sphere, on the other hand, is only 6/1000 as massive as the earth's, but it circulates rapidly enough to generate the frequent dust storms that on occasion cover the whole planet. Extreme variations of temperature between day and night and between summer and winter reflect the fact that the martian atmosphere is much more under the influence of radiative processes than that of the earth, where temperatures do vary, but to a lesser extent. Venus is thought to be at the other extreme, with nearly uniform surface temperatures of 600°C or more over the entire planet. The uniformity is thought to be due to the stabilizing influence of the circulation and results in a greenhouse climate that varies little with time of day or season. The earth, with a cloud cover of about 50 percent, is also intermediate in this respect between the normally clear martian atmosphere and completely cloud-covered Venus. In contrast to the terrestrial clouds of condensed water, those on Venus are now thought most likely to be sulfuric acid.

Although differences among the planetary atmospheres are more apparent than similarities, some analogous features do exist. Weather patterns in the winter hemisphere of Mars, for example, are thought, on the basis of known temperature data and calculated flows, to consist of unstable westerly winds like those observed in the middle latitudes on the earth, while the martian summer hemisphere may have steady easterly winds like the terrestrial tropics. A more fundamental similarity is what is believed to be the common origin of the atmospheres of Mars, Venus, and the earth—the evolution of carbon dioxide, water vapor, and other volatiles from the mantles of these planets by volcanism. On Mars much of the water vapor is thought to have escaped into space, while on the earth it condensed to form the oceans. Carbon dioxide is the main constituent of the atmospheres on Mars and Venus (water vapor may be present on Venus as well, but it has not yet been observed), but on the earth it reacted chemically with the oceans and the surface rocks, leaving nitrogen—also of volcanic origin—as the most abundant constituent. Many investigators now doubt that the earth ever had an earlier primitive atmosphere of hydrogen, of which there is no trace here or on Mars and Venus.

Investigation of planetary environments has provided new evidence of differences among the inner planets in the manner of their interaction with the interplanetary medium. The discovery of the magnetosphere, the magnetic sheath that surrounds the earth and prevents the charged particles of the solar wind from reaching the planet, was one of the major events of the early years of the space era. Mercury also seems to have a magnetosphere. Mars and Venus do not have strong magnetic fields, however, but it is now known that they are surrounded by a conducting layer of plasma in which a magnetic field sufficient to exclude the solar wind is induced.

The emerging picture of the solar system is thus one full of surprises but possessing a coherence which points to a vigorous, continuing evolutionary process. The elucidation of that process, if not immediately at hand, is now advanced to a degree that has kindled the interest of investigators from a broad range of disciplines and has raised anew fundamental questions about the conditions necessary for the origin of life. Inquiry into the nature of the solar system and its planetary bodies has turned full circle and become a subject of the greatest scientific interest at a time, ironically, when public interest in space exploration seems to have waned and political support is diminishing. As long as spacecraft continue to fly, however, the prospects for a continuing revolution in our view of the solar system, and of the earth itself, appear to be unparalleled.—ALLEN L. HAMMOND

