Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Our Debt to the Polymer Pioneers

Edward G. Jefferson[a]
[a] E. L du Pont de Nemours & Company, Wilmington, Delaware

To cite this Article Jefferson, Edward G.(1981) 'Our Debt to the Polymer Pioneers', Journal of Macromolecular Science, Part A, 16: 5, 929 — 939
To link to this Article: DOI: 10.1080/00222338108056450
URL: http://dx.doi.org/10.1080/00222338108056450

J. MACROMOL. SCI.–CHEM., A16(5), pp. 929-939, 1981

Our Debt to the Polymer Pioneers*

EDWARD G. JEFFERSON

E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

It is a pleasure to participate in this symposium and to celebrate Dr. Herman Mark, who has done so much for polymer science and the polymer-based industries. I am honored to be asked to talk about our debt to the polymer pioneers in the presence of a man who is indeed a charter member of such a group. As you all know, Herman Mark has written about and explained the history and substance of polymer development with great insight and clarity. And he has probably imparted that understanding to more people in more parts of the world than anyone else.

The accomplishments of the leaders of polymer science laid a firm foundation for the chemical industry as it exists today. The profusion of materials spawned by polymer chemistry has done much to shape how people live, dress, travel, and communicate in contemporary society.

In the next few minutes I will discuss some of those leaders and their landmark discoveries. I'll try to give you a brief glimpse of where polymers have brought us and where they may be taking us in the future.

In thinking about my subject–our debts to the pioneers–several general observations seem relevant:

First, we owe much to many people. A large corps of brilliant men and women have built the edifice of polymer science. There are those who advanced the science in a major way–and I have

*These remarks were presented before the American Chemical Society's National Symposium on Polymers in the Service of Man, Washington, D.C., June 11, 1980.

selected seven whom I will discuss in greater depth in a few minutes. But, in addition to them, there are scientists going back to the early 19th century who laid the groundwork, who were compelled by curiosity to seek knowledge about the basic structure of materials. And there are many others in this century who have made invaluable contributions.

Second, recognition cannot go solely to any one institution or any one segment of society or any one country. The development of polymers was the product of both academic theoreticians and industrial pragmatists. Praise is due not only to those who developed concepts but also to those who saw the usefulness of polymers and who took risks in developing and marketing them. We should also acknowledge the international nature of polymer developments. The great flow of information across borders, fostered by Dr Mark and others, has moved the science ahead through both the sharing of knowledge and the force of competition.

Third, polymer science has progressed very far very quickly.

This is shown graphically in Fig. 1. It charts on a logarithmic curve the pounds of synthetic polymers produced in the United States each year from the 1920s, when polymer science first began to blossom. The number at the bottom of the curve is 15 million pounds for the year 1923. At the top, it's about 49 billion pounds, which is the production figure for 1979.

Figure 1 also shows the time frames for the seven individuals who are preeminent pioneers in the field. The timelines for each of

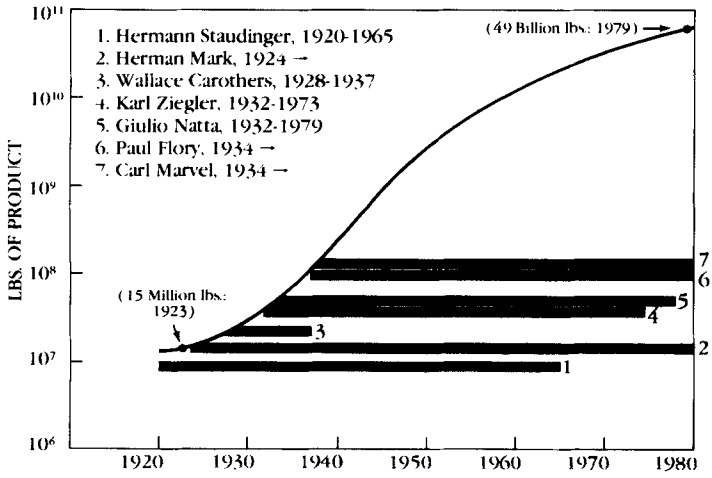

FIG. 1. United States production of synthetic polymers (lb/yr).

them begin with the year when they first published a paper or were granted a patent relating to polymers.

