Paul Flory and the Dawn of Polymers as a Science

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If Wallace Carothers was the designer, Flory was the architect and builder of the edifice of polymer science. If Carothers was the composer, Flory was the man who wrote the notes for the music. Carothers and Flory represent the quintessential qualities that are needed to make great science – intuition and rationality, experiment and theory, flights of imagination and diligent reduction to practice, exuberance and rigour.

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Paul Flory was born on 19 June 1910 in Sterling, Illinois. He obtained his first degree in chemistry from Manchester College, Indiana, a liberal arts college. As in the case of Carothers, he too was deeply influenced by his teacher of chemistry, Professor Carl Holl at Manchester College, and was encouraged by him to pursue a doctoral degree in chemistry. Flory pursued his doctoral education under the supervision of Professor H L Johnston at the Ohio State University, Columbus, Ohio, and obtained his PhD in 1934 on a study of the photochemistry of nitric oxide. Nothing in his early academic career gives a glimpse of what Flory would become in his later life; and the indelible footprints he would leave on the history of chemistry.

Much of Flory's early inspiration that led him on a road not so well trodden, came from Carothers. Immediately after completing his PhD, Flory joined DuPont where he began working with the group of Wallace Carothers. Carothers triggered his curiosity and interest in polymers. By 1935, Carothers had already laid the synthetic framework for addition and condensation polymers, and had defined the rules governing their formation, albeit somewhat empirically. One can only imagine the animated discussions between Carothers and Flory, where Carothers would have elaborated on how polymers are synthesized and their unique constitution dependent properties, while Flory asked why such reactions occur in the first place, and what molecular forces determine their

Keywords
Polymer science, polymerization, rubber elasticity, chain-growth, chain-transfer, random coils, statistical mechanics, solution properties, molecular weight distributions.

Paul J Flory

Figure 1. Paul Flory

unique properties. Flory embarked on his professional journey trying to find answers to these questions, a journey that would make the study of polymers truly a science, rooted in kinetics and thermodynamics, where rigors of statistical mechanics can be applied to understand the probabilistic behaviour of random coils of large polymer chains.

Flory admitted in his later years that he did not know what a polymer was in 1935, and that Carothers convinced him that polymers could be studied scientifically. Flory acknowledged the profound influence of Carothers saying, " It was my good fortune to be assigned to the small group headed by Dr Wallace Carothers, inventor of nylon and neoprene, and a scientist of extraordinary breadth and originality. He encouraged me to pursue my ideas. My inclinations were somewhat different from his. I was his physical chemist. It was an extraordinary opportunity."

In 1937, personally shattered by the untimely demise of Carothers, Flory moved to the University of Cincinnati. In 1940, he once again moved to the industry – the Standard Oil Development Company (which later became Exxon), where the polymer of isobutylene – polyisobutylene, was discovered by a cationic polymerization process in 1940. Polyisobutylene must have fascinated the intellectual curiosity of Flory because it was the first all-hydrocarbon rubber with no unsaturation in the chain that exhibits elastic properties. Flory's lifelong obsession with theories of polymer conformation and its effect on rubber elasticity were triggered during those years. With John Rehner, Jr., he developed a useful model of rubber networks and its application to the swelling phenomenon. In polyisobutylene solutions, he personally measured viscosities over a very wide range of molecular weights, far greater than any earlier examples, and showed their strict adherence to the Mark–Houwink–Sakurada law with a fractional exponent of 0.64.

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He later moved to the Goodyear Tire and Rubber Company in 1943, and was part of the wartime programme of the US Government to produce the first synthetic rubber that could substitute natural rubber in the manufacture of tires. What emerged as an outcome of this effort was the first synthetic rubber, a random and statistical copolymer of styrene and butadiene, produced by a unique polymerization process namely – radical induced emulsion polymerization of the organic monomers in an aqueous media.

Thus, between 1935 and 1948, Flory occupied a ringside seat, observing the evolution of some of the most exciting chemistry for making polymers: condensation reactions (at DuPont), carbocationic polymerization (at Standard Oil), and free radical emulsion chain growth polymerization (at Goodyear). This must have given abundant grist to his inquiring mind and he began formulating many of the theories of polymerization that would mature in later years as fundamental tenets of a robust science, providing an understanding of the behaviour of large macromolecules and endowing the science with predictive capabilities.

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Early in his career at DuPont, Flory realized that each molecule in a polymer must be different in terms of its chain length and that the properties of synthetic polymers can be best understood only as 'average' properties. From this emerged the concept of 'molecular weight distribution' of a polymer as one of its fundamental properties. He laid to rest a widely prevailing notion that in a condensation polymerization, the reactivity of end group decreases with increasing molecular weight. This was a conclusion based on the then prevalent collision theory of bimolecular chemical kinetics. Flory, in constructing a straightforward statistical treatment of the distribution problem, took the contrary view that reactivity under given conditions of solvent, temperature, pressure, and concentration is essentially a function only of the local structure and not of the overall molecular size. He argued that increasing size would indeed reduce the translational mobility of a molecule, but that this would be compensated by increasing the duration of each contact between reactants. Good experimental information was meager at that time, but in subsequent years, he provided with his own hands much of the kinetic data that sustained his view. The resulting distribution formula could not be simpler – the number of chains with x links decreases exponentially with x. This ‘most probable distribution’, as Flory called it, remains the norm that often describes actual polymeric products. He published this seminal work in 1936. Later, he defined the kinetic steps involved in free radical chain-growth polymerization and introduced the concept of ‘chain-transfer’, where chains are broken, thus limiting molecular weight, but other chains continue to grow with no limits on conversion of a monomer to a polymer.

