

Paul J Flory – The Man Who Laid the Foundations of Modern Polymer Science

Paul Flory's contributions to polymer science have revolutionized the field. He was introduced to macromolecules when he joined the laboratory of Wallace H Carothers at DuPont in 1934, and ever since had pioneered in the development of essentially every fundamental area of this field.

To appreciate how far polymer science had progressed during this time, one has only to consider the state of knowledge of polymers during the early part of the twentieth century. In the late 1920's the molecular nature of a polymer was still a controversial question, some preferring to regard polymeric substances as firmly-bonded colloidal aggregates. Largely due to the work of H Staudinger, K H Meyer, and H Mark, this view gradually gave way to one in which both natural and synthetic polymers were considered to be large chain molecules whose atoms were linked together by ordinary covalent bonds.

It was against this background that Carothers decided to try to unravel the mysteries of polymer formation by a synthetic approach. From Carothers' work there emerged the concepts of functionality of monomers as an important property in their polymer forming capacity, and of a recurring unit which appeared over and over again in the macromolecule.

He also distinguished between 'condensation' polymers, in which the molecular formula of the structural unit lacks certain atoms present in the monomer from which it is formed, and 'addition' polymers, in which the molecular formula of the structural unit is identical with that of the monomer from which the polymer is derived. Carothers' research laid the groundwork for the manufacture of synthetic rubber-like neoprene, synthetic fibers

such as nylon, and other polymeric materials. With the recognition of the chain structure of polymers, theoretical chemists, including W Kuhn, H Mark, and E Guth, began to treat polymers as appropriate systems for study by introducing statistical methods for examining their physical properties.

It was during the course of these developments that Flory finished his PhD work in physical chemistry at the Ohio State University, having worked in the field of photochemistry and spectroscopy under the guidance of H L Johnston. He was then hired by DuPont, and assigned to work in Carothers' group. Through this association, Flory first became interested in polymers and the exploration of the fundamentals of polymerization and polymeric substances. He was an especially fine addition to a group of very clever synthetic chemists. He could appreciate their efforts from a theoretical outlook, seeking to understand the properties of polymers on the basis of kinetic, thermodynamic, and statistical mechanical principles. His unusual mathematical ability enabled him to express reaction conditions in elegant mathematical form which provided the basis for planning further work. His initial research was devoted to a study of the production of linear condensation polymers. By assuming that the reactivity of a functional group during condensation polymerization is independent of the size of the molecule to which it is attached, in contrast to the then prevailing view that reactivity decreased with increasing molecular size, he applied statistical methods and derived the distribution for the mole and weight fractions of various species in a polymer at various extents of reaction. These were later confirmed by experiment. Flory's work on condensation polymers was brought to the attention of the world's polymer science community by Carothers in his featured lecture at the Faraday Society Symposium on 'Phenomena of Polymerization and Condensation' in September, 1935.

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A year after the untimely death of Carothers in 1937, Flory left DuPont and joined the Basic Science Research Laboratory of the University of Cincinnati for a period of 2 years. There he extended his treatment of condensation polymerization to include multifunctional monomers whose polymerization led to the formation of branched structures. Flory's research, and later work of W H Stockmayer based on it, provided a quantitative description of gelation through formation of infinite networks. This development found application not only in the field of synthetic polymers but also in biological and other systems, e.g., antigen-antibody reactions.

With the outbreak of World War II and the urgency of research and development in synthetic rubber, the supply of which was imperiled, Flory was stimulated to return to industry, first to Esso (1940-1943), and later to Goodyear (1943-1948). At Esso, he took up the problem of the thermodynamic properties of polymer solutions, a subject that was treated at the same time by M L Huggins. Showing that the ideal entropy of mixing of small molecules in solution (in terms of mole fractions) could not be expected to hold for polymers dissolved in small-molecule solvents, Flory and Huggins independently derived an extremely simple and elegant expression for the entropy of mixing in terms of volume fractions of polymer and solvent. This simple result embodies the essential physical feature of polymer solutions and spawned hundreds of applications. Its power remains unimpaired although Flory and other polymer scientists devoted much subsequent effort to improving the details. At Esso, Flory also developed a quantitative characterization of network structures and provided a statistical mechanical theory of rubber elasticity. The thermodynamics of crystallization in high polymers and the frictional properties of polymers occupied Flory's interests at Goodyear, where he began a series of theoretical and experimental investigations on

crystalline polymers and (with T G Fox) on the viscosity of polymer solutions and melts.

