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The University of Oklahoma PH.D. 1983

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GRADUATE COLLEGE

STAUDINGER, CAROTHERS, AND THE EMERGENCE OF MACROMOLECULAR CHEMISTRY

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

YASU FURUKAWA

Norman, Oklahoma

1983

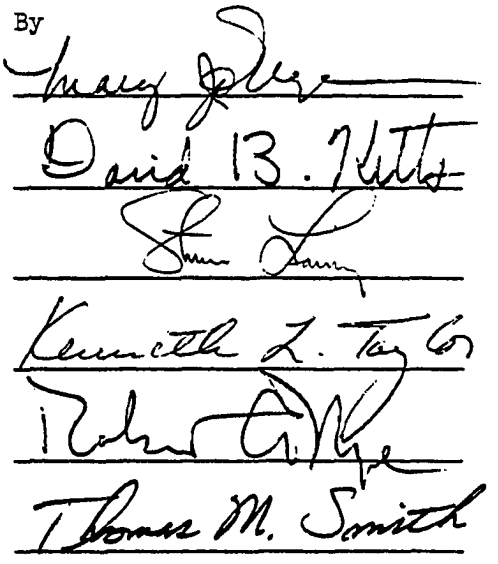
STAUDINGER, CAROTHERS, AND THE EMERGENCE

OF MACROMOLECULAR CHEMISTRY

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF THE HISTORY OF SCIENCE

By



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PREFACE

In attempting to reconstruct a picture of the emergence of macromolecular chemistry, I have focussed my investigative efforts on the scientific work and activities of Hermann Staudinger, Wallace Hume Carothers, and their research groups in Germany and the United States. The roles of the two scientists and their schools were irrefutably central to the theoretical, practical, and institutional foundations of this new field of chemical science during the interwar period. Not only does this study describe their theoretical development, but it also aims to illuminate and contrast the scientific enterprise of the two founders from various angles, such as their scientific personalities, styles in chemistry, and the peculiar institutional and social milieux in which they pursued their science. In this respect, I hope that this comparative study sheds light on contrasting characteristics between German and American science in the early twentieth century as well.

Many people at the University of Oklahoma have aided in completing this dissertation. I wish to express my deep gratitude to my major professor Mary Jo Nye (Associate Professor of the History of Science) for her careful reading of this text and for her constructive criticism, direction, and continuous encouragement. To Kenneth L. Taylor (Associate Professor of the History of Science and the Chairman of the Department of the History of Science), I owe a great debt for his prompt comments

and helpful suggestions. The other members of my committee, Thomas M. Smith (Professor of the History of Science), David B. Kitts (Professor of the History of Science), Steven J. Livesey (Assistant Professor of the History of Science), and Robert A. Nye (Professor of History), also gave me useful comments from which I have benefitted. I am very grateful to Duane H. D. Roller (Professor of the History of Science and the Curator of the History of Science Collections) and Marcia M. Goodman (Librarian of the History of Science and Rare Book Collections and Assistant Professor of Bibliography) for their valuable assistance while carrying out my doctoral research in the History of Science Collections at the University of Oklahoma. With the friendly help of the personnel of the Chemistry Library at the University of Oklahoma, I was able to consult a large amount of chemical literature published between the nineteenth century and the first half of this century. I have the pleasant duty of acknowledging the personal support and encouragement of Marilyn Ogilvie (Assistant Professor of Natural Science, Oklahoma Baptist University) and my fellow graduate students in the Department of the History of Science at the University of Oklahoma.

Special thanks are due to the Department of History of Science at the University of Oklahoma for granting me a Graduate Assistantship during my doctoral study. The travel and research grants from the Graduate College at the University of Oklahoma and from the Eleutherian-Mills Hagley Foundation enabled me to examine a rich store of unpublished sources on Carothers and the Du Pont Company at the Eleutherian Mills Historical Library in Wilmington, Delaware, in the spring of 1982. In this connection, I would like to express my thanks to Richard R. Williams

(Director of the Eleutherian Mills Historical Library) and the Eleutherian Mills Library staff for their cordial assistance and support. I am also grateful to Francis E. Parsons (Librarian of the Lavoisier Library, E. I. du Pont de Nemours and Company) for allowing me access to the Carothers File at the Lavoisier Library in the Du Pont Experimental Station, and to Adeline B. C. Strange in Wilmington, who loaned me her collection of Carothers' letters and manuscripts in which I was especially interested. As living witnesses, Herman F. Mark (Dean Emeritus, Polytechnic Institute of New York), Julian W. Hill, and Gerard J. Berchet provided me invaluable information about Staudinger, Carothers, and their own experiences in the 1920s and the 1930s through my interviews with these polymer chemists. To those who gave me kind advice and assistance regarding research materials, I owe particular thanks. They are Jeffrey L. Sturchio (Assistant Professor of the History of Science, New Jersey Institute of Technology), John K. Smith (Ph.D. candidate in the History of Technology, University of Delaware), John W. Servos (Assistant Professor of the History of Science, Princeton University), George Wise (Historian, General Electric Company), and Claus Priesner (Historian, Deutsches Museum, Munich).

For German and French quotations in this dissertation, I have used available English translations when, in my judgment, they were satisfactory. The remaining translations from foreign languages, those for which no published sources are cited, are my own. My appreciation is due to Tibor J. Herczeg (Professor of Astronomy, University of Oklahoma), for his meticulous reading of my translations from German passages and for his helpful suggestions.

Finally, I wish to express an especial thanks to my parents, Yoshiko and Masatoyo Furukawa, for their understanding, encouragement, and endless affection.

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IV. TOWARD THE CONSTRUCTION OF A NEW SCIENCE: THE GROWTH OF MACROMOLECULAR CHEMISTRY 142

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LIST OF ABBREVIATIONS

Scientific Journals

Amer. J. Sci. - American Journal of Science.

Angew. Chem. - Angewandte Chemie.

Annalen - Annalen der Chemie und Pharmacie.

Ber. - Berichte der deutschen chemischen Gesellschaft.

Bull. Soc. chim. - Bulletin de la Société chimique de France.

Chem. Abstracts - Chemical Abstracts.

Chem. Eng. News - Chemical and Engineering News.

Chem. Reviews - Chemical Reviews.

Colloid Symp. Monogr. - Colloid Symposium Monograph.

Compt. rend. - Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

Compt. rend. Trav. Lab. Carlsberg - Comptes rendus des Travaux du Laboratoire Carlsberg, serie Chimique.

Helv. Chim. Acta - Helvetica Chimica Acta.

Ind. Eng. Chem. - Industrial and Engineering Chemistry.

India-Rubber J. - The India-Rubber Journal.

J. Amer. Chem. Soc. - Journal of the American Chemical Society.

J. Chem. Educ. - Journal of Chemical Education.

J. Chem. Soc. - Journal of the Chemical Society, London.

J. Poly. Sci. - Journal of Polymer Science.

J. parkt. Chem. - Journal für praktische Chemie.

J. Russ. Phys. Chem. Soc. - Journal of the Physical and Chemical Society of Russia.

Kolloid-Z. - Kolloid-Zeitschrift.

Liebigs Ann. Chem. - Justus Liebigs Annalen der Chemie.

Monatsh. - Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.

Naturwiss. - Die Naturwissenschaften.

Phil. Mag. - Philosophical Magazine.

Phil. Trans. - Philosophical Transactions of the Royal Society of London.

Quart. J. Sci. Arts - Quarterly Journal of Science and the Arts.

Rubber Chem. Tech. - Rubber Chemistry and Technology.

Sitzungsber. Preuss. Akad. Wiss. Berlin - Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.

Trans. Amer. Inst. Chem. Eng. - Transactions of American Institute of Chemical Engineering.

Trans. Faraday Soc. - Transactions of the Faraday Society.

Z. Chem. Ind. Kolloide - Zeitschrift für Chemie und Industrie der Kolloide.

Z. anal. Chem. - Zeitschrift für analytische Chemie.

Z. Physik - Zeitschrift für Physik.

Z. physik. Chem. - Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftlehre.

Z. physiol. Chem. - Hoppe-Sevler's Zeitschrift für physiologische Chemie.

Others

EMHL - Eleutherian Mills Historical Library, Wilmington, Delaware.

SC - A. B. C. Strange Personal Collection, Wilmington, Delaware.

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INTRODUCTION

The emergence of macromolecular chemistry, the chemistry of macromolecules or large molecules, marks an epoch in the history of twentieth-century science. New conceptions inherent in this field have not only expanded the theoretical and methodological outlook of chemical science, but also have provided bases for the growth of new sciences, notably molecular biology and molecular physics. The practical aspects of this science are especially familiar to the public; synthetic fibers, synthetic rubbers, and a wide variety of plastics, on which our modern culture has come to depend, stem from applications of the chemistry of macromolecules.

Despite its significance in modern scientific development, the history of this field has not yet received adequate attention from historians of science. General textbooks on the history of modern chemistry have given few references to this subject. Some of them, which barely cover this science, have treated macromolecular science at best simply as a branch of industrial or applied chemistry.[1] While only recently a few works have thrown light on some aspects of the history of this specialty, a full-scale study reflecting the whole picture of the early development of this scientific discipline has not appeared thus far.[2]

This present study seeks thoroughly to expound details of the emergence of macromolecular chemistry between 1920 and the mid-1940s, and to fill the void in historical scholarship. Special emphasis is placed upon

the scientific work and activities of the German chemist, Hermann Staudinger (1881-1965), and the American chemist, Wallace Hume Carothers (1896-1937), both of whom laid a large protion of the theoretical and practical foundations of this field. In intellectual, social, and individual dimensions, I shall examine and contrast the origins and development of their scientific thought, and illuminate the way in which they and their German and American followers elevated their working field into a new branch of chemical science toward the 1940s.

Macromolecular chemistry is a subject-based field of science, since it deals with a class of substances with special properties (such as colloidal phenomena in solution and fibrousness or elasticity in the solid state). The substances now are often called high polymers and are exemplified by rubber, cellulose, proteins, starch, resins, and numerous synthetic polymers. In a narrower sense, the field falls within a branch (although an important branch) of organic chemistry, since the large majority of the high polymer class belongs to organic compounds. However, this is not to say that macromolecular chemistry arose merely as a consequence of the cultivation of an unexplored area of ignorance. Rather, it emerged from a fundamental reconception of existing objects of inquiry.[3]

Chapter I is devoted to an examination of conceptual developments in the study of one class of substances from the nineteenth century through the 1920s. Because of their peculiar properties, biological significance, and practical utility, natural products such as rubber, cellulose, and proteins drew much attention from scientists during the previous century. Within the framework of nineteenth-century chemistry, these compounds were identified as "polymers" in which the molecule is built up from the

recurrence of the same atomic groups. Yet there were marked differences of views on the constitution of polymers among scientists. Throughout this study, I shall illustrate the divergent points of view in light of two traditions embracing distinct approaches to polymeric substances. One of these traditions is what we may call the physicalist tradition, as represented by the colloid doctrine of Wolfgang Ostwald and its offspring, the so-called aggregate theory of colloidal substances. According to this view, polymeric compounds are the physical aggregates of small molecules held together by certain physical forces; colloidal particles in a solution are an example of these aggregates. The physicalists held that the special properties of these compounds, such as their colloidal nature, could be sufficiently explained in terms of matter and forces. This view received strong support in scientific circles during the early decades of this century.

The other tradition we will call the organic-structural tradition, which claimed that the physical and chemical properties of this class of compounds can best be understood in terms of the internal structure of the organic molecule. Rooted in the structural theory, which was developed in the second half of the nineteenth century by August Kekulé and others, this approach became the basic principle of organic chemistry. The possibility of large molecules for polymers was assumed by several chemists, including Kekulé himself, within this organic-structural tradition.[4]

The structural approach to organic compounds culminated in the work on proteins by Emil Fischer at Berlin around the turn of the century. However, in explaining the characteristics of polymers, the structural chemist Fischer emphasized the internal geometrical arrangement of atoms

in the molecule rather than the large numbers of atoms. Accordingly, organic chemists followed his claim that compounds of a molecular weight higher than 5,000 might not exist. The earlier concept of large molecules was thus discarded as superfluous within the organic-structural tradition. The aggregate theory of polymers gradually came to prevail among chemists, and the physicalist tradition appeared triumphant in scientific academic circles in the 1920s.

Chapter II analyzes the origins and development of Staudinger's macromolecular theory and the complex nature of the macromolecular debate during the 1920s. In the early 1920s, rejecting the widespread aggregate theory, Staudinger proposed his theory, according to which polymers are composed of very long-chain molecules or Makromoleküle. Conceptually and methodologically, he belonged to the organic-structural tradition. In his view, colloidal particles are themselves macromolecules which are made up of even millions of atoms linked together by "Kekulé" valence bonds, in accordance with Kekulé's structural theory. Hence, the study of colloids is, he insisted, a branch of organic chemistry, and not a part of physical or colloid chemistry. His arguments soon evoked strong oppositions among his contemporaries, including not only physical chemists, colloid chemists, and physicists, but also organic chemists, biologists, and X-ray crystallographers. In the ensuing decade, Staudinger, along with his students at Zürich and Freiburg, sought to establish experimental evidence for the existence of macromolecules. Staudinger's evidence depended on purely organic-chemical methods, whereas his opponents defended the aggregate theory on the basis of physical methods such as the X-ray diffractions. The issue came to no resolution for the time being.

Here again, the polemics largely present a picture of conflict between the organic-structural approach and the physicalist approach. The macromolecular debate continued until the middle of the 1930s when Staudinger's concept met with significant acceptance, owing particularly to Carothers' work on the mechanism of polymerization. The victory of the macromolecular theory meant the triumph of the structural tradition over the physicalist school. The concluding section of Chapter II will elaborate this point and stress that there were, however, some important differences in his concept from the classical structural approach and Fischer's views. In explaining properties of compounds, Staudinger did depart from the classical concept of molecular structure. He claimed that physical and chemical properties of polymers are not only determined by the internal structure of the molecule but more significantly by its external structure, such as its large size and shape--a facet which classical organic chemistry had not embraced. It was this point of departure from the traditional structural approach that enabled him to establish so firmly the macromolecular view, in contrast to the nineteenth-century idea of large molecules that earlier had been dropped from the organic-structural tradition.

Chapter III investigates Carothers' educational background and the American context of polymer studies before his time. It examines, as well, the details of Carothers' study of polymers and polymerization at Du Pont's Experimental Station in Wilmington, Delaware, between 1928 and 1937. In all likelihood, Carothers adopted Staudinger's macromolecular concept through his reading of German papers around 1927, when he was a Harvard instructor. As an organic chemist, he shared with Staudinger

the structural approach to polymers but developed his study into a different direction. A close examination of his background shows that there were no direct ties between Carothers and Staudinger or his German school. Recent historical literature on the emergence of American science has focussed attention on the transmission of German scientific disciplines into the United States. A common pattern for this mechanism is that American students who were trained at German universities imported a newly emerging specialty, founding research schools in American universities. The rise of American macromolecular chemistry does not fit with this conventional pattern.[5]

With no background in German chemical education from which many earlier generations of American chemists had benefitted, Carothers was a product of American pragmatic education under Roger Adams immediately after World War I. Here we find clues for understanding Carothers' style in chemistry and his approach to macromolecules, which sharply contrast with those of Staudinger. Carothers' approach to polymers was characteristically synthetic, in contrast to Staudinger's analytic approach. Carothers was concerned with the formation process or mechanism of giant molecules, while Staudinger was primarily concerned with the analysis of final products. Thus, Carothers' research program at Du Pont was not a mere importation or extension of the Staudinger school; his approach departed from that of his German counterpart from the outset of his research. This helps explain why American research, through Carothers' work, now reciprocated Germany's traditional contributions to American chemistry. His study had a fresh and new impact on German chemical circles.

The public image of Carothers as the inventor of synthetic fiber,

nylon, and of synthetic rubber, neoprene, has often overshadowed the role of his theoretical work on macromolecules. In what follows in Chapter III, an analysis of the nylon discovery (1931-1935) by his group is given in order to show how his theoretical study led to a practical application within the framework of the Du Pont corporation. Evidently, nylon was an unforeseen consequence of Carothers' own basic research. It was the Company's deliberate efforts that created the industrialization of macromolecular science in a remarkably short period. In turn, the nylon adventure turned out to be a full-scale test which proved the validity of his theory of condensation polymers. Carothers' macromolecular synthesis convinced his contemporaries, including German chemists, of the macromolecularity of polymeric substances as well as the great possibility of applications in this field.

