

NATIONAL ACADEMY OF SCIENCES

HERMAN FRANCIS MARK

1895—1992

A Biographical Memoir by
HERBERT MORAWETZ

*Any opinions expressed in this memoir are those of the author(s)
and do not necessarily reflect the views of the
National Academy of Sciences.*

Biographical Memoir

COPYRIGHT 1995
NATIONAL ACADEMIES PRESS
WASHINGTON D.C.



H. F. Mark

HERMAN FRANCIS MARK

May 3, 1895–April 6, 1992

BY HERBERT MORAWETZ

HERMAN MARK WAS WIDELY KNOWN as the father of polymer science and the contribution he made to his chosen field was crucial in many ways. His research and inspiring teaching and lecturing were only part of his activities. Being completely devoid of academic snobbery, Mark was equally at home at universities and industrial laboratories and was most influential in the phenomenal growth of the polymer industry. Deeply concerned with establishing the study of polymers as a discrete branch of chemistry, he designed the first graduate curricula in that discipline, founded a polymer journal and monograph series, and was one of the chief architects of the Polymer Section of the International Union of Pure and Applied Chemistry.

Because of the informality of his nature, Mark was affectionately called by the nickname “Geheimrat” to stress his extreme difference from the pompous professors who had been adorned with this “Secret Councillor” title. His constant cheerfulness reflected his enviable ability to recall the good part of his life’s experience while choosing to forget all the unpleasantness.

Herman grew up in Vienna as the second son of Herman Carl Mark and Lily Mueller. His father was a physician, and Herman was early impressed with the conversation around the family dinner table with guests such as the psychoanalyst Sigmund Freud, the dramatist Arthur Schnitzler, and the founder of zionism Theodore Herzl. The musical life of the period, when Gustav Mahler was conductor of the Vienna Philharmonic, made a great impression. Mark was also enthusiastic about sports, particularly skiing and soccer, and on one occasion he was a member of the Austrian national soccer team.

This idyllic life came to a sudden end with the outbreak of the First World War. Mark fought on all fronts, was wounded several times, and was awarded fourteen medals for bravery. On one occasion, when the Italian army captured Monte Ortigora and the Austrians ordered a retreat, Mark persuaded his superior officer to allow him to lead a counterattack in which the strategic peak was retaken in spite of a heavy loss of life. During the final months of the war Mark was captured. He spent almost a year as a prisoner of war in a convent near Bari; his account of the humane treatment of the prisoners in those days reads today almost like a fairy tale. To relieve the boredom of prison life, Mark studied languages and resumed his study of chemistry, which he had started two years earlier while recuperating from a battle wound. In October 1919 he learned that his father was sick. He bribed a prison guard and took a train to Vienna.

He worked on a doctoral thesis dealing with the synthesis and characterization of the pentaphenyl ethyl free radical under the direction of Wilhelm Schlenk. Many years later, Mark recalled that Schlenk repeated his elemental analysis

before he allowed him to write up the dissertation. Mark worshipped his thesis advisor and Schlenk was clearly most impressed with his student, since he invited Mark to come with him to the University of Berlin, where, in 1921, Schlenk was offered the chair previously occupied by Emil Fischer.

KAISER WILHELM INSTITUTE (1922-26)

As it turned out, the Schlenk-Mark collaboration did not last long. A year after Mark arrived in Berlin with his young wife, the former Mimi Schramek, Fritz Haber, director of the Kaiser Wilhelm Institute (KWI), asked Schlenk for a modern organic chemist for a new Institute of Fiber Research to be organized at KWI. Schlenk unhesitatingly recommended Mark. Thus, a period of almost unbelievable productivity started for Mark at what was then one of the leading scientific centers in the world. Michael Polanyi had recently joined KWI and under his inspired leadership a broad program of X-ray crystallographic studies was initiated.

Polanyi found that the X-ray diffraction from cellulose fibers indicated the presence of crystallites oriented in the direction of the fiber axis and that an analogous crystal orientation existed in metal wires. A full structure analysis of cellulose seemed beyond the experimental possibilities of the time, but Mark and Polanyi noted that the increase in the modulus of cellulose fibers on stretching seemed similar to the reinforcement of metal wires during cold-drawing. They embarked, therefore, on a detailed analysis of the changes accompanying the cold-drawing of a zinc wire.