Table 1 is a chronology of material and conceptual milestones in polymer science. This doesn't pretend to be a definitive list. I'll bet Dr. Mark might choose a few different or additional landmarks. But the purpose is to give you a quick glimpse at the "lifeline" of polymer chemistry, particularly in its early stages. In the last 25 years–beyond the period shown on the "lifeline" list–many important polymers have been developed, such as aromatic polyamides and polyimides, polyurethanes, ionomers, thermoplastic elastomers, fluorocarbon copolymers, and the epoxies, to name a few. Also, new macromolecular concepts have become accepted. But for the purpose of the "lifeline" shown here, the emphasis is on pioneering ideas and discoveries.

Let me review some history. The roots of polymer science are almost as old as organic chemistry. The Swedish chemist Berzelius first mentioned polymerization as a word in 1833. Throughout the 19th century experimentation was continuous, and major discoveries appeared from time to time. But for the most part, scientists didn't fully realize the significance of their findings. The substances which appeared in their retorts and test tubes were intellectually interesting, but of little practical use. Most of the reactions were recorded and their products and processes then set aside.

Near the turn of the century, a few perceptive chemists were getting closer to structural answers. Through some elegant and painstaking work, Emil Fischer recognized that cellulose and polypeptides were, in fact, chain structures. He actually synthesized a chain of peptide units step-by-step. The work went on and, by the end of World War I, many of the broad classes of synthetic polymers had been discovered. Industry had already introduced several synthetic polymers, such as Leo Baekeland's revolutionary phenol formaldehyde plastics, alkyd resins for paints and coatings, and some rubbery polybutadienes. But scientists could not agree on the nature and structure of these materials.

The popular theory of the day was that they consisted of small building units held together by strong but mysterious forces. The structures were defined as "associated" or "colloided" or "micellar."

Soon these theories were to be disproved. In retrospect, however, we owe a considerable debt to these very early ideas and the scientists who advanced them. Armed with only the crudest instruments and with a new method for measuring molecular weights just emerging, they blazed the trail and opened up new territory in the understanding of materials. They may have willed their successors a variety of conflicting theories to explain the behavior of these materials, but they also provided a strong base for future understanding.

The pioneer who really changed the course of polymer history was Hermann Staudinger. He pulled together almost eight decades of experiments and theories and gave that work clear meaning.

Staudinger was a scientific skeptic who refused to accept the idea

TABLE 1. A "Lifeline" of Polymer Science up to 1955

Polymeric Materials Discoveries		Macromolecular Concepts	
1839	Polymerization of styrene	1893	Cellulose as a chain
1863	Polyethylene succinate	1906	Polypeptide chain structure
1872	Polymerization of vinyl chloride	1920	Chain structures of polystyrene, polyoxymethylene and rubber
1879	Polymerization of isoprene		
1900	Polymethylene from diazomethane	1928	Cross-linked network structure for rubber
1901	Alkyd resins	1929	Condensation polymers
1901	Acrylic ester polymers	1930	Statistical methods for polymers
1907	Production of Bakelite phenol formaldehyde resins	1930	Molecular weight by viscosity
1910	Polymerization of butadiene	1934	Chain conformation
1914	Polymerization of vinyl acetate	1934	Rubber elasticity
1930	Polychloroprene	1940	Monodisperse synthetic polymers
1930	Polyester and polyamide fibers	1944	Copolymerization-radical reactivities
1930	Production of polystyrene	1948	Quantitative theory of emulsion polymerization
1933	Styrene-butadiene rubber	1950	Protein alpha-helix
1933	High pressure polyethylene	1953	Structure of DNA
1941	Polytetrafluoroethylene		
1953	High density polyethylene		
1954	Isotactic polypropylene		

that polymers were loosely bound aggregates of small molecules. In his concept, they were very large molecules in long chains held together by covalent bonds. This idea met the resistance of many scientific colleagues, but he had the determination to stand by his theory. Together with his students, he devised techniques for preparing and characterizing many common and commercially important polymers. His early papers, among the more than 850 he published during his career, also established the important relationship between solution viscosity and polymer molecular weight.

What Staudinger succeeded in doing in a fundamental way was to show that polymers are macromolecules. This perceptive insight laid the groundwork for polymer science as we know it today and, somewhat belatedly, won him a Nobel Prize in 1953.

At about this same time a university instructor and research chemist 14 years younger than Dr. Staudinger entered the picture. I refer, of course, to Herman Mark. He was among the first to support Staudinger's revolutionary concepts, and he brought a more physical approach to polymer study. An early student of crystallography, he used the techniques of that field to show that the "repeat units" in a polymeric structure could behave like small molecules in forming crystalline domains, thereby altering the polymer's physical characteristics. The finding was an important advance in the science because it greatly aided the synthesis and design of polymers with needed properties.