Chapter IV describes the Faraday Society meeting held in 1935 in Cambridge, which marked the end of the decade-long controversy between macromolecular and aggregate theory, and illuminates the roles of Staudinger's German school and Carothers' circle for the emergence of macromolecular chemistry as a new scientific specialty toward the period of World War II. Thanks to the two initiators, Staudinger and Carothers, Germany and the United States won particularly early recognition for this chemical science. But, as suggested earlier, Staudinger's school at Zürich and Freiburg and Carothers' Wilmington school exhibit a striking contrast in character. While the focus here is on the analysis of institutional and social settings in which scientists interacted, my discussion necessarily includes personal factors in the lives of the two leaders of the macromolecular schools (such as scientific personalities and leadership character-

istics), which affected the organizational modes of this science in Germany and America. The charismatic German professor, Staudinger used every means at his disposal, through a large number of advanced students and Privat Dozenten, his lectures, and his control of publication outlets, to propagate macromolecular chemistry in the German chemical community. His interest remained primarily in pure science, and applied research was not within the scope of his immediate research program. The impact of the Staudinger school on industry was less direct than on academic circles. In contrast to the charismatic leader Staudinger, Carothers served as a man of ideas in Du Pont's research organization. While working with a modest number of co-workers, the industrial researcher Carothers did not train students, unlike the university man Staudinger. Yet under his influence, there emerged the first generation of polymer chemists in American universities, who included Paul J. Flory and Carl S. Marvel. American macromolecular chemistry, which first stemmed from a fundamental research program in industry, was thus established as a scientific discipline in academia by the 1940s. The postwar period saw the United States running ahead both academically and industrially in productivity of polymer research.

In the conclusion, a few remarks will be made concerning the emergence of macromolecular chemistry in regard to the two major theses in this study, namely, the role of conceptions in the development of chemical science and the interactions between chemistry, industry, and society which marked early twentieth-century science.

NOTES

[1]Cf., Henry M. Leicester, The Historical Background of Chemistry (New York: Dover Publications, 1956); J. R. Partington, A History of Chemistry, 4 vols. (London: St. Martins, 1961-1970), vol. 4 (1964); Aaron J. Ihde, The Development of Modern Chemistry (New York: Harper and Row Publishers, 1964); Alexander Findlay, A Hundred Years of Chemistry, 3rd edition revised by Trevor I. Williams (London: Gerald Duckworth & Co. Ltd., 1965); and Eduard Farber, The Evolution of Chemistry: A History of Its Ideas, Methods, and Materials (New York: The Ronald Press Company, 2nd edition, 1969).

[2]Robert Olby has included chapters on Staudinger's macromolecular concept in his The Path to the Double Helix (Seattle: University of Washington Press, 1974). The German context of the debate over Staudinger's macromolecular theory has been extensively documented in Claus Priesner's recent study, H. Staudinger, H. Mark und K. H. Meyer: Thesen zur Grösse und Struktur der Makromoleküle (Weinheim; Deerfield Beach, Florida; and Basel: Verlag Chemie, 1980). The American context of polymer chemistry and Carothers' work has not been fully studied. The early history of macromolecular chemistry has been briefly outlined by practitioners of this field in their personal recollections or reviews: Hermann Staudinger, Arbeitserinnerungen (Heidelberg: Dr. Alfred Hüthig Verlag GmbH., 1961), especially pp. 77-93; Wallace Hume Carothers, "Polymerization," Chem. Reviews, 8 (1931): 353-426; Paul Flory, Principles of Polymer Chemistry (Ithaca, New York: Cornell University Press, 1953), pp. 3-28; Frank C. McGrew, "Structure of Synthetic High Polymers," J. Chem. Educ., 35 (1958): 178-186; Herman F. Mark, "Polymers--Past, Present, Future," in Polymers (Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research, X), ed. W. O. Milligan (Houston, Texas: The Robert A. Welch Foundation, 1967): 19-43; "The Early Days of Polymer Science," J. Chem. Educ., 50 (1973): 757-760; "Polymer Chemistry: The Past 100 Years," Chem. Eng. News, 54 (1976), no. 15: 176-189; "Polymer Chemistry in Europe and America--How It All Began," J. Chem. Educ., 58 (1981): 527-534; Carl S. Marvel, "The Development of Polymer Chemistry in America--Early Days," ibid.: 535-539; G. Allan Stahl, ed., Polymer Science Overview: A Tribute to Herman F. Mark (Washington, D.C.: American Chemical Society, 1981); and Raymond B. Seymour, ed., History of Polymer Science and Technology (New York and Basel: Marcel Dekker, Inc., 1982).

[3]The field of macromolecular chemistry is now more often called polymer chemistry in English-speaking countries, since polymers are known to be macromolecular compounds. The term polymer, as will be discussed

below, has been used since the previous century, and nineteenth-century chemists did study polymers such as rubber, cellulose, and proteins. But they were not "polymer chemists" in the sense that we use the term today. After the reconception of polymers as macromolecules in the first half of this century, the chemistry of polymers became identical with the chemistry of macromolecules. In order to avoid confusion in terminology, I adopt in this study Staudinger's original term for this field, macromolecular chemistry (makromolekulare Chemie), which indeed remains still valid.

[4]Similar conceptual confrontations existed in various phases of development of chemical science, biology, and philosophy. Historians of science have examined the conflicts between "mechanism" and "materialism" in eighteenth-century Newtonianism (Schofield), between "chemical tradition" and "physicalists" in eighteenth-century chemistry and matter theories (Thackray), between "mechanistic materialism" and "holistic materialism" in early twentieth-century physiology (Allen), and between "chemical tradition" and "physicalist tradition" in early twentieth-century physical chemistry (Servos). Robert E. Schofield, Mechanism and Materialism: British Natural Philosophy in an Age of Reason (Princeton, New Jersey: Princeton University Press, 1970); Arnold Thackray, Atoms and Powers: An Essay on Newtonian Matter Theory and the Development of Chemistry (Cambridge, Massachusetts: Harvard University Press, 1970); Garland E. Allen, Life Science in the Twentieth Century (New York, London, Sydney, and Toronto: John Wiley & Sons, Inc., 1975); John W. Servos, "Physical Chemistry in America, 1890-1933: Origins, Growth, and Definitions," (Ph.D. dissertation, Johns Hopkins University, 1979); and "A Disciplinary Program That Failed: Wilder D. Bancroft and the Journal of Physical Chemistry, 1896-1933," Isis, 73 (1982): 207-232. Of course, my demarcation between organic-structural and physicalist traditions is a relative distinction. None of Staudinger's contemporaries would have claimed to be one-hundred percent within a so-called "organic-structural" tradition nor one-hundred percent within a so-called "physicalist" tradition. While researchers in the polymer field often openly expressed their positions one way or another, however, it is clear that there was much divergence of opinion within each tradition.

[5]Cf., e.g., Margaret W. Rossiter, The Emergence of Agricultural Science: Justus Liebig and the Americans, 1840-1880 (New Haven, Connecticut; and London: Yale University Press, 1975); Owen Hannaway, "The German Model of Chemical Education in America: Ira Remsen at Johns Hopkins (1876-1913)," Ambix, 23 (1976): 145-164; R. G. A. Dolby, "The Case of Physical Chemistry," in Perspectives of the Emergence of Scientific Disciplines, eds. Gerard Lemaine, Roy MacLeod, Michael Mulkay, and Peter Weingart (The Hague and Paris: Mouton; Chicago: Aldine, 1976); "The Transmission of Two New Scientific Disciplines from Europe to North America in the Late Nineteenth Century," Annals of Science, 34 (1977): 287-310; John W. Servos, "Physical Chemistry in America"; Robert E. Kohler, From Medical Chemistry to Biochemistry: The Making of a Biomedical Discipline, (Cambridge, London, New York, New Rochelle, Melbourne, and Sydney: Cambridge University Press, 1982); and George Wise, "Ionists in Industry: Physical Chemistry at General Electric, 1900-1915," Isis, 74 (1983):7-21.

CHAPTER I

BACKGROUND: THE RISE AND DECLINE OF THE CONCEPT OF LARGE MOLECULES IN CLASSICAL ORGANIC CHEMISTRY

Chemistry, dealing with the nature and changes of matter, was both intellectually and institutionally a distinct and rapidly maturing science in the nineteenth century. One of the most remarkable features of this development was the growth of organic chemistry. The outlook of organic chemistry went through a series of drastic changes throughout the course of the century. Organic chemistry, during the first half of the nineteenth century, was essentially analytic; practitioners of this field devoted themselves to isolating organic substances, to determining their composition, and to investigating their properties. Toward the second half of the century, organic chemists were shifting their emphasis from the composition to the structure of molecules. Structural representation of molecules became a leading approach to the problem of substances associated with organic origins. Chemical vitalism lost its wide popularity in the middle of the century, as chemists embarked on the artificial synthesis of numerous organic compounds from inorganic substances, ushering in the epoch of organic synthesis. Through this transition, organic chemistry expanded its definition from the chemistry of products inherent in living things, such as plants and animals, to the chemistry of carbon

compounds.

Some theoretical elements, which shaped the emergence of the macromolecular theory, can be seen in this nineteenth century context. Such concepts as polymers, polymerization, and colloids arose during this period from various phases of investigations in the domain of organic chemistry. Chemists extended their inquiries into the elucidation of the structure and properties of a class of organic substances with colloidal nature, now known as high polymers, including rubber, cellulose, starch, proteins, and synthetic polymers. The possibility of very large molecules for these compounds was suggested by a number of scientists within the framework of organic structural chemistry. However, the concept disappeared from the main stream of science in the early part of the twentieth century, when structural chemists began to doubt the existence of the big molecules and when the aggregate theory of colloidal substances flourished. Consequently, the interpretation of polymers and polymerization was brought into a stage of radical change in chemical circles.

In this chapter, I shall examine the early development of polymer chemistry since the nineteenth century through the 1920s--around the time of Staudinger and Carothers--in order to illuminate the rise and decline of the large-molecular concept in the light of changing views and approach in classical organic chemistry.

Polymers, Colloids, and the Concept of Large Molecule

The term "polymer" originated in the work of the Swedish chemist, Jöns Jacob Berzelius (1779-1848), who recognized the existence of compounds with the same proportionate composition but having different numbers of constituent atoms. In 1833 he proposed the name "polymeric"

(polymerische, from the Greek πολύς, many) for such compounds, differentiating the idea from his notion of "isomeric" (isomerische, from the Greek ἰσομερής, composed of equal parts) which designated the case of compounds with the same compositions and the same number of atoms but having different properties. The examples he gave were olefiant gas (CH^2 as he put it) and Faraday's volatile oil "Weinöl" (C^4H^8). These are polymeric, for the relative number of carbon and hydrogen atoms is the same, but the absolute number different. The difference in the properties of these substances was therefore attributed to the difference in the absolute number of the constituent atoms.[1] Berzelius' polymer concept was soon brought into the general use of nineteenth-century chemistry. Thus, in a well-circulated chemical dictionary of the 1860s, "Bodies are said to be polymeric when they have the same percentage composition, but different molecular weights; the olefines C^nH^{2n} for example. . ."[2] Encyclopedic writers, such as Leopold Gmelin (1788-1853), compiled lists of many examples of polymeric compounds around the middle of the century.[3]

In his paper, "Liquid Diffusion Applied to Analysis," published in 1861 in the Philosophical Transactions of the Royal Society, London, the Scottish chemist Thomas Graham (1805-1869) reported that certain naturally-occurring polymeric substances in solution showed a peculiar behavior, namely, an extremely slow or even negligible rate of diffusion through membranes such as parchment. He wrote, "The comparatively 'fixed' class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme." He called such substances "colloids" (from the Greek κόλλα, glue), as distinguished from "crystalloids," that

is, normal substances that can easily crystallize and possess a high diffusibility.[4] Crystalloids and colloids, he stated, "appear like different worlds of matter."[5] In Graham's view, the colloid properties have much to do with the intimate molecular constitution of colloids. Furthermore, he recognized that such colloidal substances have a high degree of polymeric constitution:

> The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12}H_{11}O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.[6]

Graham, however, suspected that colloids represented a state or condition of matter: the same substances can exist in a crystalloidal or colloidal state. As he believed, "in nature there are no abrupt transitions, and . . . distinctions of class are never absolute."[7] For this reason, Graham assumed that the "colloid molecule" might be made up of many smaller crystalloid molecules.

Toward the second half of the nineteenth century, organic chemists were shifting their emphasis from chemical composition to molecular constitution. After a period of confusion in the use of terminology and discussions at the Karlsruhe Congress (the first international chemical congress held in 1860), chemists arrived at a general agreement on the distinction between atoms and molecules.[8] Thereafter, organic chemistry became primarily the science which deals with the molecule, the smallest

portion of a substance capable of existing independently and retaining the properties of the original substance. Organic reactions take place at the molecular level. Molecules were taken as the entity from which stemmed all chemical and physical properties and with which organic chemists primarily ought to be concerned. The concept of isomerism, which Berzelius had proposed as early as the 1830s, indicated that properties of matter depend not only on its composition but also on the arrangement of the constituent atoms in the molecule. The key to the understanding of distinct properties of organic substances now appeared to lie in the elucidation of the internal structure of the carbon-rich organic molecules.

In 1858 the German organic chemist, Friedrich August Kekulé (1829-1896) proposed some important principles concerning the architecture of organic molecules: one principle was that carbon is tetravalent or of fourfold saturating capacity; another, that atoms of carbon can combine together, forming carbon-carbon links.[9] This so-called valency theory, in which no explanation was given for the cause of the valence forces, as he thought, provided a new picture of the connection of atoms in a molecule. He wrote later that,

> Die einzelnen Atome einer Molekel stehen nicht alle mit allen order alle mit einem in Verbindung, jedes haftet vielmehr nur an einem order an wenigen Nachbaratomen, so wie in der Kette Glied an Glied sich reiht.[10]

From the valency concept followed the structural theory according to which the properties of carbon compounds depend on the arrangement of the atoms in the organic molecule more than on the kinds of component atoms.[11]

If one accepts Kekulé's theory, the question of how many atoms can be combined in one molecule occurs. Kekulé himself did not place any upper limit on molecular size. Indeed, there was no reason to deny the

possibility of very large molecules in which the atoms are linked together by the Kekulé bond. In 1877 he remarked:

> . . . ein beträchtlich grosse Anzahl von Einzelmolekeln sich durch mehrwerthige Atome zu netz- und, wenn man so sagen will, schwammartigen Massen vereinigen könne, um so jene der Diffusion widerstrebenden Molecularmassen zu erzeugen, die man, nach Graham's Vorschlag, als colloidal bezeichnet.[12]

Although Kekulé did not carry his argument any further, the possibility of the formation of a giant chemical structure of Graham's "colloidal molecule" seemed implicit in his structural scheme.

Kekulé's suggestion of very large molecules was employed by a few contemporaries, including his colleague Eduard Friedrich Wilhelm Pflüger (1829-1910). These giant molecules, Pflüger assumed, may compose the "elements of the form" (Formelelemente) of living organisms.[13] Kekulé exhibited a cautious although appreciative attitude toward Pflüger's ideas: "Es hiesse indessen den Boden des Thatsächlichen allzusehr verlassen, wollte man derartige Speculationene schon jetzt weiter verfolgen."[14]

Following Berzelius' definition of polymerism, the notion of polymerization was introduced in the synthesis of polymeric compounds in the second half of the century, the epoch of the laboratory synthesis of organic substances. In 1866, the French master of organic synthesis, Marcellin Pierre Eugene Berthelot (1827-1907), called "polymeric transformation" (transformation polymerique) the conversion reaction of certain compounds (such as styrene) to their polymerides.[15] Likewise, several cases of polymeric transformation were reported by the end of the nineteenth century, and chemists commonly referred to this process as "polymerization" designating a union of two or more molecules (of the same kind) to form larger molecules.[16] The polymerization products, notably

those prepared under drastic conditions, exhibited properties corresponding to Graham's colloids. They were gelatinous and could neither be crystallized from solution nor distilled without decomposition. Dubbed "grease chemistry," the study of these substances did not then always attract practitioners of organic chemistry, since these products did not respond to the established methods for isolation, purification, and analysis--the methods that heavily relied on crystallization or distillation.

After 1880, the possibility of large molecules was discussed often in the light of molecular weight measurements of naturally-occurring polymers. In 1882 François-Marie Raoult (1830-1901), Professor of Chemistry at the University of Grenoble, demonstrated that the depression of the freezing point of a solution was in proportion to the molecular concentration of the dissolved substance.[17] His study led to the establishment of the first quantitative method for determining the molecular weights of substances in solutions. Soon, chemists employed Raoult's method to measure the molecular weights of colloidal substances, obtaining surprisingly high values. For example, as early as 1888 the English chemists Horace Tarberer Brown (1848-1925) and George Harris Morris (1858-1902) reported to the Chemical Society, London:

> The application of this new method to starch, and to the non-crystallisable products of its transformation, soluble starch, the dextrins and malto-dextrin, seemed full of promise, since chemists are still divided in their opinions as to the true nature of these compounds, and as to whether the differences in the properties of the dextrins are such as to justify the view that they are polymeric, or, on the other hand, compounds having the same molecular weight, but differing in constitution.
>
> Certain difficulties have, however, arisen at this stage of our inquiry, owing to the very high molecular weight which these substances evidently possess. As a result of this, the freezing point of even very strong solutions is depressed to such a small extent as to render it necessary, before we can assign any approximately accurate

> numerical value to our results, to determine the limits of error of the method, which manifestly increase with the molecular weight of the substance. We have, however, convinced ourselves that the molecular complexity of these compounds is very great indeed, and we hope to lay certain results before the Society at an early date.[18]

In 1889 they arrived at a value of 32,400 for the molecular weight of "soluble starch" from their experiments of freezing point depressions, and thus gave the polymer formula $5(C_{12}H_{20}O_{12})_{20}$.[19] In the same year John Hall Gladstone (1827-1902), Graham's student, and Walter Hibbert applied Raoult's method to rubber, reporting values of 6,500 to "extremely high." They further drew the general conclusion that the molecule of a colloidal substance contains a very large number of atoms.[20] Following the study, carried out in 1887-1888 by the Dutch chemist Jacobus Henricus van't Hoff (1852-1911),[21] the osmotic pressure method for the determination of the molecular weight was also applied to colloidal substances. Using this method, Hermann Rodewald (1856-1938) and A. Kattein in 1900 obtained a similarly high molecular weight of about 38,000 for starch.[22] By the turn of the century, then, very high values of molecular weights for such colloidal substances as starch, rubber, cellulose, and proteins were being reported (see Fig.1.1),[23] and a number of chemists were led to suspect that these substances are indeed composed of very large molecules.