It is interesting to list some of the large number of materials Mark selected for his later crystallographic studies. The determination of the hexamethylene tetramine structure in 1923 was one of the first for a comparatively complex or-

ganic molecule. The graphite structure (1924) later proved important in convincing Mark (in opposition to many crystallographers of that time) that covalently bonded structures may extend beyond the crystallographic unit cell. The oxalic acid study (1924) led him to conclude that "one may assume that the carboxyl group of one molecule may attract as well the OH of water as the hydroxyl of another oxalic acid molecule." In his study of calomel (1926) he related the birefringence to the crystal structure. The crystallographic study of carbon dioxide (1925, 1926) was aimed at the determination of the carbon-oxygen bond length. A comparison of the ethane and diborane crystal structure (1925) showed that the two molecules had similar geometries—a result that was then quite surprising, since the manner in which the trivalent boron could form B_2H_6 molecules was something of a mystery. (The discovery of the similarity of the ethane and diborane structures is generally credited to S. H. Bauer's 1937 electron diffraction study, ignoring Mark's earlier work.)

Considering that Mark was originally trained as an organic chemist, it is striking how much of his effort during his years at KWI was directed at problems in physics, such as the natural width, the refractive index and the polarization of X rays, the Stark effect, and the Compton effect.

An important milestone in Mark's career was the meeting of the Gesellschaft Deutscher Naturforscher und Ärzte (Society of German Natural Scientists and Physicians) held in Düsseldorf in 1926. At this meeting Herman Staudinger, the champion of the concept of long chain molecules, was confronted with some of Germany's most distinguished chemists who viewed this idea with utmost skepticism, insisting that all effects ascribed by Staudinger to macromolecules could be explained by a colloid association of small molecules. Mark's lecture was titled "Roentgenographic Deter-

mination of the Structure of Organic, especially Highmolecular Substances.” It is important to note that the term “highmolecular” (hochmolekular) at that time carried no implication whether such substances were composed of Staudinger’s macromolecules or of his opponents’ colloidal aggregates. Mark reviewed his crystallographic work, stressing that important information may be gained from the unit cells and space groups, even if detailed molecular structures are not available. As for highmolecular substances, he was not yet ready to commit himself to long chains but suggested that the failure of such substances to break up on dissolution into small particles “indicates that lattice forces are quantitatively and qualitatively comparable to intramolecular forces: The entire crystallite behaves like a large molecule.”

I. G. FARBENINDUSTRIE

In 1926 K. H. Meyer, a director of Germany’s largest chemical corporation, the I. G. Farbenindustrie, invited Mark to become the director of a research laboratory of highmolecular compounds in Ludwigshafen. I. G. was a prominent producer of rayon and cellulose acetate fibers, and Mark was given full freedom to pursue fundamental studies as well as studies of spinning technology. His years at KWI had prepared him well for a consideration of the cellulose structure. As far back as 1921, Polanyi had pointed out that the unit cell of cellulose contains four glucose residues, but although he remarked that the diffraction pattern might be consistent with long chains composed of glucose residues, he attached no importance to that possibility. Mark made later the suggestive observation that the identity period in the fiber direction remained unchanged when cellulose was converted to its ethers or esters. Then, in 1926, Sponsler and Dore proposed in the United States a solu-

tion of the X-ray structure in which cellulose consisted of long chains of glucose residues, but this structure was inconsistent with chemical evidence that cellulose could be degraded to cellobiose. In a pioneering 1928 paper, Meyer and Mark solved the diffraction pattern to yield a structure in agreement with the chemical evidence—the first polymer crystal structure that has survived the test of time.

Another important investigation concerned Hevea rubber. While Mark was at KWI, one of his colleagues, J. R. Katz, made the surprising discovery that natural rubber, amorphous in the relaxed state, exhibits a sharp X-ray diffraction pattern when stretched. In his I. G. laboratory Mark followed up this discovery by solving with G. V. Susich the Hevea rubber crystal structure. This result was particularly important since it settled, for the first time, a question of *chemical* constitution: It had been known that natural rubber is poly(1,4-isoprene), but only the crystal structure proved that it had the *cis* configuration around the carbon-carbon double bond.