In the spring of 1948, at the invitation of P Debye, Flory delivered the Baker Lectures at Cornell, and his first book, '*Principle of Polymer Chemistry*', which has served as an important vehicle for the education of polymer scientists, had its inception at that time. In the fall of that year, he joined the Chemistry Department at Cornell, where there was considerable activity in polymer science, and remained there until 1957. To the different approaches to the treatment of polymer solution viscosity developed at that time, those of Kirkwood and Riseman and Debye and Bueche, he added the one of Flory and Fox. This was followed by extensive experimental investigations carried out by Flory and his colleagues which quantitatively confirmed the validity of the Flory treatment in which the intrinsic viscosity is proportional to the ratio of the effective volume of a polymer molecule to its molecular weight, with the proportionality constant being essentially a universal one for flexible chain molecules. The effective radius itself is proportional to an average unperturbed value which depends on only short-range interactions within the polymer chain. The effects of excluded volume and polymer-solvent interactions determine the magnitude of this proportionality constant. A particularly thorny problem at that time was the evaluation of these long-range excluded-volume effects. In one of his most important contributions to the polymer field, Flory could show that, under conditions where excluded volume effects and polymer-solvent interactions just compensate (analogous to the Boyle temperature of a real gas where excluded volume and interatomic attractions just compensate), the second virial coefficient in the expression for the osmotic pressure vanishes. The polymer appears to behave ideally, and its intrinsic viscosity in such an environment is then proportional to the cube of the average unperturbed value of the radius of the statistical coil. Such conditions

were termed θ conditions by Flory but, at a Macromolecule Symposium in Uppsala in 1953, R M Fuoss proposed that these be called 'Flory conditions'. Flory's treatment of viscosity provides the connection between frictional properties and polymer chain configuration.

The Cornell period was one in which Flory also made contributions to the theory of swelling of network structures and the role of cross-linking therein, phase equilibria in semicrystalline polymers in the presence and absence of diluents, the effect of polymer asymmetry on phase equilibria, and the theory of elastic mechanisms in fibrous proteins. The application of some of these concepts led Flory into the field of biological macromolecules, in which he dealt with the kinetic and equilibrium properties of collagen and gelatin, and into the general problem of contractility as a manifestation of polymer properties.

These problems also occupied Flory's attention during the four years he spent at the Mellon Institute, after which he moved to Stanford. At Stanford, convinced that a proper treatment of real chains required a detailed analysis of their chemistry and the potentials involved in determining their structure, Flory turned his attention primarily to polymer chain configuration, dealing with both synthetic and natural polymers. This work is dealt with extensively in his second book, '*Statistical Mechanics of Chain Molecules*'. His main approach in this research was to relate the properties of polymers in solution and in bulk to their chain character, with their bond lengths, bond angles, and interatomic interactions being no different from those in compounds of low molecular weight. He thus describes the spatial geometry of a random chain molecule in terms of rotations about bonds, "subject to a potential determined by the character of the bond itself and by hindrances imposed by steric interactions between pendant atoms and groups", the number of available configurations

being profuse. Adopting this view, he accounted for many polymer properties, including rubber elasticity, hydrodynamic and thermodynamic properties of polymer solutions, and various optical properties. By carrying out experiments under θ conditions, he focused attention on the short-range features of a polymer chain that distinguish one type of macromolecule from another, and developed theoretical methods, within the framework of classical statistical mechanics, to deal realistically with the short-range features peculiar to a given type of chain.

