Coming to an Age of Polymers in Science and Technology

H. Mark[a]

[a] Polytechnic Institute of New York, Brooklyn, New York

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H. MARK

Polytechnic Institute of New York
Brooklyn, New York 11201

ABSTRACT

Three conferences may be taken as characteristic of the early
development of polymer structure: The meeting of the Deutsche
Naturforschergesellschaft in Duesseldorf in 1926 where Staudinger
successfully upheld his concept of the existence of macromole-
cules; the Faraday Society Meeting in Cambridge in 1936 where
Carothers presented his classification of addition and condensa-
tion polymers, and the First Polymer Conference of the Inter-
national Union of Pure and Applied Chemistry in Liege in 1947
where polymer science established itself as an accepted member
of chemical disciplines. Brief accounts are given of the events
and transactions during these conferences.

Since the beginning of his existence, man has strongly relied on
the use of natural organic polymers for food, clothing, and shelter.
When he ate meat, bread, fruit, or vegetables and drank milk, he was
feeding on proteins, starch, cellulose, and related polymeric mater-
ials; when he put on clothing made of fur, leather, wool, flax, and
cotton, he used the same natural polymers; and when he protected
himself against wind and weather in tents and huts, he constructed
these most primitive buildings of wood, bamboo, leaves, leather, and
fabrics, which again all belong to the large family of organic polymers.
In addition to the above-mentioned types, there are lignin, resin, and
bark.
Even later, when higher levels of civilization were reached,

organic polymers were essential necessities in peace and war. All books in the famous library of ancient Alexandria consisted either of cellulose (paper) or protein (parchment), and they consist of these materials in all libraries of the world up to the present day. All transportation on land and sea throughout many centuries operated on wooden cars and ships which were put in motion with the aid of ropes and sails made entirely of such cellulosics as flax, hemp, or cotton. The music of all string instruments is produced by the vibrations of wooden, resin-treated boards; and all famous paintings together with many of the most valuable statues consist of cellulose, lignin, and polymerized terpenes in such materials as paper, canvas, wood, and paints. Bow and arrow are cellulose, lignin resin, and protein; catapults and siege towers were made of wood and moved with ropes and—until about 100 years ago—all sea battles were fought with wooden ships which were maneuvered with the aid of cellulosic sails and ropes.

While, in this way, natural organic polymers literally dominated the existence and welfare of all nations, virtually nothing was known about their composition and structure. In each sector—food, clothing, transportation, communication, housing, and art—highly sophisticated craftsmanship developed which was sparked by human intuition, creativity, zeal, and patience and led to accomplishments which will ever deserve the highest admiration of generations to come.

But even when the chemistry of organic compounds became a respectable scientific discipline in the early decades of the last century, the all-important helpers of mankind—proteins, cellulosics, starch, and wood—were not in the mainstream of organic chemical research.

Why?

Because somehow they did not seem attractive at that time for a truly scientific study since they did not respond to the then existing methods for isolation, purification, and analysis. The experimental backbone of organic chemistry in those days was dissolution, fractional precipitation, and crystallization or distillation; it worked and still works with all ordinary organic compounds such as sugar, glycerol, fatty acids, alcohol, and gasoline but fails with wood, starch, wool, and silk. These materials cannot be crystallized from solution and cannot be distilled without decomposition.

This fundamental and embarrassing difference between the natural organic materials and the ordinary organic chemicals warned the chemists of the last century that there might be some essential and basic difference between these two classes of substances and that one would have to develop special, new, and improved experimental methods to force the second class into the realm of truly scientific studies.

The breakthrough came in the early decades of this century, mainly through the adoption of physical methods, such as improved optical devices like the ultramicroscope, and the ones for the ultracentrifuge, new viscometers, osmometers, diffusion cells, and, most

of all, through the application of x-ray diffraction to fibers, membranes, and tissues. A decade of intense research on cellulose, proteins, rubber, and starch wound up with the following fundamental results:

1. All investigated materials consist of very large molecules. Whereas the molecular weight of ordinary organic substances such as vinegar, soap, gasoline, or sugar ranges from about 50 to 500, the molecular weight of the natural organic building materials ranges from 50,000 to several millions, a fact which earned for them, through Staudinger, the name "giant molecules" or "macromolecules."

2. Most of them have the shape of long flexible chains which are formed by the multifold repetition of a base unit. One often refers to the base unit as a "monomer" (monos is the Greek word for "one" and meros is the Greek word for "part") and to the macromolecules themselves as a "polymer" (polys is the Greek word for "many").

3. If a sample consisting of regularly built, flexible chains is exposed to mechanical deformation, the individual macromolecules are oriented and show a tendency to form thin, elongated bundles of high internal regularity which are usually referred to as "crystalline domains" or, simply, as crystallites. Depending upon the nature of the material and the severity of the treatment, a different percentage of the material undergoes crystallization whereas the rest remains in the "amorphous" or "disordered" state so that any given sample—fiber, film, rod, or disk—consists of two phases: amorphous and crystalline.

