

CHEMISTRY, MACROMOLECULES, AND THE NEEDS OF MAN

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Abstract - Having become a mature science, chemistry is no longer at the frontier in the quest for the ultimately small entities in nature. Yet, as the science most concerned with molecules, chemistry continues to be of foremost importance. It has both an opportunity and an obligation to elucidate the familiar forms of matter and to cultivate a more widespread appreciation of the nature of the substances of common experience, and of the transformations they undergo. Additionally, chemical sciences must lend support to new technologies and to the adaptation of existing ones to the needs of the present and future. Chemistry therefore has both a cultural and a technological function.

Macromolecules are singularly important in both respects. Substances comprising them are commonplace. They provide the fabric of all biological matter and perform the essential regulatory functions on which living processes depend. In the industrial domain, the rapid growth in the use of synthetic polymers witnessed in recent years seems destined to continue as they replace metals and other materials from non-renewable sources. The diversity of molecular architecture which can be incorporated in long molecular chains offers possibilities that are virtually limitless.

The base of knowledge concerning polymers, on which both the life sciences and polymer technologies must depend in the future, is precariously limited. Cultivation of deeper understanding of macromolecules therefore is urgently needed.

The emergence of chemistry as a science dates from the late eighteenth century. It was then that the conservation of matter on the one hand and the mutability of its combinations on the other came to be recognized, and the one reconciled with the other. In Europe, and also in America, this was a period of transition - a time of political upheaval and, not coincidentally, of intellectual ferment as well. Views of the physical world had been freed at last from the fetters of mysticism and from domination by sterile philosophies preoccupied with the quest for universal truth through contemplative exercise of the mind, with only secondary attention to observations.

It was a time when knowledge was held in high esteem. This was manifested not only in the vigorous pursuit of science by acknowledged scholars and others who, by good fortune, had the leisure that could be provided by wealth or the resources of a well-endowed patron. It was exemplified also by a golden age of exploration, an activity which even nations at war respected too highly to disrupt. Whereas earlier explorations had been undertaken in quest of riches or economic gain through commerce, explorers of the late eighteenth and early nineteenth centuries embarked on long and hazardous journeys to the far reaches of the globe principally to acquire knowledge of earth, of its biosphere and even of the heavens. Reports of their observations and discoveries were eagerly received by their contemporaries.

The same outlook and attitudes encouraged advancement of the then nascent sciences. Those who turned their attention to natural philosophy committed their efforts singlemindedly to the understanding of physical phenomena. Curiosity was their motivation. This curiosity was stimulated for the most part by commonplace observations within the range of experience of all. Examples are numerous and familiar. What set the natural philosopher apart from his fellowmen was his cultivated sensitivity to those observations that are most significant and

his thirst for understanding. The acquisition of knowledge was itself a sufficient goal; application of that knowledge was secondary. In this respect scientists concerned with the nature of matter, *i.e.*, chemists, broke tradition with their forebears, the alchemists. The ulterior aims of the latter were subordinated to the advancement of knowledge for its own sake.

Yet, scientists of the era I have identified were not oblivious of the practical potentialities of the knowledge that was the object of their researches. Indeed, they were convinced that the better understanding of natural phenomena must inevitably accrue to the benefit of mankind. Without attempting to identify beforehand the applications of the results of their investigations, they were confident that advances in science ultimately would be turned to practical ends. They derived deep satisfaction from witnessing applications of their work. Joseph Priestley, for example, found gratification in the fact that one of the "airs" he discovered could be used to carbonate beverages.

The power of knowledge foreseen at that time has been proved beyond the most extravagant expectations of the early pioneers of science. In the present age, however, the fruits of technological advances spawned by science are frequently called into question. Science has been under attack in modern times on various grounds: for providing armaments of war capable of achieving the ultimate in devastation, for ravishing the environment, for unleashing forces of change on a world unprepared for the incalculable consequences thereof, for failing to provide a reasonable balance between food and population while having demonstrated the capability to suppress diseases that have plagued mankind throughout recorded history, for improving the efficiency of utilization of the world's finite resources and at the same time contributing to their exhaustion; in short, for achieving both too much and too little. Like a sorcerer's magic, science is both sought after and dreaded.

Chemistry has played a major part in modern technology. Hence, chemistry may claim a major part of credit that is due, but also is vulnerable to blame for misuses of its creations by its beneficiaries.