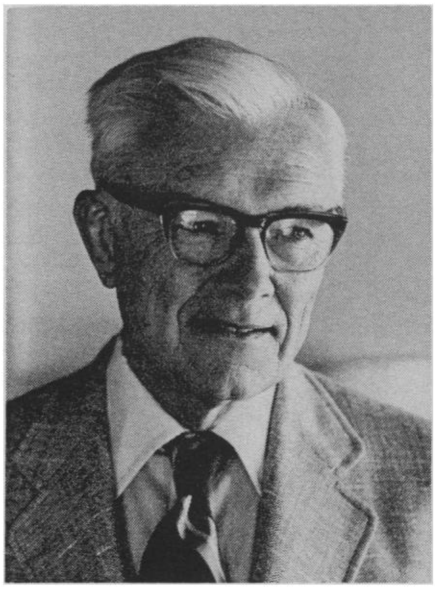
The 1974 Nobel Prize for Chemistry

The 1974 Nobel Prize for Chemistry has been awarded to Paul J. Flory of Stanford University "for his fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules." Flory thus becomes the fourth Nobel laureate to be cited for studies largely concerned with synthetic high polymers. His predecessors were Hermann Staudinger (1953), Karl Ziegler (1963), and Giulio Natta (1963). In one respect, the new award is reminiscent of Staudinger's, recognizing as it does a long series of outstanding contributions spanning an interval of almost 40 years. The fields, however, differ greatly. Staudinger was a synthetic organic chemist whose studies of cellulose, natural rubber, and polystyrene and other synthetics, supplemented by his indomitable confidence, led to the eventual recognition that such substances are composed of large molecules whose atoms are linked together by ordinary covalent bonds, rather than by some mysterious "partial valences" or "secondary forces"; and it was he who coined the now universal term macromolecule. Flory, on the other hand, is a physical chemist who, taking the essential structural principle of Staudinger as established, has done more than any other individual to demonstrate that the physical and chemical properties of macromolecular systems are fundamentally not sui generis, but understandable to the same degree as those of nonpolymeric matter in the light of the basic disciplines of thermodynamics, kinetics, and statistical mechanics.

It is scarcely possible in a short article to convey the magnitude of Flory's influence on polymer science. The examples given below have been selected arbitrarily. There are few areas within the discipline that have not been advanced and enriched by his efforts, and many of the principles he discovered have found applications not only in fundamental chemistry but also in industry and in biology. Through the publication of his *Principles of Polymer Chemistry* (Cornell University Press, 1953) he made one of the definitive contributions to pedagogy in the field. For more than 20 years this book has served as the bible for generations of polymer scientists, and it is much in use today.

Thanks to its industrial importance and its biochemical spin-off, macromolecular science has a host of practitioners, and it is pertinent to seek for the characteristics that distinguish Flory among so many. Thomas G. Fox of Carnegie-Mellon University, a longtime friend and collaborator of Flory's, put it this way on a past occasion: "I think the secret of his success is an 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's concepts and results are presented in a way that is instructive, understandable, and directly useful to the reader. This is equally true for those working in basic polymer science and those interested in industrial applications." It might be added that the intuition (faith?) that one's intuitions are correct is also an ingredient. On occasions when Flory's ideas have been opposed or regarded skeptically, he has tenaciously persisted and most frequently has been proved right.

Born in Sterling, Illinois, on 19 June 1910, Paul Flory graduated from Manchester College, Indiana, in 1931 and 3 years later received the Ph.D. degree in physical chemistry from Ohio State University. His doctoral research, guided by Herrick L. Johnston, concerned the photolysis of nitric oxide and afforded an experience in chemical kinetics that was soon put to further use. Accepting employment with DuPont in Wilmington, Flory was assigned to the research group of the great Wallace H. Carothers, inventor of nylon and other synthetics, whose name often is placed alongside Staudinger's as a founder of macromolecular chemistry.



Paul J. Flory

The formation of a condensation polymer like nylon involves stepwise repetition of a simple elementary reaction: condensation (with the elimination of water) between an amino group and a carboxyl group to form a polyamide. When Flory was first led to consider the distribution of molecular species to be expected from a reaction of this type, it was commonly supposed that the normal reactivity of a given kind of functional group would be suppressed if it were on a very large molecule: mere size per se was considered to impart a sluggishness that would bar unlimited chain growth, and existing polycondensation rate measurements were so interpreted. Flory, however, 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 local structure and not of overall molecular size. The evidence was meager, but Flory stood his ground, pointing out past errors of interpretation and subsequently providing with his own hands the incontrovertible kinetic data that sustained his views. The resulting distribution formula is beautifully simple: the number of chains with x links decreases exponentially with x. This "most probable distribution," as Flory called it, remains the norm which often describes actual polymeric products, at least approximately, and against which real systems are compared. When published in 1936, methods for direct observation of chain length distributions were inaccurate and lengthy, but today's gel-permeation chromatographic techniques have furnished many examples.

