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Article

Hermann Mark – A Pioneer of Polymer Science [a)]

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Abstract: Hermann Mark can be credited for being one of the founders of the field of polymer science and for being the father of polymer education in the United States. From the beginning, Hermann Mark understood how polymers behaved as they underwent temperature changes or as they were deformed. Over his long and productive lifetime, Hermann Mark published 20 books and over 500 articles. His Institute of Polymer Science at the Brooklyn Polytechnic University in New York served as the incubator for some of the most notable polymer scientists of the second half of the twentieth century.

Keywords: *Hermann Mark, Hermann Staudinger, polymer science, IG Farben.*

1. Introduction

In 1924, in his inaugural speech as the President of the American Chemical Society (ACS), Dr. Leo Baekeland said: "*If academics are given the opportunities to cut their teeth on some practical problems, they may grow to be of decidedly greater service to their science or its applications*".[1] He may have had many reasons to feel superior to academics; he had helped shape what at that time was already known as the plastics industry. In 1924, a thriving plastics industry was mass producing beautiful items out of cellulose nitrate, casein formaldehyde and Bakelite. His phenol formaldehyde "heat and pressure" patent,[2] had made Baekeland one of the wealthiest immigrants in the United States. However, the molecular structure of polymers remained an enigma and most plastics had not yet been invented. It was up to those academics, Baekeland criticized in his speech, to uncover the mystery of polymers.

a) Article following an oral presentation at the PHEA Plastics Heritage Congress, 29 – 31 May 2019, Lisbon.

Unbeknownst to Baekeland, that task was already underway, as two academics, Professor Hermann Staudinger and Dr. Hermann Mark were cutting their teeth on the topic of molecular structure of polymers.

2. The Science

It was four years earlier, at the German Chemical Society meeting Düsseldorf, Germany, when on June 20 1920, Professor Hermann Staudinger declared that polymers were not colloids. The post war chemists were outraged at that statement. Staudinger went further, and declared that polymers were rigid macromolecular chains. He explained that he had performed measurements and had seen that the viscosity of polymers increased proportionally to their molecular weight. He explained that longer macro-molecules impart higher friction to their neighbours, and therefore increasing the viscosity of the melt and making it more difficult to flow. Figure 1 captures this effect.

What Staudinger was not able to explain was the drastic increase in viscosity at higher molecular weights. This was done later, when Hermann Mark explained that it was due to molecular entanglements, since the polymers were flexible and not rigid as Staudinger stipulated. This is shown in Figure 2 that presents cartoons of flexible molecular chains.[3]

The shorter chains simple slide past each other, making the viscosity directly proportional to the length of molecules, which in turn is proportional to the molecular weight. This is represented using the following equation

$$\eta = k \cdot \bar{M}_v \qquad (1)$$

where, η is the viscosity, $\bar{M}_v$ is the average molecular weight and k is simply a proportionality constant.

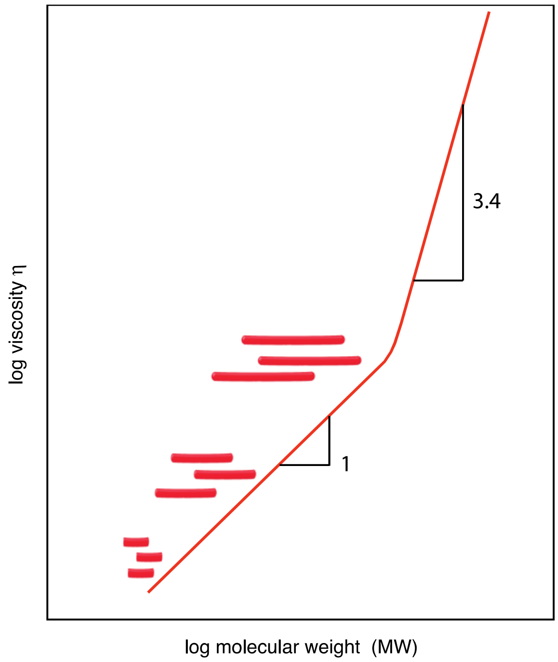

Figure 1 Staudinger's model: long rigid macromolecules impart higher friction, in-creasing viscosity proportionally to their length.

