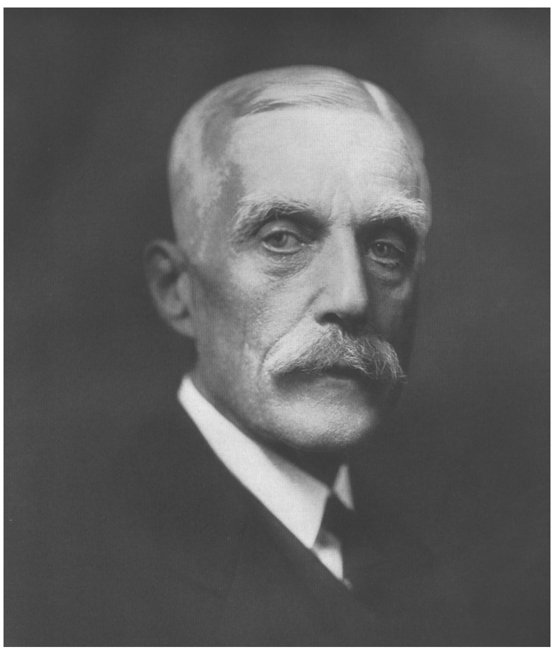
**Polymer Science in the Mellon Institute**

## Introduction

One of the institutions that provided a nurturing environment for the growth of a community of polymer scientists was the Mellon Institute for Industrial Research in Pittsburgh, PA. The founding concept that resulted in the Mellon Institute was articulated by Robert Kennedy Duncan in a series of three books: “The New Knowledge” (1905), “The Chemistry of Commerce” (1907) and “Some Chemical Problems of Today” (1911). He believed that sound industrial research should be carried out in the same location as fundamental research. The interplay of “pure” research and problem-oriented approaches benefited both groups as they exchanged the latest results and thoughts. He initially founded a program of Industrial Fellowships at the University of Kansas, where he held a Chair of Industrial Chemistry.

Robert Kennedy Duncan (1868-1914)

Two industrial pioneers in Pittsburgh, Andrew W. Mellon and Richard B. Mellon, desired to produce the same spirit of innovation in the chemical industry in America as had been demonstrated in Europe. They invited R.K. Duncan to come to the University of Pittsburgh as Professor of Industrial Research in 1911 and to initiate the same program of Industrial Fellowships. A separate entity, the Mellon Institute for Industrial Research, was founded in 1913. Although Duncan did not live to see his ideas flourish, the Mellon Institute grew and prospered under the guidance of the Mellons. Much of the credit for the success of the enterprise can also be attributed to the leadership of Edward R. Weidlein, who was a former student of R.K. Duncan at Kansas and joined the Mellon Institute in 1916. He served as its director from 1921-1956.



Andrew W. Mellon

Richard B. Mellon

Industrial firms such as Union Carbide and Gulf Oil sponsored one or more Fellows to conduct highly goal-oriented investigations in this mode. The Fellows from all the Fellowships interacted with one another and with the larger research community at the University of Pittsburgh. In 1922 the Mellon family endowed a special Fellowship in pure science. Early work in this group focused on synthetic organic chemistry and public health. Companies that sponsored Fellowships that studied polymers during this era included American Viscose, Dow Corning and Koppers . The existence of a polymer industry is one of the key factors involved in the history of polymer science.

Edward R. Weidlein

The Mellon Institute continued to grow and a magnificent building was constructed independently of the University of Pittsburgh in 1937. This facility served the Institute well and is still in use by Carnegie Mellon University. By this time there had been more than 1150 Industrial Fellowships.