These efforts were briefly interrupted by the premature death of Carothers in 1937. Soon thereafter Flory moved to the University of Cincinnati, but not before he had made another fundamental contribution to the understanding of polymerization mechanism. In a paper reviewing the kinetics of olefin polymerization, he pointed out the need for including the step known as chain transfer, whereby an actively growing chain molecule abstracts an atom from another molecule, transferring the seat of activity and ending its own growth. The practical importance of the chain transfer reaction in the control of many industrial polymerization processes, including those responsible for all the American synthetic rubber of World War II, is enormous.

At Cincinnati, Flory worked out the statistical consequences of the "equal reactivity" principle for polycondensations that start from units which bear more than two functional groups and thus permit the formation of branched structures. Such systems, in close analogy to branching chain processes that lead to explosions whether chemical or nuclear, can and do form truly macroscopic molecular networks, which first appear precisely at the critical degree of reaction predicted by Flory's theory. His equations, or extensions of them by others, have been frequently applied not only to synthetic polymer chemistry but also to antigen-antibody reactions in biological systems and to the chemistry of inorganic hydrous oxides. Moreover, closely related models have been adapted for theoretical discussions of both the structure of water and the clustering of molecules in a condensing vapor.

In 1941 Flory moved to the Esso Laboratories, where prospects for research activity were brighter. Here he began both experimental and theoretical work in two areas that have retained his attention up to the present: the thermodynamic properties of polymer solutions and rubberlike elasticity. The famous Flory-Huggins or "volume-fraction" formula for the entropy of mixing of a polymer solution, which was derived independently and announced almost simultaneously by Flory and by Maurice Huggins, dates from this period. 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 generally leads to reliable qualitative predictions. It too remains a norm to which real behavior is customarily compared.

In his subsequent research with Goodyear in Akron, Ohio, Flory continued his studies of rubber elasticity and began work on flow in polymeric systems both in solution and in the melt. At this immediately postwar stage, his concern with applied polymer science was probably at its height. For example, he studied tensile strengths of rubbery polymers in relation to flaws in network structure. In 1948 he was invited to give the Baker Lectures in Chemistry at Cornell, where Peter Debye—1936 Nobel laureate in chemistry—was just completing his term as department chairman. Flory found the atmosphere congenial and migrated there soon afterward. Although Debye and Flory never directly collaborated and in fact disagreed on some scientific questions, there is little doubt that each greatly stimulated the other.

A first fruit of the move to Ithaca was Flory's pioneering 1949 paper on the now famous "excluded-volume effect," to which Werner Kuhn had first called attention 15 years earlier. Briefly, the problem is to ascertain the consequences of the fact that real chain molecules have effective lateral dimensions and therefore cannot intersect themselves, and that furthermore their atoms experience van der Waals interactions with their close neighbors whether these belong to the same chain or to other molecules.

Proceeding beyond earlier discussions by Kuhn, by Huggins, and by Robert Simha, Flory developed a "mean field" theory, which remains in extensive use today. He showed that, except in special circumstances (which he called "theta" states and which are analogous to the Boyle temperature of a real gas), the net effect of the volume exclusion and the other interactions does not vanish. In a good solvent, a chain molecule not only expands to a greater average size than it would otherwise display, but also the numerical relation between molecular weight and effective average radius deviates from the square-root law that would hold if all interactions could be ignored. This was an unwelcome conclusion to many workers, including Debye, for the statistics of chains "unperturbed" (Flory's term) by the interactions are just those of the random flights already well understood in the theory of diffusion and Brownian motion, permitting many theoretical calculations which would otherwise become prohibitively hard to do rigorously. Today the position is inverted. The excluded-volume effect, recognized as a typical three-dimensional many-body problem, has predictably not yielded to exact analysis, but it is being attacked on many fronts: nonintersecting random walks on lattices are a favorite game for computer jocks, and elegant many-body formalisms are borrowed from other physical theories in attempts to construct better analytical approximations. The details of Flory's 1949 treatment have been superseded, but his prediction of a limiting exponent of 3/5 in the radius–molecular weight relation is regarded as very probably correct.