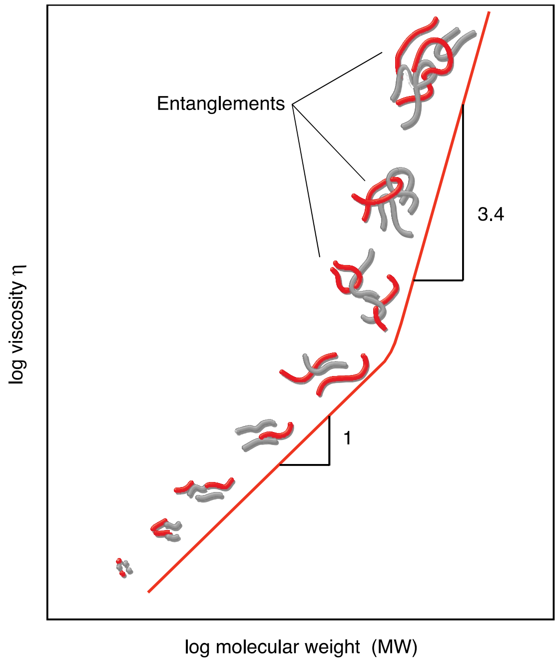

Figure 2 Mark's model: long flexible macromolecules entangle with one another, increasing the viscosity at a much higher rate.

He went further and stated that entanglements changed the above equation to

$$\eta = k \cdot \bar{M}_v^{\,3.4} \qquad (2)$$

where the viscosity increases proportional to the molecular weight to the power of 3.4.[4] Equations (1) and (2) are known as the *Mark-Houwink relation*.

It would take another 50 years before R.B. Bird, from the University of Wisconsin-Madison, using kinetic theory would prove that the exponent of 3.4, proposed by Mark, holds for all polymers and is simply due to molecular entanglement.[5]

Being able to visualize the molecular structure of polymers allowed chemists, physicists and engineers understand their behaviour during polymerisation, deformation, processing and product performance. One of the first chemists to take full advantage of this knowledge was the American chemist Wallace Hume Carothers who developed poly-chloroprene (today known as *Neoprene*), polyester and polyamide (also known as *Nylon*) during his tenure at the DuPont Company. In 1955, also at the University of Wisconsin-Madison, Ferry and his team published their now famous paper that describes the time-temperature super-position principle, which explains the relation between time scales during deformation and temperature of the polymer. This was only possible because of Mark's explanations 3 decades earlier.

2. His Life [4,6,7]

Hermann Franz Mark was born in Vienna, Austria, on 3 May 1895, to a Lutheran converted Jewish father, Hermann Karl Mark, and a Lutheran mother, Lilly Mark, née Müller. He spent his formative years in the Viennese fourth district where his father, a physician, and his mother welcomed many turn-of-the-century intellectuals into their home. One can only imagine the impact that it would have caused on young Mark when among his parent's friends were the musician Johann Strauss (son), but also among many others Sigmund Freud and Theodor Herzl, who with Chaim Weizmann went on to found the Zionist movement. Twelve years old, his life and world changed during a visit to a university laboratory. When he got home, the excited boy reported of "glass bottles and glass beakers, blue flames and Bunsen burners, bubbling liquids and those long rubber tubes through which vapours are diverted." Soon after, Hermann built his own laboratory in his room, where he conducted his own analyses and syntheses, starting a love affair with chemistry that lasted over 80 years.

The First World War forced him into adulthood. He served as a combat soldier on various fronts for a period of five years. During this time, he had two short stays in Vienna, the first to recover from a bullet wound. As usual, making the most of his time, during each stay he completed a semester of chemistry at the university. During the war, his many acts of bravery made Hermann Mark a national hero. On one occasion, Mark single-handently held a dozen Russian soldiers at bay until his whole commando reached safety. At the end of the war, after a short imprisonment in Italy, Mark, now the most decorated officer of the Austrian Army, continued his chemistry studies at the University of Vienna.

After graduating *summa cum laude* with a Ph.D. in chemistry in the summer of 1921, he moved to Berlin with his advisor Wilhelm Schlenk who succeeded Professor Emil Fischer at the University of Berlin. The year 1922 was an eventful year for Mark: after joining the Kaiser Wilhelm Institute for fibre chemistry (today the Max Planck Institute), he married Marie Schramek (Mimi). In the institute in Berlin, directed by R.O. Hertzog, Mark co-authored over 30 papers, which included his work on applying the field of X-ray diffraction when analysing crystal structures. His stay in the post-war, inflation ridden German capital gave him the opportunity to work and fraternize with people of various backgrounds and nationalities, broadening his intellect and interests. He always felt that a highlight of his years in Berlin was when he conducted experiments for Albert Einstein, using X-ray diffraction, to confirm Einstein's light-quantum hypothesis. In 1925, he finished his habilitation at Berlin University.