It was found that the crystalline domains contribute to strength, rigidity, high melting characteristics, and resistance against dissolution, whereas the amorphous areas impart softness, elasticity, absorptivity, and permeability.

As soon as the study of natural polymers had started to establish these ground rules, chemists were strongly tempted to synthesize equivalent systems from simple, available, and inexpensive raw materials. The years from 1920 to 1940 brought ever-increasing successful efforts to:

1. Provide for more and cheaper basic building units—synthesis of new monomers
2. Work out efficient reactions to string them up into link chains—mechanism of polymerization
3. Establish quantitatively the molecular weight and molecular structure—polymer characterization
4. Explore the influence of the structural details on the different ultimate properties—molecular engineering

Learning originally from nature and following up on the established principles, scientists and engineers succeeded in producing a wide spectrum of polymeric materials which outdo their original native

examples in many ways and, in most cases, are much more accessible and less expensive. All this gave a tremendous lift to the important industries of man-made fibers, films, plastics, rubbers, coatings, and adhesives and made everybody's life richer, safer, and more comfortable. Statistics show that in 1977 about 1.8×10^9 tons of man-made fibers were produced and sold in the world with a total value of more than 3×10^9 dollars; during the same year about 9×10^9 tons of synthetic plastics were produced which represent a total value of about 8×10^9 dollars. Figures of the same order of magnitude hold for synthetic rubbers, coatings, and packaging materials. As a consequence, synthetic organic polymers have become a significant factor in the economy of all industrialized countries in the world.

MACROMOLECULES WIN—AND MUSHROOM

For three decades from the 1920s to the 1950s, enormous progress was made in understanding the structure of native polymers and synthesizing artificial counterparts. Instead of giving you a detailed chronological account of these year's events, I prefer to describe three representative meetings which took place during this period which have become classical milestones of modern chemical history.

The first took place in Duesseldorf where the Gesellschaft Deutscher Naturforscher und Arzte met in 1926, the second was a meeting of the Faraday Society in Cambridge in 1936, and the third occurred in 1947 in Liege in Belgium and was the Inaugural Session of the High Polymer Commission of IUPAC (The International Union of Pure and Applied Chemistry). I had the privilege to present lectures at all three conferences and was chairman of the last.

The meeting in Duesseldorf was arranged in order to confront Staudinger, the protagonist of the macromolecular concept, with several other distinguished scientists who were still reluctant to admit the existence of giant organic molecules and adhered to the idea that these substances—cellulose, wool, rubber—consist of small units which are held together by exceptionally strong intermolecular forces like those in Werner's complex compounds or in hydrogen-bonded systems. In his lecture, Staudinger told an audience of several hundred classical organic chemists that he has established the existence of molecules which are a thousand times larger than those which they themselves were studying in their laboratories. One of them commented: "We are shocked like zoologists would be if they were told that somewhere in Africa an elephant was found who was 1500 feet long and 300 feet high."

To the classical arguments in favor of tightly knit systems of small units, which were presented by prominent scientists such as Karrer, Pringsheim, Bergmann, and Waldschmidt-Leitz, a new one had recently been added; namely, the fact that the crystallographic basic cells of cellulose, silk, and rubber are so small that they only could contain particles with molecular weights less than one thousand.

According to the then existing classical crystallographic teaching, a molecule cannot be larger than the basic cell. This is where my lecture was supposed to contribute to the discussion by explaining that, under certain conditions, a chemical molecule could well be larger than the basic crystallographic cell and could even be as large as the entire crystallite.

The presentations were followed by rather animated discussions which proved that the differences in opinion were not yet eliminated. At the end Willstaetter, who presided, summarized his position by saying: "Such enormous organic molecules are not to my personal liking but it appears that we all shall have to become acquainted with them." In fact, the "theory of the small units" lost more and more ground, and in science and engineering the macromolecular character of the principal natural polymers became an accepted fact and immediately encouraged the synthesis and study of any material which could readily be prepared from available monomers which would undergo polymerization in one way or another. So began the first phase of polymer chemistry as a rapidly expanding qualitative scouting for new polymers and their principal properties with the intention of arriving at a general survey of the width and depth of this new brand of organic chemistry.