Figure 1.1. Molecular Weights of Colloidal Substances, Reported between 1880 and 1900

Date	Author	Substances	Method	Mol. Weight
1886	Zinoffsky	haemoglobin*	Q.A.	16,700
1889	Brown and Morris	soluble starch	D.P.	32,400
1889	Gladstone and Hibbert	rubber	D.P.	6,500-
1891	Sabanijeff and Alexandrov	egg albumin*	D.P.	14,000
1893	Linter and Düll	amylodextrin*	D.P.	17,500
1900	Rodewald and Kattein	starch	O.P.	38,000
1900	Nastukoff	cellulose	E.P.	5,700-12,000

Note: D.P. = depression of freezing point; E.P. = elevation of bioling point; O.P. = osmotic pressure; Q.A. = quantitative analysis.
* = protein

Emil Fischer and the Riesenmolekülen

These reports of high molecular weights, however, were not followed by a wide acceptance of the concept of large molecules in scientific circles. On the contrary, many organic chemists were in no position to support this concept positively, and it declined in the early decades of this century within the organic-structural tradition.

One of the most influential chemists who rejected the idea of very large molecules was the German organic chemist Emil Hermann Fischer (1852-1919), the student of Kekulé and Adolf von Baeyer (1835-1917).[24] Following Kekulé, the structural theory became the principal approach to the study of organic compounds. Around the turn of the century, this approach culminated in Fischer's work on the structure of sugars, enzymes,

purines, and proteins. In elucidating the constitution of these natural products present in organisms, his method was characteristically synthetic. From simple molecules, he built up complex ones of known structure closely simulating the natural compound in question. This was followed by a comparison between the properties of his synthetic products and those of the natural products. In this way, Fischer attempted to establish the precise structure of sugars, enzymes, purines, and proteins. He argued that this synthetic approach sharply contrasted with the tendency of physics to examine matter only by dividing, subdividing, and re-subdividing:

> Die Molekularphysik wird deshalb gut tun, bei dem Studium hochmolekularer Stoffe sich an die synthetischen Produkte bekannter Struktur zu halten. Ich werde darum die Versuche zum Aufbau von Riesenmolekülen mit Hilfe des geschilderten Verfahrens fortsetzen.
>
> Sicherlich gewährt es auch noch in andrer Beziehung einen grossen Reiz, die Leistungsfähigkeit unserer Methoden zu prüfen. Bekanntlich ist die moderne Physik bemüht, die Materie in immer kleinere Stücke zu zersplittern. Über die Atome ist man längst hinaus, und wie lange die Elektronen für uns die kleinsten Massenteilchen sein werden, lässt sich nicht absehen. Demgegenüber scheint mir die organische Synthese berufen zu sein, das Gegenteil zu leisten, d. h. immer grössere Massen in dem Molekül anzuhäufen, um zu sehen, wie weit die Kompression der Materie im Sinne unserer heutigen Vorstellungen gehen kann.[25]

Although Fischer thought that proteins consist of relatively large molecules or what he called "giant molecules" (Riesenmolekülen), the reported value of the molecular weight for proteins seemed to him too high. He doubted the validity of the conventional method which attacks the problem of protein structure on the basis of molecular weight measurement. Rejecting some reported estimate of a molecular weight of 12,000 to 15,000 for proteins, Fischer claimed in 1907, "nach meiner Meinung beruhen diese Zahlen auf sehr unsicheren Voraussetzungen, da uns jede Garantie dafür fehlt, dass die natürlichen Proteine einheitliche Substanzen sind."[26]

As for crystalline hemoglobin, which on the empirical formula ($C_{712}H_{1130}N_{214}FeO_{215}$) by Oscar Zinoffsky (1848-1889) had a molecular weight of some 16,000, Fischer commented in 1913:

> Allerdings hat man für das Oxyhämoglobin, das bekanntlich hübsch krystallisiert, aus dem Eisengehalt ein Molekulargewicht bis zu 16000 abgeleitet, aber gegen solche Berechnungen lässt sich immer der Einwand machen, dass die Existenz von Krystallen allein keineswegs die chemische Individualität garantiert, sondern dass es sich auch um isomorphe Mischungen handeln kann, wie sie uns das Mineralreich in den Silicaten so mannigfach darbietet. Solche Bedenken fallen weg bei den synthetischen Produkten, deren Bildung durch Analogiereaktionen kontrolliert werden kann.[27]

Fischer urged that proteins are not composed of polymeric molecules consisting of regularly recurrent groups, but, unlike other colloidal substances, the molecules are made up of many different units, i.e., different kinds of amino acids. As he stated, "die Natur niemals lange ketten aus den gleichen Aminosäuren hervorbringt, sondern die gemischten Formen bevorzugt, bei denen die Aminosäuren von Glied zu Glied wechsein."[28] In Fischer's view, proteins are composed of "polypeptides" in which many different amino acids are linked together. His study of proteins was therefore directed to the synthesis of various polypeptide chains. In working on the constitution of polypeptides, the structural chemist Fischer made use of the Berzelian concept of isomerism; that is, that compounds of the same composition having the same molecular weight can exhibit different properties in accordance with their structural difference. A polypeptide is made up of up to thirty different amino acids. The number of possible isomers of a polypeptide chain consisting of the thirty different units was in his estimate 2.653×10^{32}.[29] The large number of possible isomers, he thought, would suffice to explain the wide variation in the properties of natural proteins. Hence, there is no need

to assume the existence of very large natural polypeptides!

Fischer admitted a molecular weight of 4021 for a starch derivative ($C_{22}H_{14}O_{58}N_4I_2$) which he and his student Karl Freudenburg (b. 1886) synthesized. At the Vienna meeting of the Naturforscher-Versammlung, held in 1913, he declared that this value of 4021 was the highest molecular weight found for any organic substance of known structure derived wholly by synthesis and for natural proteins.[30] Fischer's authority made very influential among organic chemists the claim that compounds of a molecular weight greater than 5000 do not exist. Thus, the concept of the very large molecule became superfluous within the tradition that emphasized the structure of organic molecules.[31]

In addition, the theory of large molecules was apparently made even more untenable to scientists as a consequence of the so-called aggregate theory of colloidal substances, to which we shall now turn. It is not surprising that some of the leading chemists who adopted and developed this theory were Fischer's students at the University of Berlin. A traditional Kekuléan structual chemist, Fischer placed the upper limit in the size of the Riesenmolekülen by stressing isomers, and thus paved the way toward the rise of the aggregate theory.

The Rise of the Aggregate Theory

The aggregate theory arose in the first decade of this century and soon became predominant in the study of the nature and structure of colloidal substances. According to this theory, colloidal substances, such as cellulose, rubber, starch, proteins, and resins, are the physical aggregates of small molecules held together by some intermolecular forces.[32]

There were two important elements in the development of the aggregate theory: first, the colloid doctrine, developed in the early part of the twentieth century; and second, the concept of "secondary" or "partial" valence force, introduced around 1900.

Graham's concept of colloids was altered and enlarged in the extensive study of colloidal systems by Wolfgang Ostwald (1883-1943) at Leipzig. His approach to colloids no doubt exhibited a character of the physicialist programme promoted by his father, Wilhelm Friedrich Ostwald (1840-1889), a notable physical chemist. A growing scientific discipline, physical chemistry--or "general chemistry" (allegemeine Chemie) as Wilhelm Ostwald called it--aimed at investigations of the physical nature and behavior of chemical compounds by applying the methods and theories of physics, such as kinetics and thermodynamics, to chemical phenomena. According to Wilhelm Ostwald, the current organic-structural approach is too descriptive and static to explain dynamic chemical processes and systems. He was the first to emphasize the little-known publications of Josiah Willard Gibbs (1839-1903) and the values of the phase rule and thermodynamics. Thus, he exerted a powerful influence in redirecting chemists' attention toward his physicalist scheme that interpreted chemical phenomena in terms of matter, forces, and energy.[33] In fact, Wilhelm Ostwald himself stressed colloid studies as one of the most important new fields to be explored by physical chemists. It was his son Wolfgang who practically cultivated this area with Wilhelm's ideals.

The founder of the Kolloid Gesellschaft (1922-), and editor of the two leading German journals in this field, Zeitschrift für Chemie und Industrie der Kolloide (founded in 1907) and Kolloidchemische Berichte

(founded in 1909), Wolfgang Ostwald was responsible for the foundation of colloid chemistry as "an independent division of physico-chemical science."[34] As he declared in 1914,

> Physics has until recently busied itself chiefly with the properties of matter in mass; chemistry, on the other hand, has dealt chiefly with the smallest particles of matter such as atoms and molecules. Relatively speaking, we know much of the properties of large masses and we talk much, also, of the properties of molecules and atoms. It is because of this that we have been led to regard everything about us from the standpoint of physical theory or from that of molecular or atomic theory. We have entirely overlooked the fact that between matter in mass and matter in molecular form there exists a realm in which a whole world of remarkable phenomena occur, governed neither by the laws controlling the behavior of matter in mass nor yet those which govern materials possessed of molecular dimensions. . . . We have only recently come to learn that every structure assumes special properties and a special behavior when its particles are so small that they can no longer be recognized microscopically while they are still too large to be called molecules. Only now has the true significance of this region of the colloid dimensions--THE WORLD OF NEGLECTED DIMENSIONS--become manifest to us.[35]

Ostwald defined colloids as dispersed systems consisting of particles of a size ranging between 1/10,000 and 1/1,000,000 millimeters.[36] These dispersed particles, he thought, are not themselves molecules but rather their aggregates. Unlike Graham and structural chemists such as Fischer, he rejected the molecular-structural approach to colloids, insisting that there exists "no definite connection between chemical constitution and a colloid state."[37] A colloid is a physical state of matter into which any substance might be brought; under appropriate conditions any compound can form a colloidal solution. At this point, he rather forcibly extended Graham's belief in the unity of matter. The properties of colloids, Ostwald therefore suggested, are determined not by the molecular structure but by the degree of dispersion.[38] For Wolfgang Ostwald and the adherents of this school, the ordinary laws of chemistry, including Raoult's laws of boiling point depression and van't Hoff's laws of osmotic pressure,

are not applicable to colloidal substances, since a colloidal solution is not a real chemical solution but a suspension. Hence, the molecular weights for colloids, measured on the basis of such chemical laws, do not show the real values for their organic molecules. Thus, the Ostwaldian doctrine of colloids provided a ground for the view of the physical aggregates of colloidal substances.

The concepts of "secondary valence" and "partial valence" also played an important role in the rise of the aggregate theory. In the 1890s some chemists reconsidered the nature of Kekulé's valence force, as they examined the structures of inorganic compounds and the nature of some unusual properties of various organic compounds. In 1891, attacking Kekulé's concept of rigidly directed valences, the inorganic chemist Alfred Werner (1866-1919), Professor of Chemistry at Zürich, considered chemical affinity as an attractive force from the center of an atom, acting equally in all directions.[39] In 1902 he introduced the concept of "secondary valence" (Nebenvalenz), as distinguished from Kekulé's valence or what Werner called "primary valence" (Hauptvalenz). The secondary valence, he suggested, is the residual affinity left in the atom after the formation of the primary-valence bondings in the molecule. In his view, such residual forces are strong enough to hold several molecules together to form "molecular compounds" (Molekülarverbindungen).[40] A similar concept can be seen in the notion of "partial valence" (Partialvalenz) which Friedrich Karl Johannes Thiele (1865-1918) introduced in 1899 to explain the unusual reactivity of aliphatic compounds. He stated:

> Ich nehme nun an, dass bei der Körpern, welchen eine Doppelbindung zugeschrieben wird, thatsächlich zwei Affinitäten von jedem der betheiligten Atome zur Bindung derselben verwendet werden, dass aber--

> wegen der Additionsfähigkeit der Doppelbindungen--die Affinitätskraft nicht völlig verbraucht ist und an jedem der Atome noch ein Affinitätsrest oder ein Partialvalenz vorhanden ist, eine Annahme, die sich auch thermisch begrunden lässt.
>
> In der Formel könnte man das ausdrücken
>
> C=C C=O C=N N=N u.s.w.,
>
> Wo das Zeichen . . . die Partialvalenz andenten soll. In den Partialvalenzen sehe ich die Ursache der Additionsfähigkeit.[41]

What the theories of Werner and Thiele suggested to their contemporaries was that there are secondary forces other than Kekulé's valence forces, and that these affinities can act as intermolecular forces. Thiele in particular attributed the origins of the secondary forces to the double bonds in the molecule. The concept of secondary or partial valence was soon adapted by the exponent of the aggregate view to explain the association of molecules in the colloidal particles.[42]

Between 1900 and the 1920s the aggregate structure was proposed by Carl Dietrich Harries (1866-1923) and Rudolf Pummerer (1882-1973) for rubber, by Kurt Hess (1888-1961) and Paul Karrer (1889-1971) for cellulose, by Hans Pringsheim (1876-1940) and Max Bergmann (1886-1944) and Karrer for starch, and by Emil Abderhalden (1857-1938) and Bergmann for proteins.[43] Among these scientists, Harries, Hess, Pringsheim, Bergmann, and Abderhalden were Emil Fischer's students.[44]

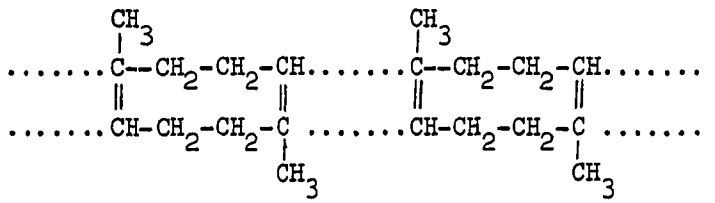
A brief examination of Harries' view of rubber structure illustrates the general grounds of the aggregate theory of polymeric compounds. Since the previous century, natural rubber, an elastic solid obtained from a milklike fluid of certain tropical trees, had aroused the interest of chemists because of its unique properties and practical utility. With

the background of a rapid expansion of the rubber industry in Europe in the early decades of the century, a number of investigators, including John Dalton (1766-1844), Michael Faraday (1791-1867), and Justus von Liebig (1803-1873), worked on the chemical analysis of this organic substance, often with the aid of the destructive distillation through which rubber was broken down into its fractional parts.[45] By Harries' days, it had been found that rubber is made up of only two elements, carbon and hydrogen, the proportions of which are respectively five to eight. Harries thought that this "isoprene" unit or the C_5H_8 unit, which might be a constituent of the rubber molecule, can be expressed by the following structural formula:

$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

isoprene unit

The apparent total absence of end groups in his chemical analysis seemed to preclude the idea of any linear-chain structure and to indicate a ring structure of the rubber molecule. In 1905 he therefore proposed the formula of an eight-membered cyclic molecule (dimethyl-cyclooctadiene), consisting of two isoprene units, for natural rubber. Colloid particles in a rubber solution are, in his opinion, the aggregates or "physical molecules" of the cyclic "chemical molecules" held together by Thiele's partial valences. The partial valence forces are derived from the carbon-carbon double bonds in the "chemical molecules."[46]



dimethyl-cyclooctadiene
consisting of 2 isoprene units

Although Harries later made minor alterations in the size of his ring formula, he maintained throughout the course of his investigations his initial idea of cyclic structure for rubber and the existence of the aggregate forces holding together the ring molecules.[47]

The rise of the aggregate theory affected the usage of terminology among chemists of the time. On the synthetic side, the word "polymerization" was used as a synonym for molecular aggregation. Thus, referring to the polymerization process of ketenes, Georg Schroeter (1869-1943), Professor of Chemistry at the Tierärztlichen Hochschule in Berlin, stated in 1916:

> Es ist aber m. E. die andere Auffassung der Molekülaggregate nicht aufzugeben, dass die einfachen Moleküle in Komplexen ihre Selbständigkeit nicht verlieren, sondern dass die Moleküle als Resultante aller in ihrem Atomverbande chemisch wirksamen Kräfte Kraftlinien aussenden, deren Wirkung den Valenzen der Atome als Molekularvalenzen selbständig an die Seite gestellt werden können; diese Molekularvalenzen vermitteln die Vereinigung der einzelnen Moleküle eines polymeren Moleküls oder Polymoleküls.[48]

Likewise, "molecular weight" referred to the weight of the physical aggregate or a colloidal particle. Thus, the apparent high molecular weights of polymers were generally not taken literally as the weights of the real chemical molecules. In this sense, Bergmann called colloidal substances "pseudo-high molecular substances" (Pseudo-hochmolekulare Stoffe).