Returning to the early years of the science of chemistry, we note that it was then at the very frontier of knowledge of the nature of matter. Its molecules and the atoms comprising them were the smallest entities known. Through the work of Hatty, Dalton, Berzelius, Avogadro and Ampère, the atomic theory of matter became well established early in the nineteenth century. This achievement is often cited as the apotheosis of the atomic hypothesis advocated much earlier by the Greek philosophers, notably by Democritus. However, the grounds were different. The hypothesis of the classic era was based on speculation rather than compelling facts of observation and critical, inductive reasoning from them. The atomic theory that would support a science of chemistry had little connection with earlier abstract reflections.

The atomistic view of matter is now well entrenched, but the quest for the smallest particles in nature continues. It is no longer the province of chemistry, however; at present it is the domain of nuclear and high energy physics. The particles that comprise the atomic nucleus, once thought to be indivisible, and the laws governing their interactions are considered to be the determinants of the properties of all matter. Thus, chemistry is no longer in the vanguard of investigations on the fundamental nature of all matter, a position it once enjoyed.

The laws of physics, when expressed in their most general form, surely must comprehend not only the properties of atomic nuclei and of atoms but of molecules as well. Hence, chemistry, loosely defined as the science of molecules and molecular behavior, is a derivative science from this point of view. It has sometimes been contended on these grounds that chemistry should be regarded as a subdivision of physics.

This reductionist view of science according to which the laws that hold for one science in the hierarchy embracing physics, chemistry, biology, etc., must comprehend implicitly the laws that govern the next science in the hierarchical sequence are philosophically impregnable. This is a virtual axiom of modern science. It is essential for a coherent view of the universe. The subdivisions of science are quite arbitrary. One merges into the other to form a continuum. Hence, the laws applicable to one of the sciences cannot be contravened in another.

Application of this axiom in the construction of the edifice we call science is something else.

Deduction of the behavior of matter in its more complex forms, living as well as inanimate, from the ultimate laws of physics as suggested by the reductionist view turns out to be impracticable. The difficulty lies in the fact that science is an activity conducted by humans, and no one has yet appeared on the scene who is capable of dealing intelligently with the complete range of the sciences. Some have attempted to do so. Their failures are illustrated by the ineptitude of physicists, from Newton on, in dealing with matters chemical. Similar criticisms could be leveled at chemists who have wandered into biology and medicine without acquiring adequate familiarity with the inherent contexture of these fields. Knowledge in one of the hierarchies of science does not confer the capability to deal effectively with a subordinate discipline. Each requires its own framework of theory and concept. These are inductively acquired through exercise of creative insights; they are not derived deductively, as the axiom of reductionism is erroneously construed to suggest.

Although molecules have relinquished their place at the frontier of knowledge concerning the ultimate nature of matter, one may confidently assert that an understanding of them will remain essential to a comprehension of the diversity of material substances that abound in the environment and serve the needs of man. The vast differences between commonplace materials - air, water, minerals, metals, wood, textiles and living matter - can only be understood in terms of their molecular constitution and their organization at the molecular level.

A more widespread appreciation of the content of scientific knowledge has become a matter of the foremost importance. Chemistry, being the science most concerned with molecules and their properties, holds the clues to differences in form and behavior of these classes of substances and of the members within each. Hence, chemistry has both an opportunity and an obligation to clarify these differences and to present them in a form communicable to a wider circle of the public at large.

The relevancy of chemistry to the common forms of matter places our science in a position of strategic importance to technology. The truth of this statement is so abundantly illustrated by past achievements and by the close liaison between chemistry and industry as not to require elaboration. The support of vast and intricate technologies has become a most important achievement and function of the science of chemistry.

Chemists generally have concentrated their efforts on simple molecules. This may be in part a response to the obvious need to conduct experiments and devise theories in circumstances of the utmost simplicity. But the task does not end with elucidation of systems that are simple and therefore lend themselves most readily to the objectives of the investigator. Nature is intricate and complex. The materials and processes of technology likewise are, for the most part, of a higher order of complexity than the systems traditionally preferred by the researcher in "pure" chemistry.

A science of chemistry that is supportive both of an understanding of the real world of common experience and of modern technology should not, therefore, confine its concerns to the simplest molecules and systems. Contrary to inferences from reductionist doctrine, principles thus established do not suffice for the elucidation of systems of higher complexity. New models and principles appropriate to the latter are required.

