

THE HARDER ONE WORKS THE MORE LUCK ONE GETS

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Thank you, thank you very much for the recognition of our work, and it is the recognition that I value most.

First, let me tell you how I became interested in polymer chemistry. Science fascinated me from childhood. In school I devoted much time to studies of physics, chemistry and mathematics. My academic carrier started after the Second World War when I joined a group under Professor Michael Polanyi in Manchester, England. I was 36 years old at that time.

I was born in 1909 in Bendzin, Poland, a small city in the southwest part of Poland. When I was three years old my parents moved to Warsaw, the capital of Poland. There I grew up, went to schools, and at the age of eighteen started my studies in the chemistry department of Warsaw Polytechnic (Warsaw Polytechnic Institute) graduating with a title of Chemical Engineer in 1932. About that time my father, a businessman representing some metallurgic factories, underwent surgery from which he never recovered. The time was bad, it was the depression of the thirties, and it was very hard to get a job. Eventually, I got a poorly paid job in a small pharmaceutical factory. My duty was to produce pharmacopoeia pure inorganic salts. At that time, in the fall of 1933, I married my present wife who was then a student in Warsaw University.

In 1935, due to the influence of my father-in-law, Hilary Frenkel, who was an active and devoted Zionist, we secured a permit to emigrate to what was known then as Palestine, a British mandate territory. We left together: my parents-in-law, my wife and I. The economic situation in Palestine was also bad. There were many professional people, doctors, scientists, etc. , who left Nazi Germany where they were persecuted, and they all were looking for employment. Therefore, it was nearly impossible to get a position in my field. After three months of fruitless search for any position, I got, with the help of my father-in-law, the privilege to work in the organic laboratory of The Hebrew University in Jerusalem as an unpaid volunteer. This allowed me to practice my profession as a chemist. The university was in the process of creation, we just started

the chemistry department and a year later we got the first chemistry under-graduates. I was engaged in teaching the students, supervising their organic laboratory, and working on the synthesis of some organo-arsenic derivatives which interested the head of the organic laboratory, Professor M. Weizmann. The latter work gained me a Ph. D degree, which I got in 1942. To earn money I was working as a night watchman, guarding the university with a rifle since we were in the midst of riots by Arabs, who attempted to burn the Jewish settlements.

In 1936 my son was born and one month later my father passed away. He was happy to see the photograph of the baby which looked like him. A heart attack killed him at the age of 56, the result of the unsuccessful surgery performed 10 years earlier from which he never recovered. My mother was left with my sisters in Warsaw. My wife lived with her parents in Tel-Aviv, my night watchman's salary was not sufficient to feed us both. One and a half years later I got a permanent, still low paid, position in the university that permitted me to bring my wife and son to Jerusalem. I felt very rich! The department was joined at that time by Professor L. Farkas, a prominent physical chemist who worked previously at Cambridge University, England in a group under Professor Eric Rideal. Physical chemistry interested me most, but no position was available in his group and I had to continue in the organic chemistry group.

In 1942, as Rommel's army landed in North Africa, the British army was in need of various products which could not be shipped from England because the sea was under Italian and German control. I got into industrial activity building small factories producing the required supplies. I was working very hard but paid well. My industrial activity brought me to Egypt and later to Beirut. At the end of the war I had enough money saved to allow me to go to a prominent English University and start a scientific carrier in the field of physical chemistry. Professor Farkas advised me to apply to Professor Michael Polanyi at the University of Manchester, England. This was my greatest luck; it changed my life.

Michael Polanyi was the most inspiring scientist, perhaps the most gifted physical chemist of his generation. I was accepted as a graduate student with no scholarship! After all I was a foreigner, hardly speaking any English, and England was economically exhausted after this terrible war. I arrived in Manchester in the fall of 1945 at the age of 36. Polanyi suggested as the subject of my research the determination

of the C-I bond dissociation energy of benzyl iodide using a pyrolytic method developed few years earlier by him and Buttler.

After a few months of hard work I came to the conclusion that this method would not lead to the desired results and suggested instead to investigate the C-H bond dissociation energy of toluene. Polanyi doubted whether the approach I proposed would work, but said "try it." This turned out to be a most successful study and as the results appeared Polanyi got enthusiastic. Within a few months I determined the C-H bond dissociation energy of toluene and proved that the PhCH₂-H bond is weaker than the Ph-CH₃ bond, contrary to the belief of those days. I extended this study to the determination of the C-H bond dissociation energies of the xylenes, in an attempt to study the effect of substituents on the bond dissociation energy. Eight months after my arrival to England I was told that I did enough work for my Ph. D thesis (the degree I got in 1947 due to the regulations), and at that time Polanyi offered me the prestigious ICI fellowship. I then brought to England my wife and two children, my daughter having been born in 1942. It was the utmost time, my savings were nearly exhausted.