In 1936 the Faraday Society arranged a meeting on "Phenomena of Polymerization and Polycondensation" in Cambridge. It was an international conference, the large size and high level of which proved the enormous progress which the young branch of polymer science had made during the last decade. There was no question anymore about the existence of macromolecules, for the contributions dealt with the mechanism of polymerization reactions, the determination of molecular weights, the properties of specific polymers as a result of their molecular structure, and potential areas of application. For the first phase the words "observation" and "preparation" were valid; for this second phase the words were "measurement" and "quantitative characterization." In addition to the old guard—Staudinger, Meyer, Rideal, and myself—a new upcoming generation of excellent scientists presented their work—Melville, Schulz, Houwink, Astbury, and others. The outstanding figure of this meeting was undoubtedly Wallace Carothers, who had come from Wilmington to give an account of the momentous studies which he and his associates had carried out during the last decade.

At the end of the symposium, everybody was convinced that polymer chemistry had grown into a full-scale science with unexpected new vistas for intensification of understanding and expansion of application. Universities and industrial organizations started to compete with each other to enter the field at any point from fundamental aspect to practical evaluation. This second, rapidly ascending phase of polymer science was first slowed down and later vigorously accelerated by World War II. The United States and Canada in particular were literally running away in basic and applied areas. Essential fundamental details in polymerization mechanisms including suspension

and emulsion polymerization were clarified, and the ground-work
for x-ray examination and IR spectroscopy of polymeric systems was
firmly established.

After the war the first close contact in science and engineering
was made by visiting professors from the United States to Europe.
Such positions were occupied among others by Alfrey, Doty, Mesro-
bian, Tobolsky, and myself, who gave several series of lectures in
Western Europe right after the war. The interest was understand-
ably very pronounced, and after contact with the president and the
secretary general of IUPAC in Paris it was decided to organize in
the summer of 1947 an International Polymer Symposium in Liege
and to initiate a Commission on High Polymers within the Division
of Physical Chemistry. There did not yet, at that time, exist scien-
tific contact with Germany, Italy, Japan, and the USSR with its satel-
lites, but all other countries where work on polymers was done sent
strong and representative delegations.

At the conference the state of the art was reviewed in a series of
comprehensive papers, and the main lines for further progress were
in the center of the discussion. Much time was spent to report prog-
ress made in England and America to the scientists on the continent.
This included synthesis and technology of such polymers as poly-
ethylene, nylon, and polyester, new methods for structure determina-
tion such as x-ray Fourier analysis and polarized infrared; and the
beginning of spin resonance and the elaborate use of light-scattering
techniques. Present were most of scientists who, within the next
decade, emerged as leaders of the various branches of polymer
science. From England came, among others, Astbury, Bawn, Bernal,
Evans, Melville, Rideal, and Thompson. Italy contributed Nasini
and Natta; France sent Champetier, Chapiro, Magat, and Sadron.
They had the opportunity to meet Hermans, Houwink, and Staverman
from The Netherlands; Errera and Smets from Belgium; Claesson
and Rånby from Sweden; Ant-Wuorinen from Finland; W. Kuhn, K. H.
Meyer, and Signer from Switzerland.

This conference initiated a vigorous and systematic cooperation
of all Western polymer scientists which soon resulted in the essential
clarification of all phases of condensation and addition polymeriza-
tion, including copolymerization, graft, and block polymerization,
in an impressive buildup of elastomer and plastics technology, in an
entire new generation of textile and industrial fibers, and in the
almost complete domination of synthetic polymers in the coatings
and packaging field. As more polymers with more complicated
structures became available, the methods for their quantitative char-
acterization had to be sharpened. All scattering techniques—light,
x-rays, electrons, and neutrons—received a thorough overhauling;
resonance processes—nuclear and electronic magnetic movements—
were built up to admirable precision and, most of all, the study of
the chemical structure as well as the state of order (regularity,
crystallinity) of polymers by vibrational (infrared and Raman) spec-
troscopy was intensified and expanded. Today this technique can be

called the most informative and powerful tool for the characterization of even very complicated polymeric systems.

INCREASING COMPLEXITY DEMANDS NEW BASIC AND PRACTICAL APPROACHES

In fact, all these methods became more and more necessary because of the enormous number of new polymers, of the increasing complexity of their structure, and of the wide variety of their application. In order to design a macromolecule for a special use, many detailed structural conditions have to be fulfilled which require very precise methods to establish their existence and to control their durability in use.

The present advanced state of vibrational spectroscopy has its roots in the late 1920s and early 1930s. One of them was the basic understanding of molecular vibrations on the basis of quantum mechanics first put in evidence by the absorption of infrared radiation and later also found in the modulations of scattered visible light in the Raman effect. The two methods complement each other dramatically because of their different response to the selection rules which control the transition probabilities between different vibrational states of a molecular framework. The other root was a gradual and substantial improvement in the experimental techniques, such as stronger and more uniform sources of the primary radiations, higher resolution in the spectroscopic part of the equipment, and, perhaps most of all, more sensitive and reliable receivers.
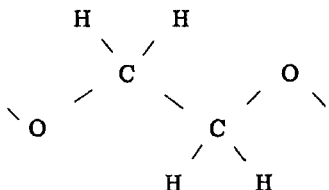
This new armamentarium—experimental and theoretical—encouraged the systematic, empirical collection of IR, absorption, or Raman bands which are characteristic of certain atomic groupings in a molecule. Literally thousands of well-defined organic substances were studied and characterized.