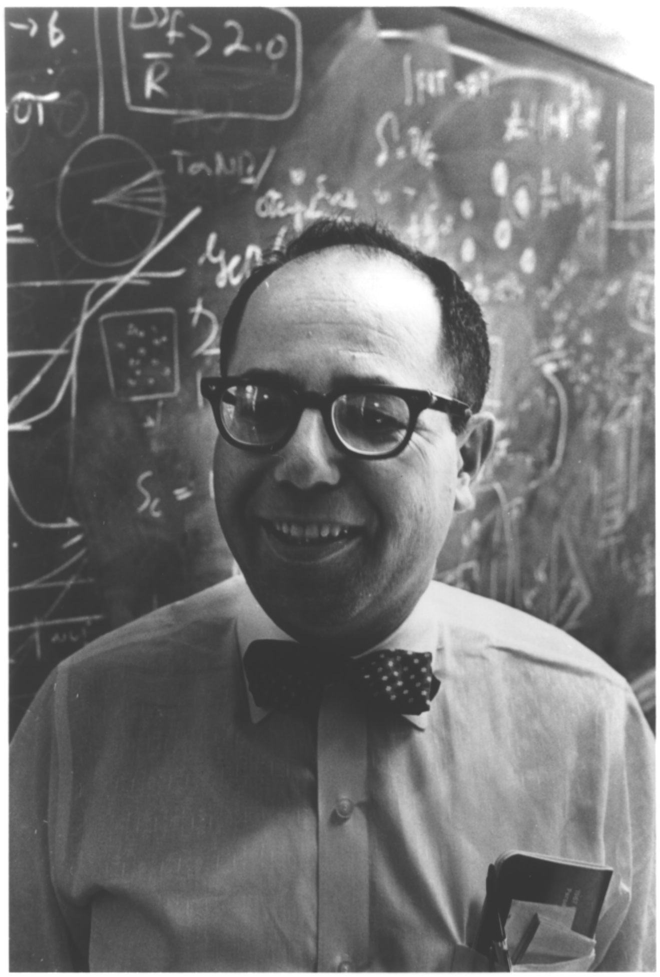
While practical searches for new polymers and new uses for polymers were well represented, the time was not yet ripe for a specific fundamental effort in polymer science. The initiation of such an effort required a source of funds that could be devoted to pioneering research. The wartime need for the production of synthetic rubber provided an opportunity to eventually generate surplus money. E.R.Weidlein was very active in Washington circles and served on the board of the Reconstruction Finance Corporation. The Rubber Reserve Company was founded in 1942 to supply the country with synthetic rubber, and both academic and industrial firms were recruited for the effort. Weidlein made sure the Mellon Institute was also a part of this program. One of the great strengths of the Mellon Institute was in Chemical Instrumentation and a Fellowship in Synthetic Rubber Instrumentation was initiated to assist the development of online plant monitoring equipment.

With the commercial success of the synthetic rubber program, the government now owned a very profitable business. Some of the proceeds of this enterprise were invested in pure research in polymers. In 1948 a pure research Fellowship in Synthetic Rubber Properties was founded in the Mellon Institute. The first member of this group was Thomas W. DeWitt. He had received his B.S. in Chemistry from Carnegie Institute of Technology in 1934 and his Ph.D. from Wisconsin in 1938. After serving as an Assistant Professor at Virginia Polytechnic and on the staff of the Tennessee Valley Authority, he was recruited back to Pittsburgh to lead the growth and development of this pioneering effort. One of the key hires was another Pittsburgher, Hershel Markovitz, who had received his B.S. from the University of Pittsburgh in 1942 and his Ph.D. from Columbia University in 1949. They formulated a program of research based on 1)careful synthesis of polymer samples, 2)chemical and structural analysis, and 3)precise measurements of the rheological properties of concentrated solutions and bulk materials.

The existence of well-characterized research samples of polymers encouraged fundamental studies using the best instrumentation. Infrared spectra of polyisoprenes were recorded and analyzed with W.S. Richardson in the Chemical Physics Department. X-ray scattering was used to derive the radial distribution function for amorphous polymers with L.E. Alexander.

The need to fully characterize the polymers also provided impetus to build new instruments and to hire people to carry out measurements. Three important techniques that were featured in the Mellon Institute were osmotic pressure, solution viscometry and light scattering. Dorothy Pollack and Paul Yavorsky served in this role. Accurate assessment of molecular weight and polymer size were essential in the interpretation of polymer properties.