Mark was keenly interested in the relationship between the molecular characteristics of polymers and their technologically useful properties. This led him to calculate, on the basis of the cellulose crystal structure and the energy required to break its covalent bonds, estimated on the basis of spectroscopic data, the ultimate strength of an ideal cellulose fiber. In this approach he was far ahead of his time. He showed that the best industrial fiber was only about 10 percent as strong as the ideal fiber—clearly owing to various defects.

With Meyer's encouragement, Mark was free to pursue during his years in Ludwigshafen a number of his scientific interests, which were not likely to translate into financial profit for the company but which gained academic prestige for the laboratory. Thus, he carried out the first electron

diffraction studies of gases, determining the bond length and bond angles for molecules such as carbon tetrachloride, germanium tetrachloride, benzene, cyclohexane, *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene. It is of special interest that he concluded, as early as 1930, that the data for 1,2-dichloroethane are incompatible with free rotation (i.e., that some values of the internal angle of rotation must be favored). The young Linus Pauling visited Mark's laboratory and was greatly impressed with these studies, as he frequently recalled in later years.

One of the most important contributions of the Ludwigshafen years was the writing, with Meyer in 1930, of the first monograph on polymeric compounds, "*Der Aufbau der hochpolymeren organischen Naturstoffe*" ("The Structure of High Molecular Organic Natural Substances"). It dealt with cellulose, Hevea rubber, gutta percha, starch, silk fibroin, and collagen on the basis of their crystallographic and solution properties. Another influential book of this period was Mark's *Physik und Chemie der Zellulose*, published in 1932.

However, the description of this period of Mark's career would be incomplete without mention of the bitter attacks to which he was subjected on the part of Herman Staudinger. Staudinger's highly charged emotional reaction was undoubtedly due to his conviction that, having first proposed the existence of long chain molecules, he had created a new fertile field of organic chemistry and could regard physical chemists and physicists who studied polymers as interlopers whom he felt free of accusing of plagiarizing his ideas. The central controversy involved Staudinger's insistence that polymer molecules are stiff rods, whereas Mark and Meyer realized that because of the hindered rotation around the bonds in the polymer backbone they must be thought of as flexible coils.

By 1932 the management of I. G. concluded that, with

the probable takeover of the German government by Hitler's party, Mark, as the son of a Jewish father, could not continue to hold a prominent position in the company. It was characteristic of Mark that he always depicted the interview in which he was told that he would have to leave in the most innocuous colors.

VIENNA (1932-38)

In 1932 Mark was appointed professor of chemistry at the University of Vienna. He embarked immediately on the design of a curriculum in polymer science, the first of its kind. The research of his students dealt with the mechanism of polymerization and the viscosity of polymer solutions, but the most important achievement of the Vienna years was the formulation, with E. Guth, of a statistical theory of the elasticity of a rubber molecule. This provided the basic ideas that led later to the theory of crosslinked rubber elasticity.

In 1935 Mark conceived an ingenious idea for combining his scientific interests with his love for mountaineering. He persuaded his friends at the Soviet Academy of Sciences to organize an expedition to the highest peak of the Caucasus to determine whether deuterium was concentrated in its ancient glaciers. The results were inconclusive but all members of the expedition had a wonderful time.

Once again a political upheaval led to a painful change in Mark's life. In March 1938 Hitler's army occupied Austria, Mark was dismissed from his professorship and arrested because of his friendship with Chancellor Dollfuss who had tried to keep Austria independent and had been murdered by Nazi conspirators during an attempted coup in 1934. Mark had to use the influence of a high school classmate, now an influential man in the new regime, to be released from jail and to have his passport returned. He told me

that the fee demanded by the "friend" for this service was his year's salary at the university.

Fortunately, Mark had been contacted during the previous year by the director of the International Paper Company plant in Hawkesbury, Ontario, who had offered him the position of research director. This offer was now repeated. Mark, his wife, and two young sons left Austria for Switzerland, ostensibly on a skiing vacation, and proceeded to England. In September Mark arrived in Canada, where he was joined by his family a few weeks later.