Although Bergmann was a student of Emil Fischer at the University of Berlin, he became a supporter of the aggregate theory in taking over Fischer's research on carbohydrates and proteins.[49] In 1926 he insisted that the classical structural theory is not suitable to the study of pseudo-high molecular substances, since the structural theory is based on Avogadro's molecule in gaseous phase and the structural formula in this theory thus gives little information about variations that the molecule undertakes in solidification, liquefaction, and solution processes.[50] The cause of colloidal properties, he said, lies largely in the magnitude of the aggregating forces--a factor to which the classical structural theory cannot be applied. He concluded:

> Darum ist das, was der Chemie der pseudo-hochmolekularen Stoffe gegenwärtig besonders nottut, die Entwicklung einer Struktur- und einer Raumchemie, deren Gegenstand ausserhalb des Moleküls, ausserhalb der Individualgruppe liegt--eine Strukturchemie, eine Raumchemie der aggregierenden Kräfte und der Aggregate.[51]

In this way, Bergmann departed from the traditional structural approach on which Fischer based his study.

The aggregate theory gained further support from X-ray crystallography in the 1920s when X-ray diffraction was employed to examine the structure of polymers. This type of research was carried out intensively at the Kaiser Wilhelm-Institut für Faserstoffchemie, founded in 1920 in Berlin-Dahlem, where Reginald Oliver Herzog (1878-1935) directed a number of physicists and physical chemists, including Michael Polanyi (1891-1976), Karl Weissenberg (1893-1976), Erich Schmid (b. 1880), Rudolf Brill (1899-), and Herman Francis Mark (1985-).[52] Rubber (when stretched) and a part of cellulose were then known to exhibit a crystalline form to which X-ray analysis was applicable. Their study of these polymers

showed that the unit cells--the recurring atomic groups in the crystalline lattice--are as small as the size of ordinary molecules. During this period, many crystallographers assumed that the molecule could not be larger than the unit cells. From this, some scientists, including Herzog, concluded that the molecular size of the polymers is likewise small.[53] To the exponents of the aggregate theory, this appeared as clear-cut empirical evidence for their view of the aggregate structure of polymeric substances.

As we see, the aggregate theory was largely formulated within the physicalist programme which stressed the colloidal state of matter and interacting forces. It compelled alterations in the classical concept of polymers and polymerization as well as in the organic-structural approach that had enjoyed its strong hold in the previous century. Theoretically and experimentally supported, the aggregate theory as a unitary theory of polymers convinced not only colloid chemists and physical chemists, but also the majority of organic chemists of the time, as illustrated by the cases of Harries and Bergmann. These organic chemists were indeed leading exponents of the theory toward the mid-1920s. The aggregate structure of colloidal substances was now overwhelmingly accepted in scientific circles. Hermann Staudinger introduced his macromolecular theory in this historical context, amidst the continued growth of the aggregate theory. It is therefore understandable that his macromolecular concept was at first rejected as laughable by many of his colleagues.

NOTES

[1]Jöns Jacob Berzelius, Jahres-Bericht über die Fortschritte der physischen Wissenschaften von Jacob Berzelius, trans. F. Wöhler, 12 (1833), p. 64. Cf., ibid., 11 (1832), p. 44.

[2]Henry Watts, A Dictionary of Chemistry and Applied Branches of Other Sciences, 5 vols. (London: Longmans, Green and Co., 1863-1868), vol. 4 (1866), s.v. "Polymerism."

[3]Leopold Gmelin, Hand-Book of Chemistry, 14 vols., trans. Henry Watts (London: Cavendish Society, 1848-1860), vol. VII: Organic Chemistry, 1 (1852), pp. 67-69.

[4]Thomas Graham, "Liquid Diffusion Applied to Analysis," Phil. Trans., 151 (1861): 183-224, on p. 183.

[5]Ibid., p. 220.

[6]Ibid., p. 221.

[7]Ibid., p. 223.

[8]On the Karlsruhe Congress in 1860, see, e.g., Clara de Milt, "Carl Weltzein and the Congress at Karlsruhe," Chymia, 1 (1948): 153-169.

[9]August Kekulé, "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," Annalen, 106 (1858): 129-159.

[10]"The separate atoms of a molecule are not connected all with all, or all with one, but, on the contrary, each one is connected only with one or a few neighbouring atoms, just as in a chain link is connected with link." August Kekulé, "Die wissenschaftlichen Ziele und Leistungen der Chemie" (Address delivered on assuming the Rectorate of the Rhenish Friedrich-Wilhelms University of Bonn, October 18, 1877), in August Kekulé, ed. Richard Anschütz, vol. 2: Abhandlungen, Berichte, Kritiken, Artikel, Reden (Berlin: Verlag Chemie GmbH, 1929): 903-917, on p. 911; trans. in "The Scientific Aims and Achievements of Chemistry," Nature, 18 (1878): 210-213, on p. 212.

[11]This is not the place to discuss the priority problem of the organic structural theory; it is still controversial among historians.

See e.g., A. J. Rocke, "Kekulé, Butlerov, and the Historiography of the Theory of Chemical Structure," British Journal for the History of Science, 14 (1981): 27-57.

[12]". . . a considerably large number of single molecules may, through polyvalent atoms, combine to net-like, and if we like to say so, sponge-like masses, in order thus to produce those molecular masses which resist diffusion, and which, according to Graham's proposition, are called colloidal ones." Kekulé, "Die wissenschaftlichen Ziele," in Anschütz, August Kekulé, pp. 912-913; Nature, p. 212.

[13]Eduard F. W. Pflüger, "Ueber die physiologische Verbrennung in den lebendigen Organismen," Pflüger's Archiv für die gesamte Physiologie des Menschen und der Tiere, 10 (1875): 251-367.

[14]"To follow such speculations any further at present would, however, be equivalent to leaving the basis of facts rather too far behind us." Kekulé, "Die wissenschaftlichen Ziele," in Anschütz, August Kekulé, p. 913; Nature, p. 212.

[15]Marcellin P. E. Berthelot, "Sur les caractères de la benzine et du styrolène, camparés avec ceux des autres d'hydrogène," Bull. Soc. chim., 6 (1866): 289-296, especially pp. 294-296; "Sur la présence du styrolène dans les huiles de goudron de huille," ibid., 296-298.

[16]Cf. A. F. Holleman, A Textbook of Organic Chemistry, 4th English ed., ed. Owen E. Mott (New York: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd., 1915), p. 139. Holleman's textbook defined polymerization as follows,"The union of two or more molecules of a substance to form a body from which the original compound can be regenerated is called 'polymerization'." On the history of synthetic polymer studies during this period, see Paul Flory, Principles of Polymer Chemistry (Ithaca, New York: Cornell University Press, 1953), pp. 12-21.

[17]François-Marie Raoult, "Loi générale de congélation des dissolvants," Compt. rend., 95 (1882): 1030-1033; "Loi générale des tensions de vapeur des dissolvants," ibid., 104 (1887): 1430-1433.

[18]Horace T. Brown and G. Harris Morris, "The Determination of the Molecular Weights of the Carbohydrates," J. Chem. Soc., 53 (1888): 610-621, on pp. 620-621.

[19]Horace T. Brown and G. Harris Morris, "The Determination of the Molecular Weights of the Carbohydrates. Part II," ibid., 55 (1889): 462-474, on p. 473.

[20]J. H. Gladstone and Walter Hibbert, "On the Molecular Weight of Caoutchoc and other Colloid Bodies," Phil. Mag., ser. 5, 28 (1889): 38-42, on pp. 39 and 42; "Molecular Weight of Caoutchoc and other Colloid Substances," J. Chem. Soc., Abstracts, 56 (1889), p. 1207.

[21]J. H. van't Hoff, "Die Rolle des osmotischen Druckes in der

Analogie zwischen Lösungen und Gasen," Z. physik. Chem., 1 (1887): 481-508; "The Function of Osmotic Pressure in the Analogy between Solutions and Gases," Phil. Mag., ser. 5, 26 (1888): 81-105.

[22]H. Rodewald and A. Kattein, "Über natürliche und künstliche Starkekörper," Z. physik. Chem., 33 (1900): 579-592, on p. 588 ff.

[23]E.g., Oscar Zinoffsky, "Ueber die Grössedes Hämoglobinmoleküls," Z. physiol. Chem., 10 (1886): 16-34; A. P. Sabanijeff and N. A. Alexandrov, "Cryoscopic Investigations of Colloids . . . III. On the Molecular Weight of Egg Albumin," J. Russ. Phys. Chem. Soc., 23 (1891): 7-9 (in Russian); C. J. Linter and G. Düll, "Ueber den Abbau der Stärke unter dem Einflusse der Diastasewirkung," Ber., 26 (1893): 2533-2547; A.Nastukoff, "Ueber einige Oxycellulosen und über das Molekulargewicht der Cellulose," ibid., 33 (1900): 2237-2243. Cf., C. E. Linebarger, "On the Nature of Colloid Solutions," Amer. J. Sci., 43 (1892): 218-223; "The Molecular Masses of Dextrine and Gum Arabic as determined by their Osmotic Pressures," ibid.: 426-428; and J. Duclaux, "Pression osmotique des solutions colloidalles," Compt. rend., 140 (1905): 1544-1547.

[24]On Emil Fischer's scientific career, see Martin Onslow Forster, "Emil Fischer Memorial Lecture," J. Chem. Soc., 117 (1920): 1157-1201; Max Bergmann, "Emil Fishcer," in Das Buch der grossen Chemikar, ed. G. Bugge, vol. 2 (Berlin: Verlag Chemie G.m.b., 1930): 1157-1201; Burckhardt Helferich, "Emil Fischer," in Great Chemists; ed. Eduard Farber, trans. R. E. Oesper (New York: Interscience, 1961): 983-995; and Dictionary of Scientific Biography, 5(1972), s.v."Fischer, Emil Hermann," by E. Farber.

[25]"Molecular physics would do well in the study of high molecular substances to confine itself to the synthetic products of known structure. I will continue the experiments on the building up of giant molecules (Riesenmolekülen) with the aid of the processes described.

"Certainly it offers in other respects a great incentive to test the productiveness of our methods. As is well known, modern physics is endeavoring to split up matter into smaller and smaller pieces. One is long since past the atom, and how long the electrons will be for us the smallest particles of matter, cannot be predicted. It seems to me that organic synthesis is called upon to accomplish the converse, i.e., to accumulate larger and larger masses in the molecule, in order to see how far the compression of matter can go, in the meaning of our present conceptions." Emil Fischer, "Synthese von Depsiden, Flechtenstoffen und Gerbstoffen," Ber., 46 (1913): 3253-3289, on pp. 3288-3289.

[26]"In my opinion these numbers are based on very uncertain assumptions since we do not have any guarantee that the natural proteins are homogeneous substances." Emil Fischer, "Synthese von Polypeptiden, XVII," ibid., 40 (1907): 1754-1767, on pp. 1757-1758.

[27]"For the beautifully crystalline oxyhemoglobin, as is well known, a molecular weight of 16,000 has been derived from its iron content, but against such calculation the objection can always be made, that

the existence of crystals in no way guarantees chemical individuality, particularly since it can be regarded as an isomorphous mixture, such as the mineral kingdom so often presents to us in the silicates. Such objections vanish with synthetic products, whose formation can be controlled by analogous reactions." Fischer, "Synthese von Depsiden," p. 3288.

[28]"Nature never creates long chains of the same amino acids, but favors the mixed forms in which amino acids change from member to member." Emil Fischer, "Proteine und Polypeptide," Z. angew. Chem., 20 (1907): 913-917, on p. 916; Emil Fischer, "Proteins and Polypeptides," Source Book in Chemistry, 1900-1950, trans. and ed. Henry M. Leicester (Cambridge, Massachusetts: Harvard University Press, 1968), 269-276, on p. 275.

[29]Emil Fischer, "Isomeries der Polypeptide," Sitzungsber. Preuss. Akad. Wiss. Berlin, Halbbd. 2 (1916): 990-1008; Emil Fischer, Emil Fischer gesammelte Werke: Untersuchungen über Aminosäuren, Polypeptide und Proteine II. ed. Max Bergmann (Berlin: Verlag von Julius Springer, 1923): 22-42, on p. 24 ff.

[30]Fischer, "Synthese von Depsiden," p. 3288. See also Emil Fischer, "Über das Tannin und Synthese ähnlicher Stoffe. III. Hochmolekulare Verbindungen," Ber., 46 (1913): 1116-1138, on pp. 1119-1120.

[31]It may be also noted here that some physicists and physical chemists expressed doubts about the possibility of large molecules from a different standpoint that if a molecule were very large and complex, containing several thousand atoms, it would be too unstable and fragile to exist. As the French physical chemist Jean Baptiste Perrin (1870-1942) stated in 1913,

> On conçoit d'ailleurs que des molécules très compliquées puissent être plus fragiles que les molécules faites de peu d'atomes, par suite puissent avoir moins de chances de se présenter à l'observation. On conçoit aussi que si une molécule est enorme (albumines?) l'entrée ou la sortie de peu d'atomes ne modifie pas énormément ses propriétés et que la séparation de corps purs correspondant à des molécules somme toute peu differentes puisse devenir inextricable. Et cela encore accroît les chances pour qu'un corps pur facile à préparer soit fait de molécules formées de peu d'atomes.
>
> (We would expect, moreover, that very complicated molecules would be more fragile than molecules composed of few atoms and that they would therefore have fewer chances of coming under observation. We should also expect that if a molecule were very large (albumins?) the entry or exit of a few atoms would not greatly affect its properties and, moreover, that the separation of a pure substance corresponding to such molecules would present no little difficulty, even if its isolation did not become impossible. And this would still further increase the probability that a pure substance easy to prepare would be composed of molecules containing few atoms).

Jean B. Perrin, Les Atomes (Paris: Librairie Felix Alcan, 1913), p. 16, n. 1; Atoms, trans. D. LL. Hammik (London: Constable and Company Ltd., 1916), p. 11, n. 1. On Perrin's work, see Mary Jo Nye, Molecular Reality: A Perspective on the Scientific Work of Jean Perrin (London: MacDonald; New York: Elsevier, 1972).

[32]The aggregate theory was also sometimes called "association theory" by some chemists.

[33]John W. Servos has given a fine account of Wilhelm Ostwald's view of allgemeine Chemie in his "Physical Chemistry in America, 1890-1933: Origins, Growth, and Definition" (Ph.D. dissertation, Johns Hopkins University, 1979), Ch. I. See also Dictionary of Scientific Biography, vol. 15, Supp. I (1978), s.v. "Ostwald, Friedrich Wilhelm," by Erwin N. Hiebert and Hans-Günther Körber.

[34]Carl Wilhelm Wolfgang Ostwald, An Introduction to Theoretical and Applied Colloid Chemistry: The World of Neglected Dimensions, trans. Martin H. Fischer (New York: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd., 1917), p. 76. This work was based on his series of lectures in America during 1913-1914, and first published in German in 1914: Die Welt der vernachlässigten Dimensionen (Leipzig, 1914). Wolfgang Ostwald's works on colloids also include "Zur Systematik der Kolloide," Z. Chem. Ind. Kolloide, 1 (1907): 291-300, 331-341; Grundriss der Kolloidchemie (Dresden: T. Steinkopff, 1909); and Kleines Praktikum der Kolloidchemie (Dresden and Leipzig: T. Steinkopff, 1920). On Wolfgang Ostwald, see A. Lottermoser, "Wolfgang Ostwald 60 Jahre alt," Kolloid-Z., 103, no. 2 (1943): 89-94; Ernst A. Hauser, "The History of Colloid Science: In Memory of Wolfgang Ostwald," J. Chem. Educ., 32 (1955): 2-9, especially on pp. 1-2; and Dictionary of Scientific Biography, vol. 10 (1975), s.v. "Ostwald, Carl Wilhelm Wolfgang," by Hans-Günther Körber.

[35]Wolfgang Ostwald, Introduction, pp. 218-219.

[36]Ibid., p. 34.

[37]Ibid., p. 6.

[38]Ibid., p. 76.

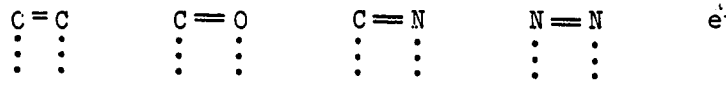
[39]Alfred Werner, "Beiträge zur Theorie der Affinität und Valenz: Über Stereochemie des Stickstoffs in der Benzhydroxamsäureihe," Vierteljahrsschrift der Züricher Naturforschenden Gesellschaft, 36 (1891): 129-169; Alfred Werner, "Contributions to the Theory of Affinity and Valence," trans. George B. Kauffman, Chymia, 12 (1967): 189-216. See also George B. Kauffman, "Alfred Werner's Habilitationsschrift," ibid.: 183-187.