The chemistry of macromolecules, or polymers, is one of the areas whose traditional neglect can be attributed in part to this misguided approach. The chemical constitution of this most ubiquitous and diversified class of chemical substances was not clearly established until the early 1930's following the monumental work of Staudinger and Carothers. For a period of nearly half a century prior to that time proteins, carbohydrates, rubber and various synthetic polymers, not to mention the polynucleotides, had been considered to consist of small molecules aggregated into colloidal particles.

The occurrence of chain molecules of great length was implicit in the earliest ideas of valency, and especially of multiple-covalency of atoms like carbon, oxygen and nitrogen. This was recognized over a century ago, virtually at the inception of concepts of valency ca. 1860. In the years immediately thereafter a few polymers were synthesized and their molecular constitution was correctly identified, as was that of some of the naturally occurring polymers. But these findings became obscured by the preoccupation of chemists with small molecules having concise, unique formulas. The assignment of low molecular formulas, typically cyclic, to polymers was therefore more compatible with the attitudes of

the times, compelling evidence to the contrary notwithstanding. Aggregation of these molecules was invoked to account for the colloidal properties of substances now known to be polymeric.

Once it came to be recognized in the 1930's that polymers are macromolecules typically consisting of chains comprising hundreds, thousands or even tens of thousands of covalent bonds in linear succession, attention turned immediately to the question of the spatial form that such an entity would assume. It was apparent that an enormous variety of spatial configurations can be generated through rotations about so many bonds. The problem seemed therefore to be of unusual complexity. It was simplified in the context of the crystalline state where a symmetrical molecular form must necessarily occur. For the numerous crystalline polymers that have been subjected to X-ray crystallographic investigation, various helices have been identified as well as the fully extended, planar conformation, depending on the polymer and its constitution. The inference that the conformation occurring in the crystal is the most stable one in terms of its intramolecular energy has been abundantly confirmed, with only rare exceptions.

With regard to the polymer molecule dispersed in a dilute solution, where the intermolecular constraints of crystal packing do not occur, it was recognized that rotations about skeletal bonds of the chain would admit of a multitude of irregular spatial configurations. This gave rise to the concept of the "random coil", a term that embraces, collectively, all of the more or less random configurations. The same randomness was assumed to prevail in the amorphous bulk polymer. These ideas were seminal in the 1930's. It soon became apparent that those characteristics of polymers that are peculiar to them are intimately related to the randomness in the conformations of their skeletal bonds that characterizes the "random coil." The properties reflecting this disordered molecular state include both the equilibrium (*i.e.*, thermodynamic) and transport (*e.g.*, viscosity) behavior of polymer solutions, the phenomenon of rubber elasticity and the diffuse scattering of radiation (light, X-rays and, recently, neutrons).

Analysis of the spatial configuration of a randomly coiled macromolecule appeared at first to be inordinantly complicated. A precise analysis would require that account be taken of skeletal bond lengths, of bond angles and, especially, of all rotations about these bonds. Simplifications were therefore sought. W. Kuhn and E. Guth and H. Mark drew analogy to the theory of random flights, a subject which had been treated mathematically in some detail by Rayleigh and others. In order to comply with the terms of this model, Kuhn replaced the molecular chain by a sequence of N hypothetical bonds of length b , each such bond being accorded full freedom in the choice of its direction without regard for the directions assumed by neighboring bonds. The average square of the distance r between the ends of this "freely jointed" chain is well known from the theory of random flights to be given by the simple relation

$$\langle r^2 \rangle = Nb^2$$

Of course, the hypothetical bond of length b must span several skeletal bonds of the real chain, and the number N of the former must be correspondingly reduced below the actual number of real bonds. However, it should be possible to scale the model to the real chain by appropriate choice of b and N , at least in the asymptotic limit of very long chains.

Much of the existing polymer theory has been propounded on the basis of this simple model. Many of the properties of macromolecular chains have thus been elucidated. Widespread use of this model continues. Yet, the model is subject to serious limitations. The scaling of b and N required to reproduce a given property differs depending on the property considered. The model is ill-suited to treatment of constitutive properties that are configuration-dependent, *e.g.*, dipole moments, and optical properties. Inasmuch as the contribution of a structural unit to one of these properties is a vector or a tensor, it cannot be referenced to a hypothetical bond that is a mere line. Moreover, an equivalent bond, b , cannot be embedded unambiguously in the chemical structure of a real chain molecule.