The results of the studies of C-H bond dissociation energy in toluene and the xylenes were prepared for publication. I brought the draft of the paper to Polanyi. He carefully went over it, explaining why he proposed some changes. The paper was retyped and Polanyi improved it again. The retyping and further corrections continued four times, and eventually Polanyi said that the final draft could be sent for publication. I asked to what journal should we send it. Polanyi replied "it is your paper you are publishing it." I still regret that I have no papers jointly with Polanyi. Subsequently, I got a larger laboratory and graduate students to help in my research. I developed a most prolific technique for determination of bond dissociation energies, referred to later as the toluene carrier technique, and applied it to many polyatomic organic compounds.

In 1947, the first postwar meeting of the Faraday Society took place in Oxford. It was an international meeting and I presented for the first time two papers: one on the C-H bond dissociation in toluene and the xylenes, the other on the formation of an intriguing quinonoid hydrocarbon, p-xylylene, and its polymerization to poly-paraxylylene. This hydrocarbon was anticipated by the theoretical chemists but never produced before. I got it as a product of pyrolysis of p-xylene, proved its structure, and thoroughly investigated its most unusual properties and its polymerization. Both

papers were well received and subsequently several distinguished American scientists visited me in my laboratory. Amongst them were Hugh Taylor, the dean of the Graduate School in Princeton University, and Herman Mark, a pioneer in polymer chemistry, who decided that I was a polymer chemist since I had discovered a new monomer and its unconventional polymerization. In fact, I did not know much about polymers and polymerization at that time. Professor Taylor asked whether I would like to visit America and go on a lecture tour of American Universities and Industrial Research Laboratories. This suggestion was attractive and Professor Taylor promised to organize such a tour.

The invitation came in 1950. Professor Taylor organized a most extensive tour taking me through virtually all the United States and Canada. I lectured in 45 Universities and Research Laboratories. It was an exciting experience, enjoyable and very educational, lasting for four months. During that visit Dr. Mark invited me to Brooklyn Polytechnic Institute and then to the Gordon Research Conference on Polymers. I met there most of the leading polymer chemists and learned much about the state of this field.

In the meantime, with the help of Dr. Kind, a director of a petroleum concern known as Petrocarbon and Petrochemicals, I applied for a patent on paraxylylene and its polymers. I became also a consultant to Petrocarbon Co. and the development work on paraxylylene was continued there. Significantly, the work on paraxylylene described in my first publication on this subject was completed in two weeks, whereas the development work that led to its commercial application took more than 10 years. It was successfully accomplished by Dr. W. F. Gorham of Union Carbide and the product is marketed now under the name of Parylene.

In 1951 I was invited again to the United States by the American Chemical Society for their 75th Jubilee Meeting. During the second visit I got an offer from Professor Edwin Jahn, then Dean of New York State College in Syracuse, N. Y., to be the Professor of Physical and Polymer Chemistry. The offer was attractive and challenging—to build a chemistry department in the newly developing State University of New York (SUNY). I accepted it, saying it would take me a year to wind up my work in Manchester. I had at that time seven graduate students.

I came to Syracuse in the fall of 1952 and brought with me my family and

three of my Manchester students. Within three months we were in full swing. I got support for our studies from the National Science Foundation and a few other government institutions. The work on bond dissociation energies was supplemented by studies of radical chemistry and simultaneously by the investigation of permeation of gases and vapors through polymeric films, an investigation carried out jointly with my colleague Vivian Stannett. The most interesting outcome of the permeation work was the development of the permeation valve, films permeating water vapor rapidly in one direction but slowly in the other one. At that time I developed also a prolific method for determining the rate constants of the addition of small radicals to a variety of aromatic, olefinic and acetylenic compounds referred to as methyl affinities. This work led also to studies of cage reactions and related problems.

In this period I had a postdoc, my former student Charles Leigh, working in Brookhaven National Laboratory on C-C bond dissociation of ethylene using radioactive tracers. I was coming to Brookhaven once a month to supervise the progress of his work. On one of these visits I met Professor Samuel Weissman. Charles and I had just published a paper on methyl affinity of aromatic hydrocarbons and Sam told me that he read it with interest because our data correlated with his on the electron affinity of these hydrocarbons. I asked how he measured electron affinities. He explained that they study aromatic radical anions and the electron transfer processes, such as: radical anion of naphthalene + phenanthrene giving radical anion of phenanthrene + naphthalene. As he talked it occurred to me that an electron transfer to styrene should produce a species that would initiate a radical polymerization from one of its ends, and simultaneously anionic polymerization from the other end, an unusual phenomenon. I asked Sam whether he investigated electron transfer to styrene. His answer was brief; "It's no use, it polymerises." I asked whether he would mind my looking into this problem, and having his consent I started the investigation of this reaction with two of my students, Moshe Levy and Ralf Milkovich. We concluded that the primary styrene radical anions dimerize into dimeric dianions and the two anionic ends initiate anionic polymerization free of termination and chain transfer. Thus, living polymers were born. The ramifications of this discovery were obvious to me and I outlined them in the first paper on living polymers published in 1956. Our papers aroused great interest and many laboratories all over the world started to work on living polymers and their application

to synthesis of polymers with controlled architecture.

Our subsequent work developed in three directions: demonstration of the synthetic potential of living polymers, i.e., preparation of block-polymers and functional polymers, study of the kinetics of polymerization of living polymers, and investigation of electron-transfer processes.