One of the techniques for which the Mellon Institute was best known was dynamic rheology. A concentric cylinder viscometer capable of studying the complex shear modulus over a range of frequency and temperature was constructed by Markovitz and Louis Zapas. They also used this technique to study the non-Newtonian normal stress effect. Both Markovitz and Zapas went on to receive the Bingham Medal of the Society of Rheology. In addition to his outstanding research, Hershel Markovitz is remembered as a dedicated educator. A common view follows.



Hershel Markovitz

By the end of 1951 the Synthetic Polymer Properties Fellowship had nine members and research was proceeding in many directions. Because the polymers produced could be rapidly characterized, systematic studies of polymerization were carried out as a function of temperature, pressure and light absorption.

One of the central concepts of polymer science is that synthetic polymers are usually characterized by a distribution of molecular weights. Many polymer properties depend explicitly on the chain length and evaluation of theories for these properties depends on the existence of well-defined fractions. Systematic studies of the phase behavior of polymer solutions resulted in successful protocols for the fractionation of samples with a broad molecular weight distribution into narrow fractions.

The viscoelastic properties of bulk polymers and cross-linked elastomers remained a prime area of interest. The rheometer was improved and applied to new problems. The ultimate strength of rubber materials was studied.

One of the goals of the Fellowship program at the Mellon Institute was to provide an opportunity for the development of young scientists. One notable Fellow from this period was Frank J. Padden. He went on to a distinguished career at AT&T Bell Laboratories and received the High Polymer Physics Prize of the American Physical Society ( jointly with H.D. Keith ). He served as the secretary of the Division of High Polymer Physics for many years.

The collaboration with L.E. Alexander also produced new understanding of the crystallization of elastomers. Natural rubber, silicone elastomer and polybutadiene were crystallized by cooling and examined by x-ray scattering. Another process that produced crystalline rubber was stretching. As the rubber is elongated, the chains tend to orient in the direction of deformation. One clear manifestation of this phenomenon is the observation of birefringence in the sample. New apparatus to measure the birefringence was constructed. With further stretching, the melting point of the rubber is elevated above the temperature of the sample and crystallization takes place. This process was also studied with x-ray scattering.

In addition to producing samples worthy of study and constructing instruments to obtain fundamental physical properties, the Mellon Institute served as a welcoming home for theorists. Bernard Coleman (Ph.D., Yale, 1954) collaborated with DeWitt and Markovitz in the explanation of the non-Newtonian properties of concentrated polymer solutions using the methods of rational mechanics. The existence of a comprehensive conceptual framework provided a rigorous basis for further understanding.

Many synthetic polymers are characterized by chains with some degree of branching. The assessment of the role of chain branching in the properties of bulk polymers and solutions was another theme pursued at the Mellon Institute. The last theorist to join the Synthetic Rubber Properties Fellowship was Edward Casassa. He had received his Ph.D. from MIT in 1953 under Walter Stockmayer, and pursued polymer science as a post-doctoral fellow at Wisconsin until 1956. His insights had an immediate impact on the program in solution properties.

In 1955 the United States Government decided to return the production of synthetic rubber entirely to private enterprise. The plants were sold and a unique era in history came to a close. But, the acquired expertise of all the research groups supported by the Office of Rubber Reserve was considered a national asset and a temporary channel was created to continue funding this work. The polymer effort in the Mellon Institute was supported by a two year grant from the National Science Foundation, but the large group was reduced to two: Hershel Markovitz and Edward Casassa.

The next period of growth in research in polymer science in the Mellon Institute was instituted by the appointment of Paul J. Flory as the Executive Director of Research in October of 1956. In order to compete in the new national environment it was decided to intensify efforts in fundamental research. Initial funding for the growth of this enterprise was provided by Mellon family funds. It was anticipated that long-term support would come from various governmental and private agencies.

Paul Flory was one of the most visible polymer chemists and his monograph, *Principles of Polymer Chemistry,* provided a unifying perspective on a wide range of topics. He was a Professor of Chemistry at Cornell University and had been supported by the same Office of Rubber Reserve. It was hoped that he could attract both a corps of outstanding scientists and the funds to support them.

The most important appointment for the future of polymer science in the Mellon Institute was Thomas G. Fox as Assistant Director of Research. He had worked in Flory's laboratory at Cornell from 1948-50 and had established a successful industrial career at Rohm and Haas. He was a superb administrator and provided both scientific and organizational leadership.