These shortcomings have been overcome in part by recent elaborations involving the adoption of a more general mathematical description of a line in space to represent the molecular chain. Refinements of this nature cannot, however, overcome the most serious deficiency of such abstractions, namely, their intrinsic artificiality. Actual bond lengths, bond angles and torsional potentials affecting bond rotations are not specifically taken into account by any model of this variety. Hence, contact is broken at the outset with the features of chemical

constitution that distinguish macromolecular chains of one kind from those of another. Such models are intrinsically incapable therefore of bridging the connection between chemical constitution and the properties that distinguish one polymer from another. This should be a primary requisite of any theory in this domain.

Over the past 15-20 years, methods have been devised for treating long chain molecules realistically on the basis of their established structures as expressed by the lengths of their bonds, their bond angles and the hindrances affecting bond rotations. It is often expedient to deal with the latter by adoption of a rotational isomeric state scheme whereby the continuous range of bond rotations is replaced by a set of discrete angles, appropriately chosen. Advantage is taken of the sequential linearity of the macromolecule in the mathematical formulation of the analysis. Methods for one-dimensional systems are therefore applicable and, as is well known, the equilibrium statistical-mechanical properties of systems in one dimension can be treated exactly. Virtually all configuration-dependent properties of interest are thus brought within the scope of a comprehensive treatment which is at once exact, applicable to any macromolecule of defined structure and congruent with that structure.

The methods briefly described are consistent and coextensive with those employed for the conformational analysis of small molecules. The principal point of departure arises in the necessity for taking averages over all of the multitude of conformations of the macromolecules. But the methods that have been developed are capable of dealing rigorously and exactly with this requirement. Hence, contact with the properties of small molecules is readily established. Identical structural and conformational parameters are applicable throughout the range from the shortest to the longest chains of a given series of homologs, as has been repeatedly demonstrated.

It follows that the properties of macromolecules can be treated quite as exactly and realistically as those of small molecules. The allegation that polymeric substances are more difficult to comprehend will be found, on close scrutiny, to be false. It is a figment of viewpoint rather than of substance.

Yet, it must be pointed out that the methods referred to have not as yet gained widespread acceptance among chemists concerned with macromolecules, and their full potential remains to be realized.

The fact, now well established, that polymer chains in an amorphous polymer adopt configurations virtually identical to those occurring in a dilute solution (when corrected for effects of excluded volume in the solution) greatly enlarges the scope of results of investigations on the spatial configurations of polymer chains. Theory leading to this conclusion put forward a quarter century ago was viewed with skepticism despite a substantial array of indirect evidence in support thereof. It remained for neutron scattering studies on deuterated polymers dispersed in the protonated species (or *vice versa*) to show irrefutably that the spatial configurations of polymer chains are little affected by the interactions with neighboring chains, which occur in profusion in the bulk polymer.

The significance of this sweeping conclusion with respect to the properties of polymers has yet to become fully appreciated. In particular, its implications concerning the molecular morphology of semicrystalline polymers, in which a given long chain molecule threads its way through crystalline and amorphous regions repeatedly, are in conflict with prevailing views. That randomly configured chains chaotically intertwined with one another in the amorphous polymer could, in the course of crystallization, disengage themselves from their neighbors and make the extensive rearrangements necessary to achieve the regularly folded arrays widely assumed as a description of the molecular morphology in semicrystalline polymers not only is inconceivable; it is incompatible with recent results of neutron scattering experiments as well. Other evidence leads to the same conclusion. Thus, a widely accepted, much publicized model must be abandoned.

This paradigm serves to remind us that the mistaken opinion that polymer molecules are colloidal aggregates, widely accepted at the turn of the century, should not be dismissed as a mere aberration of a less sophisticated era. Equally absurd opinions can persist in the present age. Their perpetration involves a kind of "science by popular consensus" in which credence is conferred by repetition of dogma, rather than by reasoned, critical examination of evidence. One may be tempted to conclude that this field is peculiarly susceptible to

irrational ideas. Careful study of the evolution of concepts in other areas probably will show them to be equally vulnerable. The history of science furnishes numerous examples of fallacious ideas tenaciously retained, even by scientists, in the face of compelling rational evidence to the contrary.

Be that as it may, the need for a more critical examination of the concepts underlying current polymer science is apparent. Additionally, these concepts need to be broadened to encompass a greater range of knowledge concerning macromolecules. It is not enough merely to dwell on existing ideas and the problems that have already been uncovered. Sharpening these with ever more precise and elegant theories will not alone suffice. The properties and behavior of macromolecules and the systems comprising them require more comprehensive exploration. New views and radical extensions into new aspects of the field are needed.