[40]Alfred Werner, "Ueber Haupt- und Nebenvalenzen und die Constitution der Ammoniumverbindungen," Liebigs Ann. Chem., 322 (1902): 261-296, especially p. 268 ff. Werner distinguished the molecular compounds from "valence compounds" (Valenzverbindungen) or ordinary compounds which are constituted by Kekulé's primary valence bonds. See also C. A. Russell, The History of Valency (Leicester: Leicester University Press, 1971),

pp. 213-223.

[41]"I now assume that in bodies to which a double bond is assigned, actually two affinities of each of the participating atoms are used for binding themselves, but that--owing to the additive power of the double bond--the strength of the affinity is not fully used, and on each atom there is still an affinity residue, or a partial valence, an assumption which can also be based on thermal grounds.

"In formulas this can be expressed



where the sign ··· signifies the partial valence. In the partial valence I see the origin of the additive power." Johannes Thiele, "Zur Kenntnis der ungesättigten Verbindungen," Leibigs Ann. Chem., 306 (1899): 87-142, on p. 89; translated in A Source Book in Chemistry, 1400-1900 (New York, Toronto, London: McGraw-Hill Book Company, Inc., 1952), ed. Henry M. Leicester and Herbert S. Klickstein, p. 510.

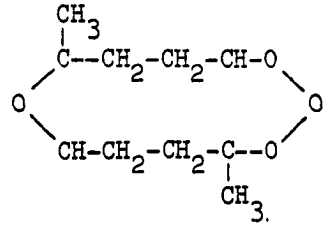
[42]Although Thiele himself did not develop the aggregate theory, he suspected that perhaps in such compounds as polystyrene the molecules of styrol are bound together by partial valences. Thiele, "Kenntnis," p. 92.

[43]Carl D. Harries, "Zur Kenntniss der Kautschukarten: Ueber Abbau und Constitution des Parakautschuks," Ber., 38 (1905): 1195-1203; Untersuchungen ueber die näturlichen und künstlichen Kautschukarten (Berlin: Verlag von Justus Springer, 1919); Rudolf Pummerer and Peter A. Burkard, "Über Kautschuk," Ber.,55 (1922):3458-3472; Rudolf Pummerer, Hilde Nielsen, and Wolfgang Gündel, "Kryoskopische Molekulargewichts-Bestimmungen des Kautschuks," ibid.,60 (1927):2167-2175; Rudorf Pummerer and Albert Koch, "Über einen Krystallisierten Kautschuk und über Hydro-Kautschuk," Liebigs Ann. Chem., 438 (1924): 294-313; Rudorf Pummerer and Wolfgang Gündel, "Über Darstellung und Molekulargrösse des Isokautschuk-nitrons," Ber., 61 (1928): 1591-1596; Kurt Hess, "Über Cellulose," Liebigs Ann. Chem., 435 (1924): 1-114; Kurt Hess, Die Chemie der Zellulose und ihrer Begleiter (Leibzig: Akademische Verlagsgesellschaft m.b.h., 1928); Paul Karrer, "Zur Kenntnis der Polysaccharide I. Methylierung der Stärke," Helv. Chim. Acta,3 (1920):620-625; Paul Karrer, Polymere Kohlenhydrate (Leipzig:Akademische Verlaggesellschaft m.b.H., 1925); Hans Pringsheim, "Über die Chemie Complexer Naturstoffe," Naturwiss., 13 (1925): 1084-1090; "Abbau und Aufbau der Polysaccharide," Ber., 59 (1926): 3008-3018; Max Bergmann, "Über den hochmolekularen Zustand der Proteine und die Synthese protein-ähnlicher Piperazin-Abkömmlinge," Naturwiss., 13 (1925): 1045-1050; Max Bergmann, "Allgemeine Struckturchemie der komplexen Kohlenhydrate und der Proteine," Ber., 59 (1926): 2973-2981; Emil Abderhalden, "Das Eiweiss als sine Zusammenfassung assoziierter, Anhydride anthaltenden Elementarkomplexe," Naturwiss., 12 (1924): 716-720.

[44]Biographies of these scientists are in J. C. Poggendorff, Biographisch-Literisches Handwörterbuch zur Geschichte der exakten Naturwissenschaften (Leipzig: Verlag von Johann Ambrosius Barth; Leipzig and Berlin: Verlag Chemie GmbH; Berlin: Akademie Verlag, 1863-), 7 vols; on Harries, see vol. 4: 587-588 and vol. 5: 500-502; on Hess, vol. 5: 530-531, vol. 6: 1101-1103, and vol. 7: 467-470; on Pringsheim, vol. 5, p. 1006, vol. 6: 2081-2082, and vol. 7, p. 633; on Bergmann, vol. 6: 185-187 and vol. 7, p. 151; and on Abderhalden, vol. 5: 2-3, vol. 6: 2-11, and vol. 7: 1-5.

[45]John Dalton, "Observations on certain Liquids obtained from Caoutchouc by Distillation," Phil. Mag., ser. 3, 9 (1836): 479-483; Michael Faraday, "On Pure Caoutchouc, and the Substances by which it is accompanied in the State of Sap, or Juice," Quart. J. Sci. Arts, 21 (1826): 19-28; and Justus von Liebig, "Bemerkung über die Methoden der Darstellung flüchtiger, durch trockene Destillation organischer Materien erhalten Produkte," Liebigs Ann. Chem., 16 (1835): 61-62. The name "isoprene" was given by Charles Greville Williams (1829-1910) in 1860. C. Greville Williams, "On Isoprene and Coutchine," Phil. Trans., 150 (1860): 241-255, on p. 244. Williams' isoprene formula $C^{10}H^8$ was later altered as C_5H_8. See also M. Gustave Bouchardat, "Sur les produits de la distillation sèche du caoutchouc," Bull. Soc. chim., 24 (1875): 111-114. The early history of rubber-composition studies was briefly outlined in G. S. Whitby and M. Katz, "Synthetic Rubber," Ind. Eng. Chem., 25 (1933): 1204-1211 and 1338-1348, on pp. 1204-1205; and Harry L. Fisher, "The Origin and Development of Synthetic Rubber," Symposium on the Applications of Synthetic Rubbers (Philadelphia: American Society for Testing Materials, 1944): 3-16, on pp. 3-4. But there is no reliable historical study of this subject.

[46]Carl D. Harries, "Zur Kenntniss der Kautschukarten," p. 1196. In order to test his theory, Harries attempted to decompose rubber through a treatment of ozone. The compositior of the ozonized product was, he found, $C_{10}H_{16}O_6$, and its molecular weight seemed in accordance with this empirical formula itself. From this he considered the ozonide's structural formula to be:



This result, Harries thought, demonstrates that the rubber molecule is dimethyl-cyclooctadiene. Harries, ibid., p. 1196. Cf., Carl Harries, "Über den Abbau des Parakautschuks vermittelst Ozon," Ber., 37 (1904): 2708-2715, on p. 2709.

[47]Harries later proposed a larger ring of five isoprene units

(1914), and eventually of seven isoprene units. Carl Harries, "Beiträge zur Kenntnis der Konstitution des Kautschuks und verwandter Verbindungen," Liebigs Ann. Chem., 406 (1914): 173-226; Chem. Abstracts, 16 (1922), 3232; and Harries, Untersuchungen. On the development of Harries' rubber formula, see G. Stafford Whitby, "Recent Work of Harries on Caoutchuc," India-Rubber J., 617 (February 12, 1921): 313-315.

[48]"The concept of molecular aggregates cannot be abandoned, which means that single molecules do not lose their autonomy in a complex. Molecules emit lines of forces as a result of all chemically active forces in their atomic groups. These forces of molecular valences have an independence from the atomic valences. Molecular valences enable single molecules to form a polymer molecule, i.e., a polymolecule." Georg Schroeter, "Über die Beziehungen zwischen den polymeren Ketenen und dem Cyclobutan-1, 3-dion und seinen Derivaten," Ber., 49 (1916): 2697-2745, on p. 2697.

[49]After receiving the Ph.D. in 1911 from the University of Berlin, Bergmann remained there as an assistant to Fischer until Fischer's death in 1919. See, e.g., Dictionary of Scientific Biography, vol. 2 (1970), s.v. "Bergmann, Max," by Joseph S. Fruton. See also references in n. 44.

[50]Bergmann, "Allgemeine Strukturchemie," p. 2973.

[51]"Therefore, what is especially needed at the present time for the chemistry of pseudo-high molecular substances is the development of a structural and spatial chemistry the object of which lies outside the molecule, outside the individual group--a structural chemistry, a spatial chemistry of aggregating forces and of aggregates." Ibid., p. 2981.

[52]For the X-ray research at the Kaiser Wilhelm-Institut für Faserstoffchemie, see Michael Polanyi, "My Time with X-rays and Crystals," in Fifty Years of X-ray Diffraction, ed. P. P. Ewald (Utrecht: International Union of Crystallography, 1962), pp. 629-636; Herman Mark, "Recollections of Dahlem and Ludwigshafen," ibid., pp. 603-607; and Herman Mark, "Polymer Chemistry in Europe and America--How it all Began," J. Chem. Educ., 58 (1981):527-534, on pp. 527-529.

[53]E.g., Reginald O. Herzog and W. Janke, "Röntgenspektrographische Untersuchungen hochmolekularer organischer Verbindungen," Z. angew. Chem., 34 (1921):385-387; and R. O. Herzog, "Zur Erkenntnis der Cellulose-Faser," Ber., 58 (1925):1254-1262. Cf., Michael Polanyi, "Faserstruktur im Röntgenlichte," Naturwiss., 9 (1921):337-340.

CHAPTER II

HERMANN STAUDINGER AND THE EMERGENCE OF THE MACROMOLECULAR THEORY

> Trotz der grossen Zahl von organischen Körpern, die wir heute schon kennen, stehen wir so erst am Anfang der Chemie der eigentlichen organischen Verbindungen und haben nicht etwa einen Abschluss erreicht.
>
> --Hermann Staudinger,
> "Die Chemie der hochmolekularen organischen Stoffe im Sinne der Kekuléschen Strukturlehre,"
> 1926.

> It is no secret that for a long time many colleagues rejected your views which some of them regarded as abderitic. Perhaps this was understandable. In the world of high polymers almost everything was new and untested. Long standing, established concepts had to be revised or new ones created. The development of the macromolecular science does not present a picture of a peaceful idyll.
>
> --A. Fredga,
> Presentation Speech to Staudinger at the Nobel Celebration in Stockholm, December 10, 1953.

> . . . I was most impressed by his [Staudinger's] tremendous enthusiasm and energy and his powerful personality, which, I imagine, would make him a most formidable opponent in any argument.
>
> --C. H. Bamford,
> quoted in V. E. Yarsley,
> "Hermann Staudinger," 1967.

The macromolecular theory was proposed shortly after the First World War by the German chemist, Hermann Staudinger (1881-1965) at the great Technische Hochschule in Zürich. Assuming the existence of macromolecules with

an almost arbitrarily large size, he explained colloidal substances, such as rubber and cellulose, as being formed by these very large-chain molecules. On the one hand, in his approach to polymers, he proved himself to be a staunch disciple of the nineteenth-century chemist Kekulé. A traditional organic chemist, Staudinger belonged to the organic-structural tradition which interpreted properties of matter solely in terms of the structure of organic molecules. In his view, colloidal particles are in many cases themselves giant molecules which are composed of between 10^3 and 10^9 atoms linked together by the "Kekulé" bonds. Macromolecular compounds are thus structured, he claimed, on the same principles as those of classical organic chemistry, namely according to Kekulé's structural theory. In this way, he strongly opposed the predominant physicalist approach to colloids. However, Staudinger was not a defender of the structural tradition of his time. As we have seen, by his time, the Fischer school and Kekulé's German successors had deliberately eliminated the classical concept of big molecules from their structural scheme. Although rooted in the organic-structural tradition, his macromolecular concept departed from this path in some crucial points.

The appearance of Staudinger's theory in the early 1920s soon provoked antipathy among his contemporaries, and he met vigorous opposition from both sides, physicalists and structural organic chemists alike. The stormy controversy over the macromolecle continued for the next fifteen years until his theory began to receive significant acceptance around the mid 1930s. The emergence of the macromolecular concept was indeed an intellectual upheaval in the German scientific community during the Weimar period.

Young Staudinger: Education and Career

Hermann Staudinger was born in Worms, Germany on March 23, 1881.[1] His father, Franz Staudinger (1849-1921), was a teacher at the Gymnasium in Worms. A well-known neo-Kantian philosopher, Franz Staudinger instilled in his son broad interests in culture, history, arts, literature, and science.[2] In Worms Staudinger studied at his father's Gymnasium and completed his qualifying examination (Abitur) in 1899. As a young student, he wished to study botany, a subject which had captured his interest from an early age. He enrolled at the University of Halle to study this field under the botanist Georg Albrecht Klebs (1857-1918). Simultaneously, he started work there on analytical chemistry in the laboratory of Jacob Volhard (1834-1910), since his father was advised that Staudinger should have a thorough training in chemistry in preparation for a future career in botany. Ironically, these "preliminary" studies in chemistry turned out to be the making of his professional career, although his interest in the biological field continued throughout his life. He was always at pains to find and pursue the connections between biology and chemical investigations, as is seen in his later study of macromolecular chemistry. After a brief period at Halle, he completed his first training in analytical chemistry at the Technische Hochschule in Darmstadt. He spent the next two semesters in Adolf von Baeyer's laboratory at the University of Munich, studying organic chemistry under Oskar Piloty (1866-1915), Baeyer's son-in-law.

After returning to Halle in 1901, Staudinger wrote his dissertation on the malonic esters of unsaturated compounds. This work, done

under the direction of Daniel Vörlander (1867-1941), was completed in 1903.[3] He served as assistant (Unterrichtsassistant) to Johannes Thiele in Strassburg in the following four years (1903-1907). During the period between 1901 and 1907, both Vörlander and Thiele gave Staudinger much inspiration in the field of theoretical organic chemistry. As we have seen in Chapter I, Thiele had just proposed his theory of partial valences which appeared to explain the unusual nature of unsaturated organic compounds.[4] Under the direction of Vörlander, Staudinger attempted to test Thiele's theory with respect to addition products of unsaturated malonic esters.[5] As an organic chemist, he was also much concerned with the classical structural theory during this period. For example, as early as 1905, he thought critically about the development of benzene theory from the ideas of Kekulé to the views of his own contemporaries including Baeyer, Thiele, and Vörlander. This review, written in his notebooks, exhibited Staudinger's cautious and critical attitude toward current theories in organic chemistry, a character which he later showed more fully in his study of high-molecular organic substances.[6]

In 1905 Staudinger made his first discovery of highly reactive unsaturated compounds, ketenes, which formed the subject of his Habilitation in the spring of 1907. Appointed associate professor at the Technische Hochschule in Karlsruhe in 1907, he continued his investigations on ketenes, studying the preparation of various ketenes and their reactivity. He, alone and together with his doctoral students, produced 57 papers in this field in the next two decades.[7] His first book Die Ketene (1912), was the fruit of these efforts, a work which won wide readership as a standard textbook on ketene chemistry.[8] During this period,

he also carried out research on aliphatic diazo compounds and oxalyl chrolides,[9] and these studies in Karlsruhe sufficiently won his early reputation as a conventional organic chemist.

In 1912 Staudinger became Professor at the Eidgenössische Technische Hochschule in Zürich, succeeding Richard Willstätter (1873-1942), the future Nobel laureate, who had moved to the newly established Kaiser Wilhelm-Institut für Chemie in Berlin-Dahlem. Staudinger remained there for the next fourteen years until his call to the University of Freiburg im Breisgau in 1926. In Zürich Staudinger's lecture attained popularity among students. According to Willem Quarles' statement, Staudinger's students "all came under the spell of this tall German [about 6 feet 4 inches] who, with his curt nervous gestures and whispering voice, penetrated into the mysteries of the carbon atom and kindled a love for the strange organic world."[10] Another student recalled, "Staudinger as I knew him was what is popularly described as a fine figure of a man. Robust, genial and kindly, I looked on him very much as a father figure . . ."[11] As a researcher, he conducted his work with tremendous enthusiasm; he paid meticulous attention to detail and was a careful planner of his experimental work. At the same time, as one of his contemporaries put it, Staudinger was "not exactly a gentle and compromising protagonist of his work"[12]--a scientific personality which he exhibited in the macromolecular debate during the 1920s and 1930s.