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## WELCOME, DR. FLORY

Dr. Paul J. Flory
Our Executive Director of Research
(See pages 3-6)

This issue of the Mellon Institute News announced the appointment and high expectations for the future of fundamental research. Many new Fellows were appointed in emerging fields of chemistry. Flory created a small group that continued to work in areas of his direct interest. A.E. Ciferri and C.A.J. Hoeve studied rubber elasticity and established the extent to which changes in internal energy contributed to the elastic properties. Hoeve also pursued the physical basis of muscle action. Flory's record of publication remained strong during his tenure at the Mellon Institute. There were many papers that were based on work done at Cornell. A series of papers on thermoelasticity were published based on the Mellon years. And a considerable number of papers on crystalline materials appeared. Flory was also a popular lecturer during this era. His position at the Mellon Institute provided a solid base for his scientific efforts. But, administrative relations with the Chairman of the Mellon Institute Board, Paul Mellon, became strained and Flory resigned as Executive Director of Research in October 1960. He proceeded to Stanford University the following year.

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DR. THOMAS G. FOX

APPOINTED ASSISTANT DIRECTOR OF RESEARCH

T.G Fox proceeded to build a community of polymer scientists that became very productive. It was organized into two groups. The Structure and Properties of Macromolecules group included Ed Casassa, who continued to develop rigorous theories of solution structure and thermodynamics. A chemist, Franz Wenger, was added to make precisely known macromolecules as part of the project to correlate structure and properties. Another former student of Flory, Thomas .A. Orofino, was also involved in this project, and followed Fox from Rohm and Haas. Systematic studies of crystals and crystallization were initiated by M.J. Richardson, in collaboration with Flory. Guy C. Berry was appointed as a Fellow after receiving his Ph.D. from the University of Michigan.

A group devoted to Continuum Mechanics and Viscoelasticity was built around Coleman and Markovitz. A new Fellow from the Wisconsin group of John Ferry, Donald Plazek, was added. Experimental measurements on bulk polymers were carried out over seven decades in time by a combination of forced oscillation, torsion pendulum and creep techniques. This collaboration was also very successful and both Coleman and Plazek also received the Bingham Medal of the Rheology Society.

A recognized group in Theoretical Chemistry also existed for a few years and included Marshall Fixman, Ed Casassa and Henryk Eisenberg. Fixman carried out seminal work in polymer solutions, including polyelectrolytes. He was elected to the National Academy of Sciences and is currently the Editor of the Journal of Chemical Physics. Eisenberg worked on the theory of light scattering and ultracentrifugation of polyelectrolytes.

Although there were distinct administrative groups, collaboration between interested Fellows was encouraged. One productive effort that had major long-term effects was the construction of a new light scattering photometer by Berry, Casassa and Plazek. Guy Berry became one of the best-known practitioners of light scattering.

The period from 1960-63 was a time of intense activity. New topological structures such as star polymers were synthesized and characterized by viscosity and light scattering. The thermodynamic theory of star polymer solutions was derived. The properties of polymer solutions depend in detail on the solvent and temperature. The global conformation of a linear chain depends on the conditions and can range from a highly swollen coil to a condensed globule. But under the right conditions, the forces of expansion are compensated and the chains have a size consistent with a random coil polymer. Extensive light scattering and viscosity studies of dilute polymer solutions under these conditions were carried out.

Polymers are often processed in the bulk or in concentrated solutions. Fox often tackled fundamental problems with clear importance to industry and developed the overall framework for understanding flow under these conditions. He was also interested in the materials that were actually used in commerce, and was able to explain some of the properties of methacrylate polymers in terms of the development of stereoregular blocks during free-radical polymerization.

At the 50$^{th}$ Anniversary celebration of the founding of the Mellon Institute, Ed Casassa was chosen to present the achievements of the Polymer Structure and Properties Group. The combination of well-characterized model polymers, systematic experimental studies and a sound theoretical framework had yielded an increasingly synoptic understanding of polymer solutions. It had also resulted in financial support from the Office of Naval Research and the Air Force Office of Scientific Research.