THE AMERICAN YEARS (1938-92)

Mark stayed in Hawkesbury for only two years, concentrating on the improvement of the manufacturing of wood pulp, cellulose acetate, and viscose. The work on viscose was particularly challenging because of its recent use in tire cord, which required fibers of new exacting quality standards. This led also to a close relationship with the Du Pont company, which proved important when Mark decided that Hawkesbury did not offer a sufficiently broad scope for his scientific interests. One of the Du Pont officers with whom Mark had dealt on the tire cord project was a board member of the Polytechnic Institute of Brooklyn and he proposed that Mark combine a Du Pont consultantship with an academic appointment at Poly.

In retrospect, the situation at Poly seemed far from auspicious when Mark joined its faculty as an adjunct professor in September 1940. This was a time when a flood of refugees from Hitler's Europe found it next to impossible to obtain academic positions appropriate to their qualifications and experience. Mark was assigned to the Shellac Bureau, whose function was the testing and chemical characterization of shellac. However, since this material was imported from Asia, the war stimulated a search for a synthetic substi-

tute and Mark's past experience was most valuable in that effort.

His activities at Poly broadened substantially as a result of research contracts with the wartime Office of Scientific Research and Development, which allowed him to hire A. V. Tobolsky, P. M. Doty, and B. H. Zimm, none of whom had experience with polymers but who later became leading figures in polymer research. Mark's influence induced a number of gifted students, such as S. Krimm and R. S. Stein, to make their career in this academically unfashionable area.

Mark also became involved in a number of rather exotic wartime projects. The most intriguing, perhaps, resulted from Mark's observation that the brittleness of ice could be largely eliminated by the incorporation of a few percent of sawdust. The British Military Mission in Washington, concerned about the shortage of landing facilities, which limited the scope of airplane attacks against German submarines, hoped that a flat iceberg made from this composition could be used as "an unsinkable landing field." A prototype was in construction when a dramatic improvement in the fortunes of war led to the termination of this effort in September 1942.

The polymer research activities at Poly led in 1947 to the foundation of the Institute of Polymer Research, the first graduate program of its kind in America. It is hard to recall today, when a number of distinguished programs of this kind are active at American universities, that this was highly controversial half a century ago. Mark's enthusiastic leadership was essential, as were his innumerable contacts all over the world, which enabled Poly's students to meet all the leading polymer scientists of that time. On Saturday mornings, symposia on subjects related to the rapidly advancing

polymer research were held in Brooklyn and were attended by people from a wide area.

At the same time, Mark's friendship with polymer scientists in all countries where polymer research was active made the polymer community an exceptionally close-knit group. Because of his inability to bear grudges, he was most helpful to German and Austrian colleagues at a time when they were frequently ostracized. He also did a great deal to bridge the gulf between the area dominated by the Soviet Union and the rest of the scientific world. He was particularly devoted to the Weizmann Institute, created in Palestine in 1944, before the end of World War II, and under his leadership Poly was used to procure equipment for what became in time one of the world's outstanding scientific centers.

Advancing age did not seem to slow Mark's activities. Although he gave up his lecture course at Poly when he turned seventy, he continued for many years to delight students and faculty by his yearly lecture on "What is new in polymers," in which he related what he had heard during his many trips overseas and in America. By his count he made about 500 overseas visits, using his native Vienna as a base. He lectured extensively at universities and industrial laboratories, acted as editor of the *Journal of Polymer Science*, and was a consultant to the polymer industry and the U.S. government. He was also a most effective expert witness at a number of important patent litigations. Two experiences of his travels were specially memorable: In 1962 he was invited to present a lecture to the Japanese Emperor. I was told that such invitations were customary when a Nobel Prize laureate visited Japan, but that it was a unique honor in Mark's case since he did not fall into that category. Ten years later, Mark was one of the first two American scientists to visit China after the communist government seized power in 1949.

Over the years Mark became the recipient of many honors. Among these were honorary degrees from the universities of Liège, Uppsala, Berlin, Vienna, Madrid, Prague, and the Technion in Haifa and memberships in the Royal Institute of Great Britain, the National Academy of Sciences, and the Soviet Academy of Sciences. He received the Hertz Medal in 1928, the Nichols Medal in 1960, the Gibbs Medal in 1975, the Humboldt Award in 1978, the Wolf Prize in 1979, the Perkin Medal and the National Medal of Science in 1980, and the Michelson-Morley Award in 1989.