Flory demonstrated that his analysis of the spatial configurations of macromolecular chains applies not only to an isolated molecule (e.g., as it exists in a dilute solution) but also, as a consequence of the statistical thermodynamics of mixing of polymer chains, to molecules in a bulk amorphous polymer, even in the total absence of a diluent. While the latter conclusion has evoked disagreeing viewpoints, Flory argued effectively that a bulk polymer has sufficient molecular flexibility to surmount problems thought to arise from dense packing and has no need for recourse to partial ordering or segregation of chains to attain the statistical configurations available to an isolated molecule. His view was vindicated by experimental evidence from rubber elasticity, cyclization equilibria, and later from neutron scattering from protonated amorphous polymers in deuterated hosts (and vice versa). The neutron scattering studies also confirmed Flory's assertion that chains in a bulk polymer have the unperturbed average dimensions characteristic of θ -conditions, i.e., that the excluded volume perturbation (which exists in dilute solution) is annulled in the bulk amorphous state. To quote Flory, "although a chain molecule in the bulk state interferes with itself, it has nothing to gain by expanding, for the decrease in interaction with itself is compensated by increased interference with its neighbors".

Another important area in which Flory made pioneering contributions is that of polymer crystallinity. Aside from providing an understanding of the kinetic and equilibrium properties of semicrystalline polymers, he put forth strong arguments to support his view of the morphology of such materials in the face of opposing views. Others had regarded semicrystalline polymers as made up of crystalline lamellae connected by amorphous regions, with the polymer molecules folded regularly; the chain is alleged to execute a sharp reversal of direction upon emerging from and re-entering a lamellae (the 'adjacent re-entry' model). In contrast, Flory regarded the crystalline lamellae as being irregularly connected, with random reentry of chains into the lamellae and profuse interconnections between neighboring lamellae. Flory based his view on, among other things, the facts that regularly folded 'adjacent re-entry' structures involve conformations that are of high free energy, and that the rate of crystal growth is too rapid to allow the chain molecule to relax in time to conform to the 'adjacent re-entry' model. Neutron scattering experiments involving deuterated polymer in a protonated host (of the type mentioned above) provided evidence which at least partially supported the Flory view. The resolution of this question was important for understanding the mechanical properties of semicrystalline polymers. In the Flory model, the application of stress, e.g., in plastic flow, leads to melting of the small crystalline regions, without chain rupture; this is followed immediately by recrystallization, resulting in 'a different array of sequences being incorporated in the regenerated crystallite in a pattern compliant with the prevailing stress'.

Flory's laboratory was always a place of scientific excitement and collegiality. He had an uncanny knack for assessing the essential physical aspects of a problem and formulating simple models that are amenable to mathematical treatment yet realistic enough to explain and predict experimental

results. He abided by very high scientific standards and was determined that these be adhered to not only by himself but by the whole scientific community. He was very highly regarded as a person and teacher by his many students and colleagues. He was always generous in his appreciation of their efforts and scientific contributions. His strong sense of honor led him to speak out courageously against, and challenge, the abridgment of human rights in areas of the world where people have been prevented from carrying out their professional activities in the spirit of free inquiry that is such an essential ingredient of science.

Flory's career was an unusual mix of industrial, research institute, and academic activity. His research contributions have charted the course of polymer science during almost half a century. His impact has been felt not only through his published papers and books, but in his effective discussions at scientific meetings and in the contributions of the many students who received their training in polymer science in his laboratory. Flory's outstanding work has been recognized in the form of numerous honors such as the Baekeland, Chandler, Debye, Gibbs, Nichols, Perkins, and Priestly Awards, the U.S. National Medal of Science, and, in 1974, the Nobel Prize in Chemistry. Flory remained at Stanford till his death on September 9, 1985, just three months after many of his friends, colleagues and past students had celebrated his 75th birthday with a scientific symposium at Stanford University.

Harold A Scheraga

Department of Chemistry & Chemical Biology
Baker Laboratory, Cornell University, USA
Email: has5@cornell.edu