Let us consider, for example, polyethylene terephthalate molecules which are supposed to be used as fiber formers. Molecular weight and molecular weight distribution are readily and rapidly available from gel permeation chromatography, but there are other more detailed questions. In general, the endgroups are hydroxyl groups but dehydration can convert them into $-CH=CH_2$ groups. Their presence has certain undesirable consequences, hence one would like to know: Are there any present, and if so, in what concentration? Infrared absorption spectroscopy gives the answer as soon as their concentration becomes large enough to be a detrimental influence.

During continuous melt polymerization, some diethylene glycol $HO+CH_2+_2O+CH_2+_2OH$ is formed through a side reaction; since it is bifunctional it enters the polymer chain and introduces ether groups into the structure. Even a small percentage of them (2 to 3 mol-percent) may cause discoloration and even degradation of the fiber under certain conditions, such as light and contact with oxidative

agents at elevated temperatures. Presently available advanced meth-
ods of vibrational spectroscopy permit the detection of ether groups
within the range of the above-mentioned concentrations and provide
a very valuable tool for product control of polyester fibers which are
used in the textile field.

But polyethylene terephthalate has also become a very important
fiber for tire cord production, and this use requires an additional
specification. There exists a certain conformational ambiguity in
the aliphatic chain between the aromatic residues:

$$\begin{array}{cccc}
H & \quad H & & \\
\diagdown & \diagup & & \\
 & C & & O \\
\diagup & \diagdown & \diagup & \diagdown \\
O & & C & \\
 & \diagup & \diagdown & \\
 & H & H &
\end{array}$$

namely trans-trans, trans-gauche, and gauche-gauche. Absorption
or scattering patterns were established for them: from CH_2 and
CH_3 over $C=C$, $C=O$, and $C\equiv N$ to ether, ester, amid, urethane, and
ureid bonds. As the experimental data increased in quantity and
quality, encouragement was given to the next step, namely to con-
centrate attention to one of these groups, e.g., the ester group or
the benzene ring, to calculate all possible vibrations of the system
and to predict the complete IR and Raman spectrum of that particular
group. Efforts of this type were facilitated through the availability of
improved force constants for stretching, bending, and rocking mo-
tions, and for the repulsive actions of hydrogen atoms attached to
neighboring members of the chain skeletons. This procedure yielded
the main experimental pattern and also gave many additional impor-
tant refinements.

In those chains which are located inside of a laterally well-
ordered (crystalline) domain, the trans conformation prevails, but
in the other molecules there exist gauche and maybe even cis confor-
mations. Their presence has a reducing influence on the modulus
of the fiber but increases its elongation to break and moisture absorp-
tion capacity. Hence quantitative information on the proportion of the
conformational distribution as a result of processing conditions—
spinning, drawing, heat setting, and texturizing—is of interest. The
only method which provides such information is the vibrational spec-
troscopy in its various existing forms of application. In the field of
elastomer science and engineering there are many important prob-
lems which have been successfully clarified by the same techniques.
Here, in the ethylene-propylene copolymers, there are again confor-
mational questions—trans, gauche, cis in the polyethylene segments and
helicoidal or not wherever propylene units prevail. But here and in all
materials which contain butadiene or iosprene there exist many

different configurational arrangements—isotactic vs atactic and cis vs trans. All existing evidence shows that particularly the configurational character of an elastic co- or terpolymer is of great importance for all its significant practical properties. Here it is again the vibrational spectral analysis which is capable of providing rapid and reliable answers to many pressing questions.

Another interesting and rewarding task is the investigation of organic adhesives and coatings. Even a tiny piece of lacquer permits an almost instantaneous indication of the group of coatings to which the material belongs—alkyd, polyester, polyamide, or polyacrylic; whether and to what extent it has been reacted with fatty substances; and which other and what kind of additives, antistatic agents, flame retardants) it contains.

This established general utility of the vibrational spectroscopy has recently been greatly enhanced by the addition of differential methods and particularly by the computerized Fourier transform technique based on interferometric spectroscopy.

Thus, many relatively complex polymeric structures can be correlated in great detail with their vibrational spectra. This obviously called for a systematic collection of relevant data—a formidable task which was undertaken by D. O. Hummel and his associates at the University of Cologne and led to the immensely useful standard work which permits a rapid and reliable identification of even very small (less than a milligram) quantities of polymeric materials, such as a piece of a fiber, a film, a coating, or an adhesive.