys. Rev. Lett.*, **42**, 1698–1701 (1979).

[36] W. Feast and J. Winter, An improved synthesis of polyacetylene, *J. Chem. Soc. Chem. Commun.*, 202–203 (1985).

[37] H. Naarmann and N. Theophilou, New process for the production of metal-like, stable polyacetylene, *Synth. Metals*, **22**, 1–8 (1987).

[38] T. Yamamoto, K. Sanechika, and A. Yamamoto, Preparation of thermostable and electric-conducting poly(2,5-thienylene), *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 9–12 (1980).

[39] G. Kossmehl and G. Chatzitheodorou, Electrical conductivity of poly(2,5-thiophenediyl)-arsenic pentafluoride-complexes, *Makromol. Chem., Rapid Commun.*, **2**, 551–555 (1981).

[40] A. Diaz, K. Kanazawa, and G. Gardini, Electrochemical polymerization of pyrrole, *J. Chem. Soc: Chem. Commun.*, 635–636 (1979).

[41] A. F. Diaz and J. A. Logan, Electroactive polyaniline films, *J. Electroanal. Chem.*, **111**, 111–114 (1980).

[42] J. Bargon, S. Mohmand, and R. J. Waltman, Electrochemical synthesis of electrically conducting polymers from aromatic compounds, *IBM J. Res. Dev.*, **27**, 330–341 (1983).

[43] J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, Electron-spin-resonance studies of pyrrole polymers – evidence for bipolarons, *Phys. Rev. B*, **28**, 2140–2145 (1983).

[44] J. C. Scott, J. L. Bredas, K. Yakushi, P. Pfluger, and G. B. Street, The evidence for bipolarons in pyrrole polymers, *Synth. Metals*, **9**, 165–172 (1984).

[45] M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Akhtar, Z. Kiss, and A. J. Epstein, Polyaniline: solutions, films and oxidation state, *Molec. Cryst. Liq. Cryst.*, **160**, 151–163 (1988).

[46] A. Andreatta, Y. Cao, J. C. Chiang, A. J. Heeger, and P. Smith, Electrically-conductive fibers of polyaniline spun from solutions in concentrated sulfuric acid, *Synth. Metals*, **26**, 383–389 (1988).

[47] J. Yue, Z. H. Wang, K. R. Cromack, A. J. Epstein, and A. G. MacDiarmid, Effect of sulfonic acid group on polyaniline backbone, *J. Am. Chem. Soc.*, **113**, 2665–2671 (1991).

[48] X.-L. Wei, Y. Z. Wang, S. M. Long, C. Bobeczko, and A. J. Epstein, Synthesis and Physical Properties of Highly Sulfonated Polyaniline, *J. Am. Chem. Soc.*, **118**, 2545–2555 (1996).

[49] Y. Cao, P. Smith, and A. J. Heeger, Counter-ion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers, *Synth. Metals*, **48**, 91–97 (1992).

[50] Y. Cao and P. Smith, Liquid-crystalline solutions of electrically conducting polyaniline, *Polymer*, **34**, 3139–3143 (1993).

[51] F. Jonas, G. Heywang, W. Schmidtberg, J. Heinze, and M. Dietrich, Method of imparting antistatic properties to a substrate by coating the substrate with a novel polythiophene, US Patent 5035926, 30 July 1991.

[52] G. Heywang and F. Jonas, Poly(alkylenedioxythiophene)s – new, very stable conducting polymers, *Adv. Mater.*, **4**, 116–118 (1992).

[53] M. Dietrich, J. Heinze, G. Heywang, and F. Jonas, Electrochemical and spectroscopic characterization of polyalkylenedioxythiophenes, *J. Electroanal. Chem*, **369**, 87–92 (1994).

[54] I. Winter, C. Reese, J. Hormes, G. Heywang, and F. Jonas, The thermal ageing of poly(3,4-ethylenedioxythiophene). An investigation by X-ray absorption and X-ray photoelectron spectroscopy, *Chem. Phys.*, **194**, 207–213 (1995).

[55] J. S. Miller, Conducting polymers – materials of commerce, *Adv. Mater.*, **5**, 587–589 (1993).

[56] J. S. Miller, Conducting polymers – materials of commerce, *Adv. Mater.*, **5**, 671–676 (1993).

[57] D. W. DeBerry, Modification of the electrochemical and corrosion behavior of stainless steels with an electroactive coating, *J. Electrochem. Soc.*, **132**, 1022–1026 (1985).

[58] S. Karg, J. C. Scott, J. R. Salem, and M. Angelopoulos, Increased brightness and lifetime of polymer light-emitting diodes with polyaniline anodes, *Synth. Metals*, **80**, 111–117 (1996).

[59] S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock, and J. C. Scott, Polymeric anodes for improved polymer light-emitting diode performance, *Appl. Phys. Lett.*, **70**, 2067–2069 (1997).

[60] A. Kraft, A. C. Grimsdale, and A. B. Holmes, Electroluminescent conjugated polymers – Seeing polymers in a new light, *Angew. Chem. Internat. Ed.*, **37**, 402–428 (1998).