Since the start of these studies, many of my associates have contributed to the development of this field. I cannot name all of them, only a few who were amongst the early contributors. Dr. David Richards, known to us as Rick, was the first to produce in my laboratory the interesting block polymers of the hydrophobic polystyrene and hydrophilic polyethylene oxide. His work included also the studies of functionalization of the end-groups of living polymers. Later, on his own, Rick pioneered in developing the methods of conversion of the active end-groups of the growing polymers to allow the modification of the mechanism of propagation, say, from an anionic to a cationic or radical mode of growth. His most promising career was terminated by his untimely death. Johan Smid, Battacharyya and Chi-Long Lee were the first to recognize the role of ions and ion-pairs in anionic polymerization. This work performed in Syracuse was paralleled by the independent studies of Professor G. V. Schulz in Mainz, Germany, who published his results shortly after the appearance of our own reports. At that time Johan Smid was my closest co-worker. He gained a well-deserved reputation for his own original studies of contact and solvent separated ion-pairs accomplished jointly with another of my students, Theo Hogen-Esch, presently a professor in the University of Southern California in Los Angeles, USA. Johan, who stayed in Syracuse and was elevated to the rank of professor, is contributing prolifically to polymer chemistry. The synthesis of polymers having crown ether groups attached to their chain and the interesting application of these novel materials as catalysts exemplify some of his many achievements. Chi-Long moved to Dow-Corning Co. and developed there the living polymerization of polysiloxanes. He holds presently a prestigious position in that company.

Many innovations in our studies result from the contributions of my Japanese associates. Professor Ryuzo Asami, now retired from Nagoya University, helped to unravel some aspects of the electron-transfer initiation of polymerization by studying the dissociation of the dimeric dianions using isotope labeling.

Professor Mikiko Shima was the first to carry out extensive studies of crosspropagation in anionic polymerization. The work of Professor Minoru Matsuda contributed to the studies of initiation of polymerization by electron-transfer through his investigation of the reverse process. Dr. Makoto Shinohara demonstrated the striking action of some solvating agents on the rate of anionic polymerization and accounted quantitatively for the results. Dr. Takatoshi Shimomura revealed the role of solvent separated ion-pairs in the anionic propagation by demonstrating the negative activation energy of some of these processes. Dr. Kiyoshi Shimada showed how an electron transfer between the end-groups of polymer chains reflects its rigidity. Professor A. Yamagishi resolved the behavior of di-lithiated initiators in their interaction with living polystyrene, and clarified the effect of aggregation on some co-polymerizations proceeding with lithium counter-ions. The time limitation prevents me from discussing the work of my other Japanese students, and I apologize to them for this regrettable omission.

However, the truly exponential growth of the field of living polymers is due to the original contributions of many researchers throughout the world. Their work led not only to new products and novel techniques but also to the extension of the living polymerization process to other modes of propagation than the anionic one utilized in the early studies. Indeed, six years after the discovery of the first living polymers it was demonstrated that the cationic ring-opening polymerization of heterocyclic monomers may also proceed as a living propagation. Some new features of this reaction were observed in the course of its study. The simultaneous participation of ionic and covalent species in these processes was recognized first by Professor Takeo Saegusa and this idea was fruitfully expanded by the extensive work of my former associate Professor Stanislaw Penczek.

New kinds of living polymers were reported in the following years. The group-transfer polymerization developed by the DuPont team headed by Dr. Owen Webster, the discovery of living polymerization proceeding by metathesis of cyclic di-olefines pioneered by Professor Richard Grubb, and the co-ordination polymerization reported by Professor Inoue, are the most spectacular additions to this field.

Finally, the cationic polymerization of vinyl ethers was developed in the last decade by Professor Toshinobu Higashimura, who expanded his studies in cooperation

with his associate Dr. Mitsuo Sawamoto. The independent extensive studies of Professor Joseph Kennedy demonstrated a similar living character of the cationic polymerization of isobutene when initiated by esters or ethers activated by BCl_3 or TiCl_4 .

One cannot predict the future developments in this field, but the promising studies of organo-metalic complexes by Professor Teiji Tsuruta are significant. Such complexes are able not only to initiate and propagate a polymerization, but they also govern efficiently their stereochemistry.

As you may see from this story, my introduction to polymer chemistry and the discovery of living polymers were results of unexpected events. Undoubtedly I was lucky. However, here is a point deserving stressing. The harder one works the more luck one gets. This should be remembered especially by young people. Another point is worth emphasis. Unexpected events happen quite often. It is important to note them and to realize their significance. Then there is another problem. Should we investigate the unexpected phenomenon or should we leave it, perhaps keep it in mind, and continue with our previously planned work. This decision is crucial. To follow every unexpected event may lead to chase of wild geese. One may spend time and effort on an insignificant problem. On the other hand, a gold mine may be missed by not pursuing the new opening. There are no rules that guide one's decision. It helps to understand the phenomenon and to use one's intelligence and intuition. These problems are general. They are encountered in ordinary life as well as in research and their proper judgment is often vital.