During World War I, when there was a shortage of food in Germany, Staudinger worked on the synthesis of a pepper substitute and on the aroma of roasted coffee. As a structural chemist, he especially investigated the relation between properties of these substances (e.g., the

taste of pepper and coffee flavor) and their chemical constitutions.[13] He also continued his research on ketenes. But it was during this period that he first developed his interest in the study of polymers. Because of his growing interest in this field during the last years of his stay in Zürich (especially between 1920-1926), he set aside his investigations on ketenes and other low-molecular compounds. When he moved to the University of Freiburg in 1926, he virtually discontinued the work of his early research areas and devoted himself to the study of polymers. Perhaps it is not surprising, given the success of his early work in the field of low-molecular chemistry, that his colleagues were skeptical about this change. Staudinger recalled:

> Diejenigen Fachgenossen, denen meine früheren Publikationen auf dem Gebiet der neidermolekularen Chemie bekannt waren, fragten mich, warum ich diese schönen Arbeitsgebiete verlasse und mich mit so unerfreulichen und wenig definierbaren Verbindungen, wie mit Kautschuk und synthetischen Polymeren, beschäftige, deren Verhalten man damals vielfach als Schmierenschemie bezeichnete.[14]

However, it was in this unpleasant field of grease chemistry (Schmierenchemie) that Staudinger brought about an upheaval in modern chemistry and eventually established his reputation as the founder of a new science, macromolecular chemistry. While entering into an entirely new field, it was his background as a classical organic chemist that played an important role in the development of his interests and ideas in this subject, as will be discussed below.

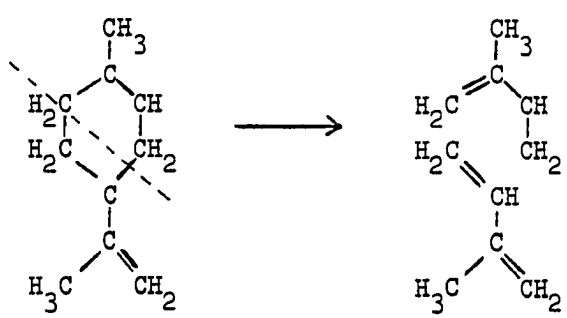
The Origins and Development of Staudinger's Macromolecular Theory

Staudinger began his study of polymers in 1920 at the age of thirty-eight when he was Professor of Chemistry at the Eidgenössische Technische Hochschule in Zürich. In this year he proposed his general

view of the structure of long-chain molecules for polymeric compounds and embarked on a series of investigations on the existence of these giant molecules or macromolecules.[15]

Staudinger had developed some interest in the polymer structure already in the early 1910s when he was investigating ketene compounds. He observed that highly reactive ketenes readily polymerize to four-membered cyclic dimers, derivatives of cyclobutane. Such four-membered ring molecules were easily split by pyrolysis. This observation induced him to examine the pyrolytic decomposition of other ring systems, particularly those of the six-membered rings such as terpenes ($C_{10}H_{16}$). In 1911 Staudinger reported that, among terpenes, limonene and its isomer, dipentene, decompose with very good yield (up to about 70%) into isoprene (C_5H_8), a substance known as the basic unit of natural rubber.[16]

(limonene and dipentene) (isoprene)



Therefore it is understandable that, shortly after this study (probably around 1911), Staudinger performed experiments to polymerize isoprene to polyisoprene, that is, synthetic rubber. However, he found that while synthetic rubber resembled natural rubber, it differed in a number of properties such as colloidal nature. According to Staudinger's recollec-

tions, "Gerade diese Unterschiede in machen Eigenschaften [zwischen synthetischem und näturlichem Kautschuk] regten die Bearbeitung dieses Gebietes, hauptsächlich die Untersuchung der kolloiden Lösungen dieser Stoffe, an."[17] In short, from the work on ketenes originated Staudinger's interest in isoprene and its polymerization, which in turn stimulated his developing interest in rubber structure in the early 1910s.

Staudinger's 1911 paper on isoprene briefly referred without criticism to Carl Dietrich Harries' interpretation of the aggregate structure for rubber.[18] However, we find that six years later, he rejected it and first expressed a view in favor of the long-chain structure for rubber. In a lecture, "Über Isopren und Kautshuk: Kautschuk-Synthese," given in October, 1917, before the 32th general meeting of the Schweizerischen Gesellschaft für chemische Industrie, Staudinger remarked:

> Bei seinen wichtigen Arbeiten über die Einwirkung von Ozon auf organische Substanzen konnte Harries im Jahre 1904/1905 dem Einblick den Weg bahnen, wie sich die Isoprenmoleküle zu dem Kautschuk zusammenlagern. Auf seine anfängliche unrichtige Annahme, dass dem Kautschuk ein Kohlenwasserstoff der Cyclooctadienreihe zugrunde liege, will ich hier nicht näher eingehen. Ich nehme anschliessend an die Arbeiten von Pickles an, dass bei der Kautschukbildung sich die Isoprenmoleküle an den Enden, also in 1-4-Stellung zusammengelagert haben und dass Hunderte von Isoprenmolekülen die grossen Kautschukmoleküle, die durch das Ultramikroskop sichtbar gemacht werden können, und die die kolloidalen Eigenschaften des Kautschuks bedingen, gebildet haben.[19]

It is clear from this statement that he followed the view proposed by the English rubber chemist, Samuel Shrowder Pickles (1878-1962).

A relatively unknown researcher at the Imperial Institute in South Kensington, Pickles had expressed views at variance with Harries' theory at the York meeting of the Chemical Section of the British Association as early as 1906. His discussion at the meeting was not

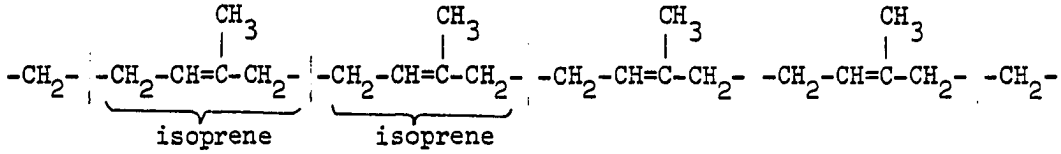
printed and not widely known until his paper, "The Constitution and Synthesis of Caoutchouc," appeared in 1910 in the Journal of the Chemical Society.[20] This paper was primarily directed against Harries' view of rubber structure as the physical aggregates of dimethyl-cyclooctadiene molecules ($C_{10}H_{16}$) consisting of two isoprene units (C_5H_8). According to Pickles, Harries' formula is unsatisfactory, "as its arrangement demands vague and unnecessary conceptions of polymerisation." "The single molecule [dimethyl-cyclooctadiene]," he wrote, "is regarded [by Harries] as the 'chemical' molecule, and the polymerised aggregate as the 'physical' molecule. The extent of polymerisation . . . is undefined." If rubber is aggregates of small molecules held together by loose physical forces, one should obtain these simple molecules by heating or through chemical treatments of rubber, such as the saturation of the double bonds in the molecules. However, Pickles urged, this is contrary to chemical experience. Pointing out that the polymerization of isoprene into rubber is not physical but "strictly chemical," he suggested an alternative view that the isoprene units are united in long chains of the structure:

$$\text{. . . . } CH_2.\overset{\overset{Me}{\cdot}}{C}{:}CH.(CH_2)_2.\overset{\overset{Me}{\cdot}}{C}{:}CH.(CH_2)_2.\overset{\overset{Me}{\cdot}}{C}{:}CH.(CH_2)_2.\overset{\overset{Me}{\cdot}}{C}{:}CH.(CH_2)_2 \text{ . . . .}$$

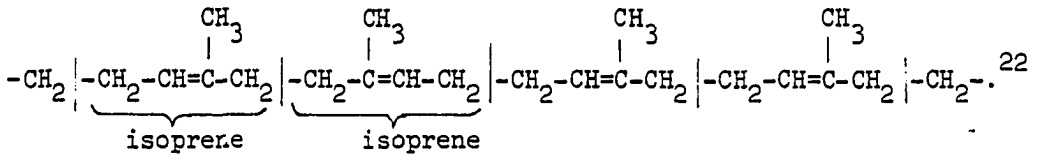
Pickles' formula was, however, not a linear chain structure. As he added, "the two ends of the chain should be linked together, which, of course, leads to the formation of a ring . . . Rubber probably contains at least eight C_5H_8 complexes . . ."[21] Thus, Pickles shared with Harries the idea of ring structure for the rubber molecule; the difference between their opinions apparently lay in the ring size. While soon going into the rubber manufacturing industry as a practical chemist, Pickles did not

pursue further demonstrations on this issue. Nevertheless, his 1910 paper drew particular attention from some of his contemporaries, particularly from Staudinger.

Although Staudinger did not accept Pickles' assumption of the closed chain formula, he did adopt some of the important arguments in Pickles' paper, namely that the polymerization of isoprene is a purely chemical process, and that through this process the isoprene molecules unite to form very long chains. In his 1917 lecture, mentioned above, Staudinger suggested a long chain formula in which hundreds of isoprene units build up the large molecules of natural rubber:



He proposed a similar but slightly different structure for the synthetic rubber prepared from isoprene:



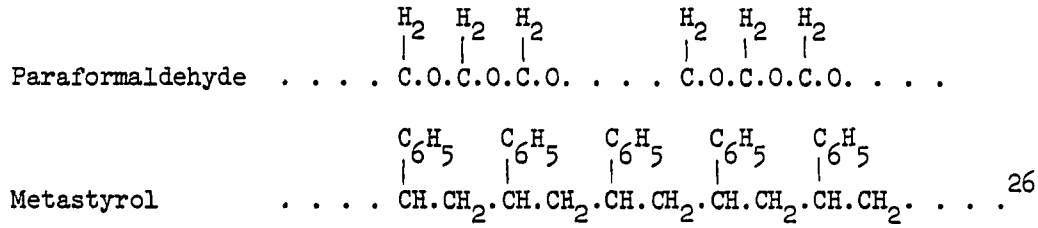
Unlike natural rubber, in the formation of synthetic rubber, the isoprene units are thus not arranged side by side regularly. For this reason, synthetic rubber, he thought, exhibits properties different from those of natural rubber. As we can see, Staudinger's view of rubber was based wholly upon Kekulé's classical structural theory according to which the properties of compounds depend on the arrangement of atoms in the molecule.

By 1920 Staudinger extended his idea of long-chain structure of

rubber to the general theory of polymer structure. This year he published his landmark paper, "Über Polymerisation," in the Berichte der deutschen chemischen Gesellschaft.[23] In this paper he suggested that the polymerization products can be explained satisfactorily by normal or Kekulé valences. He did not think it necessary to assume that the molecular compounds are held together by secondary-valence forces:

> Und doch glaube ich, dass nach dem vorliegenden Beobachtungsmaterial solche Annahmen [von Molekülverbindungen, die durch Nabenvalenzen zusammengehalten werden] zur Erklärung des Enstehens der Polymerisationsprodukte nicht gemacht zu werden brauchen; vielmehr können die verschiedenartigsten Polymerisationprodukte, wie ich im Folgenden zeigen möchte, durch normale Valenzformeln eine genügende Erklärung finden; und gerade in der organischen Chemie wird man so lange wie möglich sich bemühen, die Eigenschaften der Verbindungen durch Formeln mit Normalvalenzen wiederzugeben.[24]

Maintaining the Berzelian definition of polymerism, Staudinger asserted that polymerization is a chemical reaction in which two or more molecules combine into a product of the same composition, but with a higher molecular weight.[25] In this way, he gave long-chain formulas for such polymerization products as paraformaldehyde (polyoxymethylene) and metastyrol (polystyrene) as well as rubber:



[26]

The colloidal properties of these substances were attributed entirely to the sizes of their primary valence molecules, which he guessed might contain on the order of a hundred units. In contrast to the ring structure which formed the basic conception of the aggregate theory, Staudinger's chain formulas appeared to contain the problem that there might exist

unsaturated atomic groups at the ends of the long chain. Yet he simply suggested that those free valences at the ends of very long chains would be unreactive owing to the size of the molecule:

> Nehmen wir z. B. hunderte von Molekülen Formaldehyd, so haben wir im unpolymerisierten Zustand zweimal hunderte reaktionsfähige Atome. Nehemen wir an, dass diese hunderte von Molekülen sich zu einem Paraformaldehyd-Molekül polymerisiert haben, so haben wir dort nur zwei ungesättigte Stellen, die Reaktions-fähigkeit ist also mehrhundertfach geringer. Dies stimmt mit der Beobachtung überein, dass die hochmolekularen Verbindungen weit weniger reaktionfähig sind als die monomolekülaren Ausgangsprodukte, dass sie aber noch zum Teil die Reaktionen der monomolekülaren Körper zeigen.[27]

Staudinger's 1920 paper did not carry any substantial experimental support for his concept of long-chain molecules of polymeric compounds. Unlike earlier exponents of the idea of large molecules (such as Horace T. Brown and John H. Gladstone),[28] he did not use the data of the molecular weights of colloids as evidence. At this stage, he rather pointed out the technical difficulties in measuring the molecular weight of these substances.[29] It was not until two years afterwards that he proposed what he called "the first evidence for the existence of macromolecules" (erste Beweise für die Existenz von Makromolekülen).[30] Perhaps, as his contemporary Herman Francis Mark later stated, Staudinger "had postulated intuitively" an idea of long-chain molecules before developing his evidence.[31] The idea occurred to Staudinger first, and its experimental evidence or justification came later. Yet, as we have seen in his 1917 lecture and 1920 paper, his "intuitive postulate" was conceptually grounded on his firm belief in the classical structural approach, as opposed to the prevailing physicalist views of polymers.

Staudinger's evidence in 1922 was based on an experiment on the

hydrogenation of rubber which he carried out with his student, Jakob Fritschi. As mentioned earlier, Carl D. Harries had concluded that colloidal particles in a rubber solution are aggregates of relatively small molecules of ring structure. The partial valences holding these molecules together, Harries thought, are generated from the unsaturated double bonds of the molecules. Harries' theory predicted that hydrogenation of rubber should yield a normal low molecular substance, because saturation would occur and destroy the partial valences between the molecules. In their experiment, however, Staudinger and Fritschi obtained a contradictory result. The properties of the saturated hydrorubber, they found, were quite similar to those of natural rubber; it did not crystallize but gave a colloidal solution like rubber. Thus, they concluded that colloidal particles of rubber are not the aggregates of small molecules held together by partial valences, but are instead giant molecules. They now used the term Makromoleküle to designate such molecules for the first time.[32] In 1924 Staudinger defined macromolecule in organic-structural terms as follows:

> Für solche Kolloidteilchen, bei denen das Molekül mit den Primärteilchen identisch ist, bei dem also die einzelnen Atome des Kolloidmoleküls durchnormale Valenzbetätigung gebunden sind, schlagen wir zum Unterschied die Bezeichnung Makromolekül vor. Derart konstituierte Kolloidteilchen, die entsprechend der Bindfähigkeit des Kohlenstoffs vor allem in der organischen Chemie und in der organischen Natur auftreten, bilden die eigentlichen kolloiden Stoffe. Hier sind die Kolloid-Eigenschaften eben durch den Bau und die Grosse des Moleküls bedingt . . .[33]

He stressed that Thomas Graham, the founder of colloid chemistry, had suspected that the colloidal nature is determined by the chemical structure of the substance. Colloidal particles, Staudinger claimed, are themselves giant organic molecules.[34] Hence, according to him, the

interpretation of colloidal phenomena should be based on the principles of organic chemistry rather than the doctrine which explained colloidal phenomena in physico-chemical terms, the aggregation forces and the unity of matter. Staudinger thus reinterpreted Wolfgang Ostwald's realm of colloidal dimensions by considering it to be a field within organic chemistry.

Through the 1920s Staudinger continued to investigate synthetic polymers as model substances which he boldly thought would serve to explain the structure and behavior of the more complex natural polymers. For example, the insoluble polymeride, polyoxymethylene, was used as a model for cellulose, and polystyrene for rubber. He prepared various degrees of these synthetic polymers from simple compounds and showed that physical properties, such as the viscosity of their solutions, correlate with the degree of polymerization--a characteristic shared with the homologous series of ordinary paraffin hydrocarbons. This result seemed to him to support his view of the macromolecular structure of colloidal substances.[35] He also subjected these polymerization products to chemical reactions, such as hydrogenation, methylation, and nitration, but he found that the degree of polymerization was not affected. In other words, the polymers were converted into their derivatives without their sizes being changed. The method whereby such conversions are made, later called "polymer analogous reaction," acquired growing significance for Staudinger as a demonstration of macromolecularity.

