MACROMOLECULES

ORIGIN, DEVELOPMENT, SIGNIFICANCE

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ABSTRACT Natural polymers such as wood, cotton, wool, starch, and rubber have been known and used for a long time even though their composition and structure were unknown. At the beginning of this century systematic efforts were started to analyze these materials, elucidate their molecular pattern, and fit them into the framework of organic chemistry. It was found that they all are characterized by the presence of chain-like molecules with very high molecular weights ranging from 10000 to several millions. It was also found that these chains can be oriented by mechanical deformations and assume a laterally ordered crystal-like supermolecular arrangement. As soon as these facts become known as systematic search for synthetic counterparts of natural polymers was started which led to the laboratory preparation and large scale production of many synthetic materials which cover a wide range of properties and applications and which are becoming an increasingly important factor in science and industry. With growing understanding and know-how it also became possible to synthesize polymers with biochemically interesting properties such as the polyelectrolytes and other biopolymers.

Natural polymers such as wood, cotton, wool, silk, lacquers, rubber, and many types of gums have been used for centuries in all kinds of practical applications. Their chemical composition and structure were unknown; improvements made in the course of time were mainly through breeding, selection of the best raw materials, and through advances in the mechanics of the manufacturing processes. A few very important though probably accidental chemical discoveries were made which affected the chemical composition and structure of certain natural polymers such as the *vulcanization* of rubber, the *mercerization* of cotton, hemp, and flax, the *tanning* of leather, and the loading of silk. They led to significant technical results and were constantly improved in an empirical fashion.

Scientific work began around 1880 on the chemical composition, structure, and morphology of cellulose, wool, silk, starch, and rubber; it was largely descriptive and qualitative but provided a very useful background for further quantitative approaches. During this period the first synthetic (or artificial) polymers were made, particularly condensation products of formaldehyde with phenol, urea, and proteins (bakelite, Pollopas and Galalit) and derivatives of cellulose (nitrate and acetate); they acquired a considerable commercial importance but their development was purely empirical and their properties were, in most cases inferior to those of the corresponding natural products. Hence they were generally considered as *substitutes* or *ersatz* and were given such names as *Kunstseide, Kunstleder,* or *Kunstostoffe.* Most of their development took place in Europe, particularly in Germany, France, and England.

The ground work for the *organic chemistry* of polymers or macromolecules was laid around 1905 in the Institute of Emil Fischer in Berlin. His work on sugars and amino acids clarified in a complete manner the composition, structure, and stereochemistry of these substances and opened the way to a stepwise synthesis of progressively larger and larger molecular species. Emil Fischer himself remained strictly in the domain of classical organic chemistry of which he was the unsurpassed master and only reached the lower limits of polymer chemistry (molecular weights between 1000 and 1500) but his coworkers pioneered in all fields of true polymer research—Freudenberg, Helferich, and Hess in the field of polysaccharides, Leuchs and Bergmann in the domain of polypeptides, and Harries and Pummerer in polyhydrocarbons, particularly rubber. At the same time Ostwald and Svedberg developed *physicochemical* methods for the investigation of colloidal systems by the measurement of *diffusion, sedimentation, viscosity,* and *turbidity* and laid the fundament for the quantitative study of polymer solutions. Finally, the basic discovery of x-ray diffraction by von Laue, Bragg, Debye, and Scherrer showed the way to apply this method for the elucidation of the fine structure of the solid state even in microcystalline materials, which eventually led to the x-ray investigation of such polymeric materials as cellulose, proteins, and rubber.

The combined application of *all available* methods, organic, physiocochemical, and physical, was systematically promoted from 1920 to 1930 and led to a systematic clarification of a number of basic facts such as: synthesis of many new polymers, determination of their average molecular weight, the behavior of their solutions, and the details of their structure in the solid state. Most results were still qualitative or semiquantitative but a wide field was opened for further research and numerous attractive problems posed themselves on various topics. The industrial application of different polymers started to develop and it became evident that many valuable properties could be obtained in great variety and at low cost. A few prominent names of this period are W. A. Carothers, K. H. Meyer, E. K. Rideal, and H. Staudinger.

During the next decade there occurred a continuation of the systematic synthesis of many new polymers in the field of fibers, plastics, and rubbers, particularly through the preparation of new monomers, the discovery of new catalytic systems, and of the principle of copolymerization. There was a *quantitative formulation* of the kinetics of polymerization processes and understanding of their individual steps. Development of the statistical thermodynamics and hydrodynamics of polymer solutions leading to a *quantitative* understanding of osmotic pressure, diffusion, sedimentation, and viscosity took place. There was also a clarification of the solid state structure of polymers: theory of rubber elasticity, transition phenomena, crystallinity—amorphous system and relaxation behavior. Some prominent names in these fields are P. J. Flory, E. Guth, L. M. Huggins, W. Kuhn, W. H. Melville, and G. V. Schulz.

After 1940 we can witness a successful extension, amplification, and refinement in all directions. Specifically many new monomers, many new powerful catalytic systems, and many new polymerization techniques were developed with refinement of the statistical treatment of macromolecules in solution and in the bulk state, development of new methods for the characterization of polymers such as light-scattering, small angle x-ray diffraction, polarized infrared absorption spectroscopy, rotatory dispersion measurements, nuclear magnetic resonance signals, differential thermal analysis or sedimentation, and diffusion in a density gradient cell. There was also clarification of the mechanism of polymerization under various conditions such as in solution, suspension, and emulsion, at high pressures, high and low temperatures, and in the form of living polymers. Enormous growth in the industrial production and practical application of all polymers took place.

The following important progress can be forecast without too much risk for the near future:

(*a*) Lowering of the selling prices of all standard plastics and rubbers into the range between 20 and 30 cents per pound with some coming down as far as 15 cents. Lowering of the selling prices of most standard staple fibers into the range between 40 and 60 cents per pound with some of them coming down as far as 25 to 30 cents.

(*b*) Synthesis of polymers which will remain flexible and supple as far down as −100°C and of others which can stand temperatures of 500°C for prolonged periods.

(*c*) Development of adhesives which will make it possible to build houses, cars, and airplanes without nails, screws, or rivets.

(*d*) Polymerization at low temperatures in the liquid or solid state permitting rapid continuous production of many polymers with convenient control of molecular weight and of high purity.

(*e*) Further improvement of the methods for the characterization of polymers, particularly NMR, flow birefringence, optical activity, and differential thermal analysis.