The above account may suggest that the excluded-volume problem is a mathematician's dream but a practical chemist's useless nightmare; yet such a conclusion would be misleading. Armed with his understanding of that problem, Flory next turned to an interpretation of polymer solution viscosity, a favorite experimental fingerprint of macromolecules since Staudinger's day. Recognizing that certain possible hydrodynamic complications suggested by previous theories were rarely likely to be serious in practice, Flory with Fox showed that the increase in solution viscosity produced by each chain molecule is proportional to the cube of its effective radius, and that the proportionality constant is close to being universal for all flexible chains in all solvents. There was thus made available a simple method for extracting from a vast body of existing data information about chain conformations. The relation between conformation and chain structure has since become one of Flory's major preoccupations. His book on the *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969) summarizes much of the mathematical and experimental material.

Soon after the viscosity work, Flory with Leo Mandelkern and Harold Scheraga provided a similar treatment of sedimentation velocity in the ultracentrifuge, and showed that from both measurements taken together it was possible to estimate closely the molecular weight of the macromolecule. Until the recent development of laser light-scattering techniques, this combination demanded less sample than any other molecular-weight method, and it thus has been much used by biochemists.

Cornell to Mellon to Stanford

Flory left Cornell in 1957 to become executive director of the Mellon Institute, and 4 years later went to his present location. At Stanford he has served his term as department chairman, and currently holds the Jackson-Wood professorship. Many honors have come to him before the recent crowning one, including the Debye award and the Gibbs and Priestley medals of the American Chemical Society, and election to membership in the National Academy of Sciences.

It would be illuminating to dwell on many of Flory's other research efforts, such as those on elasticity in fibrous proteins or on the conformations of proteins and polypeptides, but we must be content with two final examples. A very important source of experimental information on the energetics of chain conformation is the temperature dependence of the elastic force in rubbery polymers, provided that the excluded-volume effect can be ignored. Flory has always insisted that this is a valid assumption; in his own words, "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." Nonetheless, in recent years it was frequently argued, mainly in order to account for certain features of electron-microscope pictures of amorphous polymer surfaces, that there must be considerable nonuniformity in bulk polymer structure, with attendant deviations from the Flory view. Within the past 2 years, neutron-scattering studies by German, French, and English groups at the Grenoble and Julich reactor sites have provided unequivocal confirmations of Flory's assertion. Taking advantage of the big difference in neutron-scattering cross sections between deuterium and hydrogen, these workers directly ascertained that the mean dimensions of polystyrene and other chains in undiluted amorphous samples were identical to those in "theta" states.

When polymers crystallize in thin plates from dilute solution, the elongated chains are found to lie in a direction perpendicular to the lamellar plane. As the chain length typically exceeds the lamellar thickness by a factor of 10 or more (100 nanometers compared to 10 nanometers), the chains must therefore fold back and forth many times. When polymers crystallize in bulk, although many complications can arise, lamellar crystals also frequently form. A question currently at issue, and one which is important in the interpretation of the mechanical and other properties of solid crystalline polymers, is whether the chains usually fold sharply at the crystal surface and reenter the lattice in adjacent position, or whether they mainly make larger loops before finding reentry at some distance away. The latter "telephone switchboard" model is strongly favored by Flory, while the "adjacent reentry" model also has many strong and able supporters. Crucial experiments to distinguish between these alternatives are not easily designed, but may be expected within the next few years. Although nobody can win them all, experienced Flory-watchers are placing their bets.

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