No matter where Herman Mark worked in this period–whether in the university or the industrial laboratory–he made significant contributions. At I. G. Farben he developed commercial routes to polystyrene, the vinyls, and acrylics and made essential improvements in rayon to make it useful as tire cord. At the University of Vienna his studies of high polymer formation were critical to the advance of polymer science in the 1930s.

Altogether, his work importantly influenced the evolution of polymer science. But his later career as a teacher, mentor, and consultant after coming to America in 1940 is just as important. I will have more to say about it after considering some other pioneers.

Another scientist who has special meaning, particularly to us at Du Pont, is, of course, Wallace Carothers. He proved experimentally what Staudinger had proposed theoretically–that polymers were large molecules whose properties depended on their constitution. It was a powerful breakthrough.

We owe Carothers and his small band of research scientist a great debt. They started us on the road to neoprene and the development of such fiber families as the polyesters and the polyamides. They stimulated major experimental effort around the world that led to a tide of practical fibers, plastics, elastomers, and other synthetics.

Let me pause here to make a few observations about the development of polymers up to this stage. If you want to call the early explorations of Fischer, Baekeland, and others Stage One in polymer history, then you can call the Staudinger-Mark-Carothers era

Stage Two. It was the "Golden Age of Polymers" when theories were being advanced and consolidated and when new structures and products were virtually "exploding" on the commercial scene.

My first observation is that much interplay went on between industry and the universities in cultivating polymer chemistry as a science. It was one of those exemplary cases in science where pragmatist and theoretician collaborated well. The separation often found between academic and industrial science was absent in the work that centered on polymers.

Today, there is still much interest in polymers on the academic level, but in the United States it is mainly concentrated in engineering and materials sciences departments at about 30 universities. To meet the challenges of the future, more attention in physics and chemistry departments at major universities is needed. This is important if we are going to continue to train exceptional scientists and maintain growth in the polymer industry.

Comment number two is a statement of the obvious. As in the case of any developing field of science or technology, polymer scientists built on the ideas of others. Dr Mark, in one of his many articles on the history of polymers, stated the principle well. He wrote: "Evidence must be amended and modified as soon as new concepts and techniques become known which bring with them a higher level of preparative perfection and of structural understanding." That approach has permanent validity for all disciplines and for industry.

Successively, higher levels of understanding in polymers continued to be reached well after the breakthroughs of the 20s and 30s. Four other pioneers moved the science forward in a major way. Like Staudinger, Mark, and Carothers, all four had the unique ability to think on both practical and theoretical levels.

The names of Ziegler and Natta are frequently linked because of their separate but complementary efforts for which they shared the Nobel Prize in 1963. Ziegler's discovery of catalysts which cause low pressure polymerization of ethylene and other olefins and Natta's published elucidation of the steric structures of crystalline polypropylene by x-ray analysis contributed significantly to the rapid development of these polymers.

Ziegler began a new era in polymer chemistry and the plastics industry by uncovering his now famous "growth reaction" of aluminum alkyls and refining it. When he discovered, late in 1953, that certain transition metal-aluminum alkyl catalysts led to rapid polymerization, he uncovered a very important route to high density polyethylene.

Natta, Ziegler, and others quickly extended Professor Ziegler's ethylene polymerization reaction to the synthesis and characterization of stereoregular high polymers from propylene and other olefins. Crystalline polypropylene, prepared by various modifications of Ziegler's catalysts, is a major commercial polymer today, selling in the billions of pounds.

Paul Flory, another Nobel laureate, applied the techniques of the physical chemist to the definition of polymer properties. He introduced

and then clarified the concepts of chain transfer and cross-linking, two phenomena that have had profound influence on polymer properties. While in industry and at Cornell and Stanford, he quantified the behavior of polymers. At first, these concepts were applied only to dilute polymer solutions. Subsequently, they've been applied to polymers in bulk form. It can be said that Paul Flory's work led to an understanding of why polymers behave the way they do.

In any discussion of Flory's work, his classic reference books deserve special mention. To most of us in this room, they are like the Old and New Testaments of polymer science. They have probably explained polymer behavior more clearly to more people than any other books ever published.

The final pioneer on my list is Carl "Speed" Marvel. In 1917, his first of over 500 papers should have told us something about his ability to recognize important areas of study. It was on turbidity in beer. After analyzing that problem, he shifted to polymer chemistry and has spent a lifetime doing deliberate, craftsmanlike synthesis of polymeric molecules. A friend of mine recently put "Speed's" contributions in perspective. "Wallace Carothers," he said, "got the practical side of polymer synthesis underway, but 'Speed' Marvel defined the continental limits." It is hard to believe how many reactions Dr Marvel has run. And out of this prolific work has come a host of new and unusual polymers, including some with extraordinary heat stability.