His personal life was deeply affected by the death, after a long struggle with angina pectoris, of his wife Mimi in 1970. Another blow was the death of his son Peter in 1979. During the last two years of his long life Mark lived with his son Hans, who was chancellor of the University of Texas. There I visited him in the spring of 1991. The Geheimrat was in a wheelchair, but there seemed little change in his spirit as he told me about preparations for a lecture on conducting polymers.

NOTE

FOUR YEARS BEFORE Herman Mark's death, Jeffrey I. Seeman asked him to contribute an autobiographical sketch to the series of such memoirs of outstanding organic chemists published by the American Chemical Society under the title "Profiles, Pathways and Dreams." Mark accepted with enthusiasm, and I had the unique pleasure to work with him on the editing of that booklet, which was published in 1993. This memoir presents a picture of Mark's vivid character that cannot be conveyed second hand.

SELECTED BIBLIOGRAPHY

1922

With W. Schlenk. Über das freie Pentaphenyl-äthyl. *Ber.* 55:2285-89.

1923

With H. Gonnell. Roentgenographische Bestimmung der Strukturformel des Hexamethylentetramins. *Z. Phys. Chem.* 107:181-218.

With K. Weissenberg. Über die Struktur des Pentaerithrits und eine graphische Auswertung von Schichtliniendiagrammen. *Z. Physik* 17:301-15.

With M. Polanyi and E. Schmid. Vorgänge bei der Dehnung von Zinkkristallen. *S. Physik* 12:58-116.

1925

With E. Pohland. Über die Gitterstruktur des Äthans und Diborans. *Z. Kristall.* 62:103-12.

1926

With H. Kallman. Über einige Eigenschaften der Comptonstrahlen. *Z. Physik* 36:120-42.

With L. Szilard. Die Polarisation von Röntgenstrahlen durch Reflexion an Kristallen. *Z. Physik* 35:743-47.

Über die röntgenographische Ermittlung der Struktur organischer, besonders hochmolekularer Substanzen. *Ber.* 59:2982-3000.

1928

With K. H. Meyer. Über den Bau des kristallisierten Anteils der Zellulose. *Ber.* 61:593-613.

With K. H. Meyer. Über den Aufbau des Seidenfibroins. *Ber.* 61:1932-36.

With K. H. Meyer. Über den Kautschuk. *Ber.* 61:1939-48.

With G. v. Susich. Über geregelte Mizellstrukturen von Kautschuk. *Kolloid-Z.* 46:11-21.

1929

With G. v. Susich. Über die natürliche Breite der Röntgenemissionslinien. *Z. Physik* 65:253-65.

With R. Wierl. Über die relativen Intensitäten des Starkeffekts-Komponenten H_{β} and H_{δ} . *Z. Physik* 53:526-41.

With R. Wierl. Starkeffektintensitäten im Längseffekt. *Z. Physik* 57:494-500.

Zur Theorie der Flüssigkeitsinterferenzen. *Z. Physik* 54:505-10.

The determination of particle size by the use of X-rays. *Trans. Faraday Soc.* 25:387-89.

1930

With J. Hengstenberg. Röntgenographische Intensitätsmessungen an gestörten Gittern. *Z. Physik* 61:435-53.

With K. H. Meyer. *Der Aufbau der hochmolekularen organischen Naturstoffe*. Leipzig: Akademische Verlagsgesellschaft.

With R. Wierl. Die Ermittlung von Molekülstrukturen durch Beugung von Elektronen an einem Dampfstrahl. *Z. Elektrochem.* 36:675-76.

1932

Über den Aufbau der hochpolymeren Substanzen. *Scientia* 51:405-21.

1937

With E. Guth. Statistische Theorie der Kautschukelastizität. *Z. Elektrochem.* 43:683-86.

With K. H. Meyer. *Hochpolymere Chemie*. Leipzig: Akademische Verlagsgesellschaft.

1940

Intermicellar hole and tube system in fiber structure. *J. Phys. Chem.* 44:764-88.

1950

With A. V. Tobolsky. *Physical Chemistry of High Polymeric Systems*. New York: Interscience Publ.