> Der entscheidence Beweis für die Existenz der Makromoleküle wurde nach den Methoden der klassischen organischen Chemie durch polymeranaloge Umsetzungen geführt, also dadurch, dass ein makromolekularer Stoff in Derivate verwandelt wird, ohne dass sich sein Polymerisationsgrad dabei ändert. Die Beweiskraft wird noch erhöht,

> wenn deratige polymeranaloge Umsetzungen an höher- und niederpolymeren Gliedern einer polymerhomologen Reihe durchgeführt werden, wie es in vielen Fällen geschah. Diese Beweisführung für die Existenz der Makromoleküle basiert auf den gleichen Überlegungen, wie ein Jahrhundert früher der Beweis fur die Existenz von kleinen Molekülen in der organischen Chemie: Wöhler und Liebig . . . konnten 1832 bei ihren Untersuchungen über das Radikal Äthyl und Benzoyl organische Stoffe in Derivate mit ganz anderen Eigenschaften überführen, wobei ein grosser Teil des Moleküls, das Radikal, in seiner Grösse unverändert blieb, was damals sehr überraschend war. Bei geeigneten chemischen Umsetzungen mit Makromolekülen kann in der gleichen Weise nachgewiesen werden, dass deren „Makroradikale" in der verschiedener Derivaten in unveränderter Grösse erhalten bleiben.[36]

Thus, by using purely classical techniques of organic chemistry for ordinary compounds, Staudinger attempted to show that colloidal substances are composed of macromolecules in which atoms are linked together by powerful main valence forces. The conservative organic chemist Staudinger was undoubtedly quite content with his approach, for he believed that problems of organic compounds must be solved only by means of organic chemistry. Despite his confidence, this theory provoked antipathy among his contemporaries, including inorganic chemists, X-ray crystallographers, colloid chemists, physical chemists as well as organic chemists. Thus began a decade-long controversy over the existence of the macromolecule.

The Macromolecular Debate, 1924-1930

The line of evidence which Staudinger marshalled was not enough to convince many of his contemporaries. Instead, he encountered their vigorous opposition. Influenced by Emil Fischer's opinion against the existence of very large molecules and the predominant aggregate theory of polymers, many chemists of the time considered Staudinger's view untenable. Staudinger's colleague, Heinrich Wieland (1877-1957), the 1927 Nobel Prize winner in chemistry, advised him:

> Lieber Herr Kollege, lassen Sie doch die Vorstellung mit den grossen Molekülen, organische Moleküle mit einem Molekülargewicht über 5000 gibt es nicht. Reinigen Sie Ihre Produkte,wie z. B. den Kautschuk, dann werden kristallisieren und sich als niedermolekulare Stoffe erweisen![37]

In defense of his theory of the aggregate structure of rubber, Harries in 1923 stated simply that Staudinger's conclusion, drawn from the experiment on hydrogenation of rubber, was "premature" (verfrüht), since the experimental conditions appeared to him to be insufficient.[38]

From the perspective of X-ray crystallographers like Johann Rodorf Katz (1880-1938), Staudinger's arguments contradicted their interpretations. Katz recalled:

> At the meeting of the Naturforscherversammlung in Innsbruck in September, 1924, I first heard him [Staudinger] defend this theory [of macromolecules], especially for the case of polyoxymethylenes, but also some other cases. Neither I myself nor some others to whom I spoke were convinced by his very interesting exposition. His conception seemed possible, but, many of us thought, not proved. And the whole subject did not yet look attractive to many of us.[39]

Staudinger recalled a meeting of the Züricher chemischen Gesellschaft held in the following year:

> Als ich . . . 1925 einen längeren Vortrag hielt und glaubte, an den Beispielen des Kautschuks, des Polystyrols und Polyoxymethylens den Beweis für einen makromolekularen Bau erbracht zu haben, da stand der bekannte Mineraloge Paul Niggli auf und sagte als einzige Disskussionsbemerkung: „So etwas gibt es nicht!"[40]

The principal objection to Staudinger's view which emerged during the meeting again came from the data of X-ray analysis that appeared to suggest that the molecules of polymers are small.[41] In contrast, Staudinger's arguments for the macromolecule were based solely on the principles and methods of classical organic chemistry, with few references to the new physical technique, X-ray analysis. Indeed, to supporters of the aggregate theory such as Paul Niggli (1888-1953), Staudinger's theory flew in

the face of results obtained through procedures based on the X-ray diffraction--results that ostensibly were better established scientifically. The issue came to no resolution, as a witness reported:

> Alle anwesenden Grössen: der Organiker Karrer, der Mineraloge Niggli, der Kolloidchemiker Wiegner, der Physiker Scherrer und der Röntgenograph (und nachmalige Zellulosechemiker) Ott trachteten vergeblich, Staudinger von der Unmöglichkeit seiner Konzeption zu überzeugen, weil sie im Widerspruch zu exakten wissenschaftlichen Daten stand. Die stürmische Sitzung endete mit einer „Hier stehe ich, ich kann nicht anders"--Haltung Staudingers.[42]

In the middle of the 1920s, Staudinger found himself isolated in the face of criticism. However, it should be remembered that he was an organic chemist of established prestige who had already worked in different fields (such as ketenes) and along conventional lines. Thanks to this reputation, his opinions demanded careful consideration in any gathering. In Zürich between 1920 and 1926, he worked on macromolecules with seventeen doctoral students who, under his direction, piled up a mass of data on polymerization and the structures of rubber, cellulose, polysaccharides, polyoxymethylene, polystyrene, and polyindene.[43] Moving to the University of Freiburg in 1926, Staudinger continued his research with a strong conviction that his theory was valid. By this time the debate between the macromolecule and aggregate conceptions had become widely known in Germany, and the Gesellschaft Deutscher Naturforscher und Ärzte arranged a symposium on the subject at its annual meeting in Düsseldorf in September, 1926.

At this symposium Max Bergmann and Hans Pringsheim presented several arguments in favor of the aggregate structure of proteins, inulin, and other polysaccharides. They stressed the significance of the aggregation forces which might determine the properties of these

colloidal substances.[44] On the other side, Staudinger defended his theory using the data of his experiments on homologous series of various polymers and the hydrogenation of rubber, polyoxymethylene, and polyindene. Emphasizing the classical concept of the molecule, he again insisted that such polymeric compounds are built up according to Kekulé's structural theory. "Die Möglichkeit der Existenz der Makro-Moleküle," he declared, "lässt sich aus ganz allegemeinen Betrachtungen ableiten."[45] Staudinger now added proteins to his list of macromolecular compounds for the first time. Aware of the biological implication of his work, he closed his speech with the following remark before an audience of several hundred organic chemists:

> Die Welt der organischen Verbingungen liegt gewissermassen zwischen den einfachsten Kohlenstoff-Verbindungen, dem Methan, den Kohlenoxygen, dem Cyan, und den allergrossen Molekülen, dem hochpolymeren Kohlenstoff. . . .
>
> Troz der grossen Zahl von organischen Körpern, die wir heute schon kennen, stehen wir so erst am Anfang der Chemie der eigentlichen organischen Verbindungen und haben nicht etwa einen Abschluss erreicht.[46]

Another speaker at the session in Düsseldorf was Herman Francis Mark who had been working for the last four years on the X-ray analysis of organic substances at the Kaiser Wilhelm-Institut für Faserstoffchemie under Reginald O. Herzog.[47] Well aware of the issues of the controversy over the existence of macromolecules, Fritz Haber (1868-1934) had asked Mark to speak at the symposium about the question of whether X-ray structure examinations are in conflict with the concept of very large molecules. Although Mark apparently belonged to the school of the aggregate theory, his position at the meeting turned out to be neutral. He referred to the work by Alfred J. Reis (1882-1951) and Karl Weissenberg (1893-1976) which suggested that there are some cases in which the molecule

can be larger than the crystallographic unit cell.[48] He remarked that these cases could happen when primary valences penetrate through the whole crystal. Therefore, he thought, the fact that the unit cells are small does not exclude the existence of macromolecules; nor does it prove their existence.[49]

As happened in 1925, no agreement on the issue of macromolecules was reached. But Richard Willstätter, who presided over the symposium, was moved to favor Staudinger's view. According to Mark,

> Willstätter thanked all lecturers and discussion speakers in friendly words and said: "For me, as an organic chemist, the concept that a molecule can have a molecular weight of 100,000 is somewhat terrifying, but, on the basis of what we have heard today, it seems that I shall have to slowly adjust to this thought."[50]

In Staudinger's own recollections, Willstätter was particularly impressed by Staudinger's argument on the hydrogenation of polystyrene.[51] Many of the audience, however, seem to have felt more personal distaste than Willstätter for such enormous organic molecules--molecules which are a thousand times larger than those which they themselves were studying in their laboratories. Mark remembered one of them saying, "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."[52] The X-ray crystallographer, Katz who also attended the Düsseldorf symposium, reported that "Staudinger's conceptions did not seem to many of us really convincing, nor was the decisive value which X-ray spectrography could have for the subject yet understood at this meeting."[53]

Staudinger's lecture at the Düsseldorf meeting did not contain any decisive argument as to the problem posed by many X-ray crystallographers, although he believed that he had given sufficient evidence for

his theory on the basis of organic chemical methods. During the period between 1926 and 1927, activity in the field was steadily expanding. In keeping with Mark's conclusions some scientists rejected the assumption that the molecules of polymers must be smaller than the X-ray elementary cell of crystals. For example, in 1926, the American botanists, Olenus Lee Sponsler (b. 1879) and Walter Harrington Dore (1882-1956), pointed out that the repeating unit molecule of cellulose ($C_6H_{10}O_5$) is very much larger than the elementary cell.[54] In 1927 Staudinger's colleagues at the University of Freiburg, Gustav Mie (1883-1952) and Josef Hengstenberg (1904-), working in close collaboration with Staudinger, published papers on the X-ray analysis of polyoxymethylene. They observed that the X-ray diffraction pattern of polyoxymethylene has a characteristic interference pattern which varies with the number of CH_2O- groups in the polymer. Thus, they demonstrated by X-ray analysis the chain structure of polyoxymethylene, along which the unit CH_2O- repeats itself. The elementary cell contained only four CH_2O- groups which corresponded to only a small portion of the entire molecule. Therefore, they concluded, "Die Molekülgrosse hochmolekular Köpper lässt sich danach nicht nach der röntgenometrischen Methode bestimmen."[55] To X-ray investigators such as Katz, this work by Hengstenburg and Mie seemed to be "the first direct experimental evidence of Staudinger's hypothesis, and a decisive one."[56] Niggli also changed his viewpoint around this time.[57] After 1927 the issue of the small elementary cell no longer played so important a part in macromolecular debate, as it did before.

Although one of the arguments for the aggregate theory thus apparently lost ground, opinions of many organic chemists remained

unchanged. This is illustrated by Staudinger's record of a colleague's view around 1928:

> Etwa 2 Jahre nach meiner Berufung nach Freiburg sagte mir deshalb ein älterer Kollege meiner Freiburger Fakultät, er habe aus Erlangen gehört, dass durch Pummerers Arbeiten die Frage nach der Konstitution des Kautschuks abgeschlossen und dass meine Auffassung dadurch hinfällig sei. Ich fragte diesen Kollegen darauf, ob er und die Fakultät nunmehr der Meinung seien, eine Fehlberufung gemacht zu haben![58]

Mark seems to have come over to Staudinger's view of long-chain molecules shortly after the Düsseldorf meeting,[59] applying the idea in a different fashion. Moving to the I. G. Farbenindustrie as a head of the Ludwigshafen laboratory in early 1927, he worked with Kurt Heinrich Meyer (1883-1952) on the crystal structure of cellulose. From 1928 to 1930, they developed a theory which appeared to compromise between Staudinger's macromolecular theory and the aggregate theory. According to them, colloidal particles in a solution are not themselves macromolecules. Rather, colloidal particles are "micelles" (Micellen), a term which had been used by the Swiss botanist, Carl Wilhelm von Nägeli (1817-1891), in the previous century for the crystalline building blocks of starch.[60] Because Meyer and Mark considered that the micelles are the aggregates of primary valence chains (Hauptvalenzketten) or long-chain molecules held together by "special micellar forces" (besondere Micellarkräfte), they claimed that the molecular concept may not be applied to the micelle, that is, the colloidal particle. The weights of these particles, determined by physical methods (e.g., osmotic pressure measurements), do not represent molecular weights, but "micellar weights" (Micellargewichte). The micelles are stable in solution because of the considerable cohesive power of the Van der Waals-type micellar forces.

The colloidal properties are dependent on the micellar structure of the colloidal particles rather than on the structure of the long-chain molecules. Meyer and Mark estimated the size of the micelles from the widths of the X-ray diffraction spots. For example, a cellulose micelle, they suggested, is formed by 40-60 primary valence chains, each of them composed of 30-50 glucose units ($C_6H_{10}O_5$). This micellar size of 30-50 glucose units was taken to be the molecular length of cellulose. A micelle of 40-60 chain molecules is like a match box; the match box is the same length as each match (see Fig.2.1).[61]

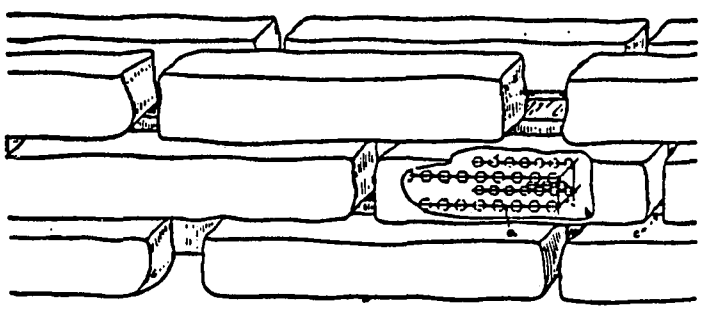


Fig. 2.1.

Meyer's sketch of the micellar structure of cellulose. Each box indicates a micelle in which primary valence chains (a) are arranged regularly.[62]

Staudinger recognized the physicalist approach inherent in what he called the "new micelle theory" (neuer Micellarlehre) of Meyer and Mark, because they stressed molecular cohesion and physical molecules in their explanation of colloidal properties of polymers. In published papers and personal correspondence, Staudinger opposed Meyer and Mark. He believed their estimate of the main chains to be too short. To Staudinger, the 40-60 chains would be, in the match-box model, connected

through primary valences to form a very long but thin chain-molecule. This led Staudinger to deny the existence of the micelles. The colloidal particle is identical with the macromolecule which determines colloidal properties of the polymer. Against the claims of X-ray crystallography, Staudinger maintained that neither the size of the elementary cell nor that of the crystallite bears any direct relationship to the length of the polymer molecule.[63] Although they were fundamentally in agreement on the long-chain structures of polymers, the difference in methodology led Staudinger to a more serious attack on Meyer and Mark. As Mark has said in retrospect,

> We [Staudinger and Mark] both favored the concept of long-chained molecules. He [Staudinger] did, on the basis of organic chemistry; and I did, on the basis of X-ray diffraction. He only trusted organic chemistry. I said trust both (techniques) ; we have two methods which do not contradict. My God, they could have contradicted![64]

Perhaps, this statement well illustrates Staudinger's position as a non-physicalist organic chemist throughout the debate.

Meyer in particular responded strongly to Staudinger's attack, which undoubtedly left considerable bitterness between the two chemists.[65] Time and again, they made their standpoints clear, emphasizing their difference in perspectives, rather than seeking to find common ground. On certain occasions, Staudinger and Meyer argued with each other more vigorously than with the defender of the aggregate theory. One aspect of the debate between them was that it developed into an argument of priority. Agreeing with the existence of long-chain molecules, Meyer used the term "primary valence chains" (Hauptvalenzketten) instead of "macromolecules" (Makromoleküle). Staudinger felt that Meyer employed Staudinger's concept as if it were his own idea. In a letter to Mark

dated October 31, 1928, Staudinger wrote:

> Ich kann ihm [Meyer] in 2 Punkten nicht zustimmen. Einmal sind meines Erachtens die Ausführungen von K. H. Meyer nicht neu, sondern decken sich im wesentlichen mit den Ansichten, die ich seit Jahren vertrete und experimentell begründet habe; dann aber glaube ich, dass mit der Einführung von Hauptvalenzketten statt Makromolekülen der Klärung dieser Frage nicht gedient ist.[66]

In response to Staudinger, Mark suggested that the "primary valence chains" and the "macromolecules" are identical, and that those who agreed upon the concept of large molecules should march hand in hand together against the school attacking their common ground.

> Ich glaube, dass wir bei der Stellungnahme zu dieser Frage gemeinsam vorgehen und nicht gewisse, meiner Meinung nach geringe Differenzen zwischen unseren eigenen Anschauungen betonen sollten, sonst könnte das hochpolymere Lager leicht in den Fehler verfallen, der aus der Politik nur allzu bekannt ist; dass wegen kleiner Differenzen benachbarter Meinungen ein grosser Gesichtspunkt nich genügende Beachtung und nicht nachhaltichen Ausdruck fand.[67]

However, this suggestion was not followed. While Staudinger continued to reproach Meyer for his use of the "primary valence chains" and "micelles," Meyer objected to Staudinger's presenting Meyer's opinions as his own.[68] This was due to the fact that Staudinger did not exclude the possibility of inter-macromolecular forces (of the order of the magnitude of the Van der Waals forces), at the same time that he rejected the possibility of micellar forces. Further, Staudinger held the idea of crystallite--a crystalline part of polymeric substances which, he thought, consists of a bundle of macromolecules--an idea which appeared somewhat similar to the concept of micelles. Their polemics involving the priority issue continued until the middle of the 1930s.[69]

The emergence of the Meyer-Mark micelle theory, which embraced aspects of both the macromolecular concept and the aggregate theory, gave rise to renewed debate in German scientific circles. On the one

hand, the theory drew much favorable attention from the advocates of the aggregate theory. On the other hand, the work of Meyer and Mark played a significant role in disseminating widely the concept of long-chain molecules, especially among cellulose chemists.