"Speed" Marvel has also had tremendous impact as a teacher on the study and development of macromolecules. During his tenure at the University of Illinois from 1920 to 1961, more than 10% of all PhD's in organic chemistry in the United States received degrees from that institution. And because Dr Marvel was interested in polymers, many students followed his example. Many of his over 300 PhD's and postdoctorates are in key roles in industry and the universities today.

Like all outstanding people in any field, these pioneers were leaders, visionaries, stimulators, and exemplars. Some conveyed the important explorative nature of their work simply by doing. Others thrived on the open, vigorous exchange of opinion and advocated the vast potential of their unfolding young discipline. Whether they worked in industry, universities, or straddled both worlds, the pioneers stamped colleagues who worked with them and students who trained under them with a thirst for knowledge, a solid grounding in the art of inquiry, and an eagerness to "stretch" the horizons of polymer science. For these qualities alone, we owe them much.

While all the pioneers did brilliant, original work, none perhaps has filled so complete a role in the advance of polymer science as Herman Mark. Dr Mark uniquely spans the whole range of polymer development. He has made important scientific contributions in his own right; he set up the leading academic research institute on polymers in the United States; he has consulted and lectured in industry for decades, providing ideas and inspiration wherever he has gone;

and he still serves as a global conduit of information on polymer advances through his journals, travels and meetings. As the New Yorker magazine said of him 20 years ago, Dr Mark is the "most peripatetic polymer chemist anywhere around." And, remarkably, that still holds today in his 85th year.

Equally important as his many broad-ranging contributions is Herman Mark, the person. His informality, personal warmth, and enthusiasm have attracted students and scientists to the Institute of Polymer Research for more than 30 years. To a great degree, Herman Mark has left his "mark" on just about everybody who has ever worked in the field of polymers. His influence on polymer scientists reaffirms the fundamental nature of scientific progress, in that one generation learns from another and continues this cycle of knowledge growth.

Dr Mark has gained a wide reputation for his dedication to polymer advancement. This, combined with his desire to know and the force and magnetism of his personality, helped him establish a special camaraderie among polymer scientists throughout the world. In a real sense, the spirit of fellowship found in polymer meetings from New York and Washington to Rome and Tokyo represents the spirit of Herman Mark.

All of the other pioneers I have mentioned were "giants" in science and education. But none quite fits the mold of Herman Mark. We at Du Pont remember him traveling all night, arriving at a plant in a rural community at six in the morning, and then lecturing chemists new to polymers and consulting with research managers for an entire day without once losing his zest for the subject. As promoter, promulgator, and "energizer" of polymer chemistry, Herman Mark is proof that the exceptional individual still matters in the world of science and technology. In the special issue of the Journal of Polymer Science celebrating Dr. Mark's sixtieth birthday, Sir Eric Rideal summed it up well. He said, "There are no workers in the world in polymer chemistry who at some point in their investigations are not indebted to his pioneering work."

It is unlikely that the polymer pioneers ever envisioned the total impact of their work. But it's no exaggeration to say that the fruits of their labor have, in some way or another, touched most of the world. In the industrialized world, new living styles and standards, new uses of resources, new concepts of materials have evolved due, in part, to highly functional, low-cost polymers.

In recent years, it has become fashionable to disparage the so-called "plastic" society. This is nonsense. Synthetic products based on polymer chemistry are central to a society that must face up to the tough reality of rapid change. We are moving to a conservation ethic and will need to turn increasingly to polymers to gain efficiency, to save energy, and to survive in a competitive world of scarce resources.

I need only to cite a few facts to clarify my point:

A recent paper by the Worldwatch Institute, an organization that studies emerging global issues, concludes that the use of man-made fibers, plastics, and elastomers requires less energy, in many cases, than natural materials. The report states: "In an oil-short world, we may actually end up using more rather than fewer petrochemically based materials."

Lightweight plastic in the average automobile today provides total annual energy savings in fuel consumption equivalent to an estimated 14 million barrels of crude oil. The use of engineering plastics in automobiles is expected to double by 1985, with further significant increases in fuel savings.

And when comparing the total energy requirements of a polyester/cotton blend shirt with an all-cotton shirt, a National Science Foundation study found that the blends outperformed cotton fabrics. It takes 25% more energy to make a polyester/cotton blend shirt than to make one entirely of cotton. However, blend fabrics last longer and require less maintenance than all-cotton fabrics do. So the life-cycle energy requirements of all-cotton clothing in the United States were estimated to be as much as 90% higher than the blends.