In the summer of 1926, Professor Kurt H. Meyer, one of the research leaders at the I.G. Farbenindustrie chemical giant's BASF labs in Ludwigshafen, visited Mark in Berlin and proposed that the young scientist move to industry to apply his basic research abilities to industrial problems. Mark accepted Meyer's offer and in January of 1927, moved to Mannheim, where he and his family would live for the next five years. This dramatic change, along with Mark's association with Meyer, his immediate boss at I.G. Farben, and his collaboration with Hermann Staudinger and other German academic scientists of the time, served as one of the catalysts that propelled the field of polymer science into the spotlight. In 1928, Mark and Meyer proposed a crystal structure for cellulose, stretched rubber and silk, nearly identical to the ones still accepted today. Their theory was supportive of Staudinger's high molecular weight theory and refuted the commonly accepted colloidal association theory of the time. Mark's model for polymer molecules differed from Staudinger's in that the molecules were flexible, not rigid, as Staudinger suggested. In the relatively short time at I.G. Farben, Mark produced an impressive list of publications, which included over 80 papers, 17 patents and 3 books.

With the political winds in Germany shifting to the right, and because of their Jewish ancestry, both Hermann Mark's and Kurt Meyer's positions at I.G. Farben became uncertain in the summer of 1932. The advice that came from the top of the company was that Mark look for an academic position, preferably outside of Germany. However, since I.G. Farben did not want to lose a certain degree of control on Mark's research, he was promised financial support for his future academic work. And so, Hermann Mark, his wife, Mimi, and two young children moved to Vienna in the fall of 1932, where he became director of the First Chemistry Institute at the University of Vienna. His friend and closest collaborator, Kurt Meyer, moved to Geneva that same year. With I.G. Farben funds, Mark was able to assemble an impressive team of scientists that included Eugene Guth, Robert Simha and Fritz Eirich. In Vienna, Mark published many fundamental papers on polymer physics including ground-breaking theories on polymer relaxation, poly-merisation kinetics and molecular weight distribution. However, leaving Germany was not enough; during the thirties, the Austrian political airs also started turning brown, culminating 15 March 1938, when the Nazis marched into Vienna. Mark was arrested the following day, and released without his passport four days later. The next eight weeks were spent recovering his passport and securing a position in Canada, to get Canadian and Swiss visas. To finance his trip to North America, the resourceful Mark purchased over one kilogram of platinum wire that he carefully wrapped around coat hangers. With visas in-hand, and their precious currency, the Marks and their niece attached a Nazi flag on the hood of their car and placed rope and skis to the roof and headed up the Alps. They drove into Switzerland on 10 May 1938. After bribing their household possessions out of Austria, the Marks spent the summer in Switzerland, France and England. Mark started his new position at the Canadian International Paper Company in September of 1938.

After almost two years in Canada, Mark moved to New York in the summer of 1940 where he founded, now as Herman Francis Mark, the Institute of Polymer Science at the Brooklyn Polytechnic University in New York. This marks the official start of polymer science education in the United States. The Institute of Polymer Science was the first American institution to award the Ph.D. degree in polymer science, and thus, became the incubator of many American scientists and educators. He advised over 100 scientists that included Fritz Eirich, Edmund Immergut, Herbert Morawetz and Charles Overberger. Some of his students went on as educators, multiplying the polymer science education all over the world. Eirich stayed at Brooklyn, Guth went to Notre Dame, Simha to Caltech and later to Case Western. Other pupils of Mark served as editors and writers such as Immergut, who had several editorial positions, including with Hanser Publishers between 1980 and 1997, which resulted in a vast polymer engineering and science book library, that has served as a reference and resource to many students, engineers and scientists. During his years at Brooklyn, Mark wrote hundreds of papers, many books and was the founder and editor of various journals including the Journal of Polymer Science. He also served as a consultant to DuPont, Polaroid, and others, and maintained relations with industry in his native Austria.

Hermann Mark's lifetime achievements were recognized by many: he received 17 honorary doctorates, numerous medals and awards, and served as an honorary member to dozens of scientific academies and professional societies. Hermann Mark, the war hero, scientist and teacher, died at age 96 in April 1992 in Austin (TX, USA).

More information about Hermann Mark's life can be found in the literature.[8,9]

Figure 3 Herman F. Mark at his office in Brooklyn; he had the last laugh.

4. Conclusion / Summary

Because Hermann Mark could fully understand the morphology of polymer molecules, explaining entanglement, crystallisation and other physical responses of polymers as they undergo temperature changes or are deformed, we can safely credit him for being the father of polymer science. His contributions continued throughout his life. His academic children, and their children continued to enrich the field of polymer chemistry, physics and science until this day.

Acknowledgement

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