Doubtless, his outstanding achievement of those years was the development of the famous Flory–Huggins, or the ‘volume fraction’ formula for the entropy of mixing of polymer solutions[1]. This now classic formula plays a role analogous to that of the van der Waals equation of state for real gases because although approximate, it conveys the essential physics and leads to reliable qualitative predictions. It remains the norm to which real behavior is customarily compared. He later extended his treatment to polymer solutions of arbitrary complexity.

He extended the concept of ‘excluded volume’ to polymers stating that it is not possible for one of the parts of a long chain molecule to occupy a space which is already taken up by other parts of that molecule. He provided a method to calculate the apparent size of a polymer molecule in a ‘good solvent’. He also provided a theoretical framework for understanding phase transitions in polymers. It is not surprising that Flory’s name is associated with most of the fundamental concepts in polymer science (*Box* 1). His lifetime contributions to the understanding of solution thermodynamics, hydrodynamics, molar mass distribution, glass transition, crystallization, melt viscosity, polymer chain entanglements, rubber elasticity, cross-linking, polymer networks, liquid crystals, and chain conformation, belies our imagination.

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In 1948, he was invited by Peter Debye to lecture at Cornell University as the George Fisher Baker Non-resident Lecturer in Chemistry. Flory, in a series of scintillating lectures, laid bare his phenomenal understanding and foresight concerning polymer molecules. This was to emerge later as a book entitled, *Principles of Polymer Chemistry* in 1953. This book marked a watershed moment in the history of chemistry and defined the coming

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[1] This result was obtained essentially simultaneously by Maurice L Huggins in the United States and by A J Staverman in Nazi-occupied Holland.

Box 1. Flory's Contributions to Fundamental Concepts in Polymer Science

- *Flory–Huggins Theory*: Defines dilute solution properties and entropy of mixing of polymers.
- *Flory Interaction Parameter*: Defines the nature of interaction between a polymer and a solvent.
- *Flory Theta Temperature*: A temperature at which polymer–solvent interaction parameter vanishes.
- *Flory–Rehner Equation*: Extent of swelling of cross-linked polymer.
- *Schulz–Flory Distribution*: Most probable distribution of molecular weights, determined by the rate of chain transfer.
- *Flory–Fox Equation*: Predicts that for a truly random copolymer, the Tg is a weighted average of the Tg's of the respective homopolymers.

of age of polymer science. It was the first definitive and authoritative treatment of a new class of materials called polymers, and placed in perspective, the formation and behaviour of such materials within the framework of well-accepted theories of kinetics, thermodynamics, and statistical mechanics. The book is a classic and a compulsory read for any student of polymer science. Polymer science has witnessed an explosive growth in the past sixty years since the publication of this book, yet it is fair to say that none of the 'principles' that Flory proposed has been violated. This speaks for the incredible intellect of this man. Flory continued on the faculty of Cornell for nine years.

In 1961, Flory moved to Stanford University as a professor where he stayed until his death. On September 10, 1985, Flory was scheduled to lecture at the American Chemical Society meeting in Chicago on his analysis of the abrupt collapse of randomly coiled polymer chains in a poor solvent. He was also slated to argue his case that at small stretching forces, rubber is stiffer because the cross-linked junctions are entangled with the neighbouring chains. As the force increases, the junctions slip free of the entanglements and the rubber becomes less stiff at larger stretching forces. Sadly, as he was working on his lectures at his weekend home in Big Sur, overlooking Monterey Bay, he died of a cardiac arrest. He was 75.

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Flory was awarded the Nobel Prize in Chemistry in 1974 for his

Box 2. Flory on the Importance of Basic Research

"Significant inventions are not mere accidents. This is an erroneous view. Happenstance usually plays a part, but there is much more to invention than the popular notion of a bolt out of the blue. Knowledge in depth and breadth are virtual prerequisites. Unless the mind is thoroughly charged before hand, the proverbial spark of genius, if it should manifest itself, probably will find nothing to ignite Creative invention without a firm grasp of underlying principles becomes increasingly rare This assertion contradicts the prevalent view that measure of practical value of basic research lies in its success in uncovering nuggets of truth that can be commercialized I am convinced that basic research has a more pervasive mission in advancing knowledge, in providing incisive concepts an in sharpening insights. These are the ingredients that nurture enduring innovations of the broadest scope Basic research must not be treated as an dispensable adjunct whose cultivation can be postponed at the pleasure of the profit margin."

Paul Flory
Priestely Medal Lecture, 1974

"fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules." He was the first chemistry faculty member of Stanford to have won the Nobel Prize.

Paul Flory was a strong believer in the power of basic research leading to creative invention (*Box* 2). Flory's enduring legacy was that he saw polymers through the prism of physical chemistry, and was able to delineate the molecular concepts behind polymer science. Polymer science, after Flory, emerged as a discipline in its own right, but with strong connectivity to organic chemistry, physical chemistry, and physics. Through his work, he also underscored the relevance as well as provided a rationale for basic research, something Charles Stine had contemplated when he built the programme of basic research at DuPont in 1928, and invited Carothers to join this endeavour. The foresight of Stine, the creative burst of Wallace Carothers, and the diligent pursuit of important questions regarding the nature of polymers by Paul Flory not only led to the emergence of polymer science, but also that of an industry that led to the creation of a multitude of products for the good of mankind.

In the words of his long time collaborator, Thomas Fox, the secret of his success was "unparalleled intuition for grasping the physical essentials of a problem, for visualizing a phenomenon in terms of simple models amenable to straightforward treatment, and productive of results that are valid to the degree required by the original statement of the problem." Consequently, Flory was able to present his concepts and results in a way that was instructive, understandable, and directly useful to the readers working in the area of basic polymer science, as well as those interested in industrial applications.

Suggested Reading

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