Another debt we owe the pioneers is the lesson of technological evolution inherent in their work.

In most polymer-based products–from fibers to plastics to elastomers–industry has developed two, three, four, and more generations of polymer systems with others yet to come. In each step along the way, the properties have become more refined and their uses more sophisticated.

Look at what has happened in man-made fibers, for example. The initial generation of polymeric fibers met basic needs in clothing, home furnishings, and industry. With the next wave of improvement, fibers became easier to dye, easier-to-care-for, more stain- and fade-resistant, and more durable. The next generation filled specific needs. In clothing, fibers were given more stretch to conform to body movement; in carpeting, they were designed to be soil resistant and to reduce static electricity; and in industrial uses, they were made flame-retardant and abrasion resistant to meet all sorts of different demands. Now, fibers are being engineered even more precisely. They are being spun to match natural aesthetics, blended and combined to increase strength and reduce weight in automobiles and aircraft, and engineered for use in difficult industrial environments.

The same kind of evolutionary progress has taken place in plastics. Early brittle polystyrenes have been supplanted by more impact resistant, toughened versions or ABS. New engineering plastics have been developed such as polycarbonate and super-tough nylon. Sophisticated specialty plastics have replaced metals in demanding precision moldings, temperature- and corrosion-resistant parts, and lightweight electroplated structures. And the development of plastic materials for even more demanding uses continues.

Similar generations of polymer development can be traced in elastomers, films, finishes, and coatings.

What lies on the horizon for polymers? You've heard much about the prospects over the last three days. If there is any one, ongoing legacy that the pioneers left us, it is both the tradition and the determination to forge ahead, to see where else polymer chemisty–and physics, and biology–may lead us.

As I've shown in my fibers and plastics examples, polymer systems are adaptable and capable of impressive growth. Some might argue that man-made fibers and plastics and elastomers are mature industries. I am skeptical of such judgments. The opportunity for change is only as far away as the nearest research laboratory.

For instance, polymers have historically filled structural roles, whether it be as a piece of clothing or a plastic part. Today, they are more and more being designed to perform active or dynamic roles. Polymeric membranes are already helping to purify water and produce large-volume chemicals in an environmentally safe way. Photopolymers have high promise for image-making innovations. Optical fibers are making inroads in light and data transmission. Possibly in the future, variants of these active polymers and systems based on them can perform electromechanical, signal amplification, data storage, and data manipulation functions.

Major advances are also being made in analytical processes. Polymer chemistry was first put on a scientific footing by characterization methods that identified them as macromolecular chains. Now, through new approaches in instrumentation, spectroscopy, and the use of computers, the way is being paved for new resins, raw materials, and applications. One benefit is already being reaped and it's in keeping with our interest in conservation. Instrument hookups to computers are being used to monitor chemical reactions and send data back to operators within seconds. With more such instant feedback in the future, rapid process adjustments will become commonplace and will reduce waste, save energy, and improve product quality.

Then, there are areas of polymer science where we have just begun to scratch the surface. One such area is the study of biological macromolecules. Polymers form the basis for life. Proteins, nucleic acids, and oligosaccharides are complex polymers which control biological processes. But we are only beginning to understand them, and we have much to learn when it comes to duplicating what nature does in stitching together monomers into macromolecules.

However, through the study of life sciences and biological polymers, we may be able to expand our level of understanding enough to develop highly specific drugs and agricultural chemicals or to catalyze reactions to mass produce chemicals. The field is full of intellectual challenge. It is also capable of yielding quantum leap discoveries. It might not be too far-fetched to say that in another 50 years somebody might be making a speech on our debts to the pioneers of biological polymers. One can already visualize the early "lifeline,"

starting with the contributions of Linus Pauling and including the elegant body of experimentation by scientists such as Maurice Wilkins and co-workers, which culminated in James Watson's and Francis Crick's remarkable insight into DNA structure.

What this all amounts to is that those first insights by the pioneers have brought us a long way. A man such as Herman Mark, who was there at the beginning, can surely attest to the long road traveled. But I'd venture to guess that Dr. Mark would be the first to suggest that he and other polymer pioneers really only laid a grand foundation upon which we and succeeding generations must continue to build. That's the greatest legacy the pioneers could possibly leave us: The success of yesterday and the promise of tomorrow. It is our good fortune that Der Geheimrat continues to add much to that promise.