This will be especially apparent if one considers the relation of macromolecular science to biology. Polymers provide both structure and function in all biological systems. It may be asserted with cogent argument that a rational understanding of biological molecules and their behavior in living systems must rest on a science of macromolecules. Yet, it will be evident also that most of the fascinating complexities of biological systems are beyond the reach of macromolecular science at its current level of development. Must the sequence of sciences from basic physical laws to biology and beyond, to which earlier reference was made, be broken at this point? The answer should be postponed until the frontiers of polymer science have been advanced much further. The creation of a science eventually capable of dealing rationally with the intricacies of the behavior of biological systems at the molecular level should be a major reason for encouraging research to expand fundamental knowledge of polymers and the molecules comprising them.

During the past half century, we have witnessed the introduction of synthetic polymers as articles of commerce in quantity and in variety with few parallels in the annals of technological advance. Some of them have replaced polymers of natural origin; notable examples are the synthetic fibers and synthetic rubbers. Others, because of their special properties, have found novel applications without precedent in the traditional uses of natural materials. The usage of polymers has grown to the point where the total volume produced per annum exceeds that of all metals combined. According to projections, the production of polymers measured in weight may surpass the total weight of metals produced before long. Synthetic fibers matching steel in strength, and with only about one-sixth the density, have reached commercialization in this decade. The end is not in sight.

Polymers, being made up of many discrete units connected in linear sequence, admit of almost endless variations in constitution. This capacity for variation finds expression in the ranges of the physical, chemical and mechanical properties exhibited by diverse polymeric materials. As a class, polymers are singularly versatile in the characteristics and properties that can be infused in them. Future generations, with benefit of the perspective of history, conceivably may denote the present and coming era as the age of polymers, just as we refer to the stone, bronze and iron ages.

As we enter a period of dwindling sources of raw materials, scarcities of which have long been foreseen by chemists, renewable replacements for those in limited supply are urgently needed. The central role chemistry must play in response to this need is obvious. Amongst the prospective candidate materials to replace those whose availability is limited, polymers offer the most promising alternatives. They can be made from renewable raw materials. Some of them match or excel metals in strength, rigidity and durability. They offer a wider range of useful properties than any other class of materials. And the limits attainable remain to be determined.

Other pressing problems to which I have alluded earlier also place heavy demands on chemistry. Amongst these are the safeguarding of the environment and the ecological base of life on this planet; chemotherapy against diseases for which cures are yet unknown (and this includes most diseases); means for augmenting the production of food through research at the interface between chemistry and biology; and so forth. Regardless of one's assessment of the tally of benefits of science versus its detrimental consequences, one prediction beyond dispute is that the future calls for the utmost science can offer. Only through advancement of the frontiers of scientific knowledge will alternatives be uncovered which can be turned to the alleviation of the problems that are pending.

The over all importance of science and scientific research does not, however, confer equal justification for furtherance of each of its many subdivisions. Some researches are certainly more significant and promising than others in their potential contribution to the integrated body of scientific knowledge and understanding on the one hand and to the material needs of mankind on the other. Parenthetically, these two legitimate goals of the scientific enterprise are, in my view, more often in concert than in mutual conflict. Valid judgments on the merit of a scientific investigation are difficult at best. However, science as a whole has become so large and its frontiers so extensive that its perimeter cannot be manned by the available number of qualified scientists. Furthermore, much of scientific research has become expensive, and the limits on financial support are no longer to be ignored. Hence, choices must somehow be made.

Scientists themselves are best qualified to reach decisions on which scientific activities should receive preferential attention. Up to the present time directions of scientific effort have been largely in the hands of members of the scientific community. Retention of this prerogative in the future will, in my opinion, require a broader view of the responsibilities of science, both as regards its contributions to material human well-being and its cultural and intellectual values as well.

Scientists urgently need to acquire a greater awareness of the significance of their work beyond the confines of the necessarily narrow objectives of the immediate researches that absorb their efforts. The parochial goal of gaining the attention and approbation of a handful of specialists cannot be tolerated as a sufficient criterion. Scientific research must earn, and deserve, the support of society at large. In order to do so, its efforts will have to be cast in directions that are consonant with positive goals beyond the gratification of the scientific community. Adoption of this precept seems imperative if science is to flourish at a time when the demands upon it may become staggering. Basic research is already under attack in many quarters. Its goals and functions need therefore to be critically examined by the scientific community.

In closing, let me reiterate the conviction that the advance of scientific knowledge is essential both for the material needs of the future and for the preservation and growth of cultural values. In this, chemistry must play a major role.