Around 1930 the interpretation of polymeric compounds diverged between Staudinger's school at Freiburg, Meyer and Mark at Ludwigschafen, and supporters of the aggregate view who included a large number of colloid chemists. Considering this situation, the Kolloid-Gesellschaft held a discussion meeting on "Organische Chemie und Kolloidchemie" in Frankfurt in September 1930. Wolfgang Ostwald, the German leader of colloid chemistry, presided over this meeting. Staudinger, Meyer, Mark, Herzog, Kurt Hess, and Rudolf Pummerer were the principal speakers.

In his lecture, "Über hochpolymere Verbindungen: Organische Chemie und Kolloidchemie," Staudinger stressed before an audience of colloid scientists that colloidal substances should be examined on the basis of organic chemistry, rather than relying on traditional colloidal doctrines, and that the study of these substances represents a new field within organic chemistry.[70] On this occasion, he presented the well-known Staudinger Law of Viscosity which expressed a relationship between the viscosity and the molecular weight of polymers in dilute solutions. He had developed this concept in early 1929, breaking with the tradition of colloid scientists, according to which there is no linear relationship between viscosity and the molecular size of colloids.

The Einstein equation which relates molecular weight to viscosity was known to be applicable only to spherical molecules. Staudinger put two of his students to work on the problem. In 1929 and 1930, Ryuzaburo

Nodzu (1892-1957) and Eiji Ochiai , both from Japan, experimentally confirmed that the Einstein equation does not apply to low-molecular linear chain compounds, but they did find that there is a proportionality between viscosity and chain length.[71] The implication was clear to Staudinger: viscosity depends on the shape and length of the molecule, and he applied this notion to linear macromolecules. At the Frankfurt meeting, using various degrees of polymers (polystyrene, polyoxymethylene, and decomposed cellulose and rubber), Staudinger demonstrated that their molecular weights, measured by end-group analysis and the depressions of freezing point, are in proportion to the viscosity of solution.[72] On the basis of this relation, he was able to obtain the molecular weights of high polymers (which could not be determined previously by available methods) simply by means of viscometry. According to his estimate by the viscosity method, natural rubber is composed of macromolecules of about 1000 isoprene units (C_5H_8), and a cellulose molecule consists of 500 to 1000 glucose units ($C_6H_{10}O_5$). Confident of his findings, Staudinger contrasted his macromolecular viewpoint with the new micelle theory and the aggregate theory: for example, the chemical formula of rubber is $(C_5H_8)_{1000}$ according to Staudinger; $(C_5H_8)_{100}$ according to Mark; and $(C_5H_8)_8$ in Pummerer's view.[73]

Meyer and Mark confronted the audience with an impressive array of data on cellulose, starch, silk fibroin, and rubber.[74] Although their lectures were based on the micelle theory, they stood on Staudinger's side in supporting the concept of long-chain structure for these colloidal substances. After the lectures from the camp of large molecules, Herzog, Hess, and Pummerer defended the aggregate theory of cellulose

and rubber.[75] Realizing that the aggregate view was facing a difficult situation, the cellulose chemist Hess closed his lecture with the following words:

> Meine Ausführungen bezweckten nicht, die Auffassung zu widerlegen, dass die Zahl der C_6- Gruppen im Zellulosemolekül sehr gross sein kann. Es solten in den vorangehenden Ausführungen nur die experimentellen Erscheinungen ein wenig schärfer, als es bisher möglich war, beleuchtet werden. Man wird sich des Eindurcks kaum entziehen können, dass die Erscheinungen komplizierter sind, als es zunächst den Anschein hat und dass neues Versuchsmaterial notwendig ist, um sie weiter zu klären.
>
> In diesem Sinne bin ich ein Freund der in neuer Form durch die Arbeit der Herren Meyer und Mark zu neuem Leben erwachten alten Vorstellung Emil Fischer's und Bernard Tollens, wenn sie zu neuen Versuchen herausfordert und fördert. Möge dann diese Vorstellung auch eines Tages wieder verlassen order revidiert werden müssen, ihren grossen Wert wird sie behalten, denn auf diesem schwierigen Gebiet gilt mehr als für viele andere das Wort: „Wahr ist, was fruchtbar ist!"[76]

Hess evaluated highly the work of Meyer and Mark; the new micelle theory, if not Staudinger's macromolecular theory, appeared to him to be acceptable. He implicitly reminded the audience that any scientific theory is destined to be rewritten some day, which may hold true for the aggregate theory as well; yet the contributions of the aggregate school to the development of this field must not be forgotten. Impressed by Hess' cry, the champion of the colloid doctrine, Wolfgang Ostwald who chaired the speech, could not help exclaiming, "Bravo!"[77]

While having a feeling in favor of the Meyer-Mark theory, Hess, one of the most powerful defenders of the aggregate view, sought to maintain his own standpoint for years after the Frankfurt meeting of the Kolloid-Gesellschaft. Hess' attitude during this period is well illustrated by a statement of his Japanese student, Ichiro Sakurada (1904-

):

一九三二年の春，私はくっ革研究室を去ったが，そのとき先生は，「いま自分がこの研究を投げ打ったならば，世間ではセルロースの高分子説はドイツの学者によって確定せられたということであろう。しかし，事実は彼らの考えるごとく簡単ではない。まだたくさんの仕事，解決されるべき多数の問題が残っている。自分はカラー，マイヤーのごとくこの問題から逃避せず，徹底的にこの研究を今までの立場から続けようと思う。」といわれた。[78]

However, by the mid-1930s the climate of opinion was shifting to the side of the macromolecular theory. Many of the arguments on polymers around 1935 were concerned with the details of the long-chain structures rather than with the question as to the existence of very large molecules. As we have seen earlier, X-ray crystallographers' reception of macromolecules since about 1927 and the impact of the Meyer-Mark theory, which acted as a bridge between the macromolecular view and the aggregate theory since 1928, had paved the way toward this shift. The Staudinger school of macromolecules had grown; by 1935 he had trained 23 doctoral students at Freiburg; the total number of his doctoral students was now 40, including those graduated from the Zürich Technische Hochschule.[79] He had published his masterpiece textbook, Die hochmolekularen organischen Verbindungen (1932) in which he summarized the results of his and his co-workers' decade-long research on macromolecular compounds.[80] His theory was now supported by the work of some scientists outside Germany as well as by his own students. Among the significant new developments were molecular weight measurements with the ultracentrifuge which the Swedish scientist Theodor Svedberg (1884-1971) had introduced in 1926 and, which estimated the molecular weight of some proteins to be several millions.[81] Yet, one of the most crucial movements in the domain of organic chemistry was put forward by a young

American researcher, Wallace Hume Carothers (1896-1937), who established the macromolecular view through a series of investigations, inaugurated in 1928, on the mechanism of polymerization, as will be discussed in the next chapter. By the middle of the 1930s, many of the champions of the aggregate theory, including Bergmann, Pringsheim, and Hess himself, came to accept Staudinger's macromolecular concept. Meyer no longer invoked his theory against Staudinger's view. Polemics now behind him, Staudinger began to gain a reputation as the founder of a new science.

Polymers and their Properties: From Organic Chemistry to Macromolecules

The macromolecular debates in the 1920s and the early 1930s exhibit largely a conceptual and methodological clash between Staudinger and his opponents, a clash between the organic-structural tradition and the physicalist tradition. As Mark testified, during the controversy,

> Many of his colleagues in high academic positions remained for a long time skeptical and overcautious. They did not approve of the strong terms with which Staudinger elevated his own working field to a "new branch of organic chemistry," and they displayed mistrust in a number of his methods and results.[82]

Because of his strong adherence to traditional organic chemistry, Staudinger has been called "one of the last great organic chemists of the old school."[83] The triumph of Staudinger's approach in the field of polymeric substances meant a victory for the old school of organic chemistry. When he received the Nobel Prize in 1953 in chemistry in recognition of his work on macromolecular chemistry, his former student Emil Ott (b. 1902) stressed that, "Staudinger succeeded where others failed because he knew and believed in organic chemistry."[84] As we have seen, Staudinger brought back the organic-structural approach to the study of colloidal substances, whereas this field had been dominated by the physicalist

view of colloids as a state of matter. Seeing colloidal particles as giant organic molecules, he claimed that these macromolecules are structured on the same principles as those of low molecules, that is, in accordance with Kekulé's classical structural theory. In this respect, it may be argued that Staudinger established his concept of macromolecules by returning to classical organic chemistry. Given this context, one may raise the question: was Staudinger's macromolecular theory merely the revival, or the extension, of the classical concept of low molecules; that is, to what degree was it based on classical structural chemistry? To answer this question, it is important to examine more closely Staudinger's view of the properties of polymers.

As an organic chemist, Staudinger regarded the molecule as the entity from which stemmed all physical and chemical properties of the substance. He shared the structural concept with traditional chemists such as Emil Fischer, holding that the properties of compounds largely depend on their molecular structure, especially on the arrangement of the constituent atoms in the molecule. This point of view was in contrast to Max Bergmann's claim that the properties of polymers can best be understood by the study of the physical conditions outside the molecule rather than inside. Likewise, the structural concept differed from the Meyer-Mark micelle concept which stressed the intermolecular-micellar forces rather than the structure of primary valence chains. While chemists traditionally maintained that a pure substance consists exclusively of a single and definite molecular component, Staudinger broke with this belief. He wrote in 1926:

> Dabei besteht allerdings zwischen einem einfachen, einheitlichen

> Stoff und einem Hochmolekularen ein wesentlicher Unterschied, dessen Nichtbeachtung hinderte, dass man hier den Molekül-Begriff anwandte. Bei einem einfachen, einheitlichen Stoff besitzen alle Moleküle gleiche Grösse; die hochmolekularen Verbindungen setzen sich dagegen meist aus einem Gemisch von ähnlich gebauten, aber verschieden grossen Molekülen zusammen. Eine Trennung in einheitliche Stoffe ist hier wegen der zu geringen Unterschiede der physikalischen und chemischen Eigenschaften nicht durchführbar. Wenn also bei diesen Hochpolymeren Molekulargewichte angegeben werden, so kann es sich nur um Durchschnittswerte handeln.[85]

Polymers are, he stressed, composed of molecular chains of different lengths owing to their great size; the molecules in the compound are not completely identical in size. In other words, macromolecular substances are "polymolecular" (polymolekulare). Therefore, the molecular weights have certain ranges and can be expressed only by average values rather than by definite numbers. In this respect, the macromolecular conception differed from the traditional notion of chemical compounds which was held both by structural chemists and by the exponents of the aggregate theory.

The structural chemist, Fischer, while unaffected by the aggregate theory of colloidal particles, doubted the existence of giant molecules. For, as mentioned above, he believed that isomerism alone would suffice to explain the complexity of natural organic compounds such as proteins; and hence that the assumption of giant molecules ought to be superfluous. Staudinger went even further; he insisted that because of the size of macromolecules (1,000-100,000 times the size of low molecules), there is an almost infinitely large number of structural possibilities for the molecules. This is, he thought, especially true in the case of protein molecules, in which even slight differences in the structure would yield different biological properties.[86] Furthermore, according to Staudinger, the great variety of the shapes of macromolecules

causes numerous variations in the properties of polymers, such as fibrousness, elasticity, tensile strength, viscosity, and swelling phenomena. For example, he classified macromolecules into two large groups, linear and spherical, according to their shape. Substances with spherical macromolecules, he said, are usually powder in the solid state. They dissolve in water without swelling and form solutions of low viscosity. Glycogen belongs to this group. Linear macromolecular substances, on the other hand, are fibrous and tough, and dissolve with considerable swelling to give gel solutions of high viscosity. Cellulose is, he claimed, a typical polymer of this group.[87] Thus, as he stated, "the shape of macromolecules affects the physical and chemical properties of the substances considerably more strongly than is the case with the low molecular compounds."[88] With his emphasis upon the molecular size and shape in explaining the properties of the polymer, Staudinger departed from the tradition of Fischer, who confined his study to the arrangement of the atoms within the molecules.[89]

Staudinger claimed that the macromolecule as a whole, just as a building, exhibits its own unique properties which cannot be simply deduced from those of the low molecular units.

> . . . die Moleküle und ebenso die Makromoleküle lassen sich mit Bauwerken vergleichen, die im wesentlichen aus nur wenigen Sorten von Bausteinen, den Kohlenstoff-, Wasserstoff-, Sauerstoff- und Stickstoffatomen, aufgebaut sind. Liegen nur einige Dutzend oder Hunderte davon vor, so kann man damit nur kleine Moleküle und entsprechend nur relativ primitive Bauwerke konstruieren. Beim Vorliegen aber von 10000 oder 100000 Bausteinen lassen sich unendlich verschiedenartige Bauwerke herstellen: Wohnhäuser, Fabrikhallen, Hochhäuser, Paläste, etc., und es lassen sich dann auch Konstruktionen ausführen, deren Möglichkeiten man nicht ahnen kann, wenn man nur wenig Baumaterial zur Verfügung hat. Gleiches gilt für die Makromoleküle. Es ist einleuchtend, dass hierbei natürlich auch neuartige Eigenschaften auftreten, die bei kleinen Molekülen niedermolekularer Stoffe nicht möglich sind.[90]

In short, the whole is not a mere sum of its parts, but more than that. For this reason, he focussed his attention on the properties of the giant molecule itself, e.g., size and shape--a factor with which the Kekuléan structural chemistry was little concerned.[91] Here Staudinger no doubt registered a biological holistic point of view that distinguished him from many of his contemporaries.[92]

The appreciation of the whole rather than its isolated parts also differentiated his view from the mechanistic trend that reduced colloidal phenomena to smaller units and forces. Staudinger's friend, Berhnard Welte (b. 1913), remarked in an address to Staudinger in 1956:

> Inmitten der durchgängigen quantitativen Methodik der modernen Chemie sind Sie, und dies scheint mir überaus denkwürdig, aufmerksam geworden auf eine Zone im chemischen Aufbau unserer materiellen Welt, innerhalb derer das Quantum, die Zahl der Bausteine und Elemente der materiellen Stoffe nicht mehr nur Quantum ist, vielmehr in die Qualität übergeht, um hier einen Gedanken aus HEGELs Logik heranzuziehen. Sie sind aufmerksam geworden auf Formen und Gebilde, bei denen Gesetz, Ordnung und Form, -z. B. die Form von Ketten und Ringen der mannigfaltigsten Art, - wichtiger werden als die blosse Zahl der Bausteine oder der elementaren Wirkungskräfte. Vielleicht darf ich diese Schwelle, an der das Quantum in die Qualität übergeht, mit einem Gleichnis bezeichnen. Gehen wir mit Ihnen und Ihrer Forschung diesen Weg der Natur, den Sie zuerst mit ihr denkend und forschend gegangen sind, den Weg aus der klassischen quantitativen Chemie zur makromolekularen Chemie, dann ist es, als wären wir zuerst über einen grossen Bauplatz gegangen, angefüllt mit einer Menge kostbarer Werkstoffe, Steine, Eisenträger, Hölzer und vielerlei Dingen dieser Art, und als seien wir nachher vor ein Haus getreten, vor ein grosses Haus, vielleicht vor eine Kathedrale. Vor eine Kathedrale, welche ganz gewiss mehr ist als die blosse Summe der vielen einzelnen Werksteine und Werkstoffe, welche in sie verbaut sind. Sie ist mehr, weil in ihr das Viele der einzelnen Bauelemente zu einer geformten Einheit höherer Ebene und höheren Ranges verbunden ist. Aus dem Quantum ist ein Quale geworden.[93]

Quality comes from the whole rather than the parts. In this regard, Staudinger stated that macromolecular compounds exhibit properties which "cannot be predicted even by a thorough study of the low molecular

substances."[94] It was such a conviction that led Staudinger to consider macromolecular chemistry as "a new field of organic chemistry" (ein neues Gebiet der organischen Chemie), as distinguished from classical organic chemistry which deals with low molecular substances.[94]

In sum, the following remarks can be made about the emergence of the macromolecular concept. Staudinger's theory of macromolecules was rooted in the organic-structural tradition, both theoretically and experimentally. However, in explaining the properties of compounds, Staudinger departed from the classical concept of chemical structures. He claimed that the physical and chemical properties of polymers are determined not only by the internal structure of the molecule but more significantly by its external structure, such as its size and shape. Perhaps it was this departure from the traditional structural approach that enabled him to establish so firmly the macromolecular view, in contrast to the nineteenth-century concept of the large molecule that earlier had been dropped from the organic-structural tradition. Staudinger's holistic conception of matter that stressed the whole rather than its individual parts played a crucial role in this departure. His strong rejection of mechanical reductionism in the physicalist approach to polymers can also be understood in the light of his holistic conception. Thus, as we can see, the rise of Staudinger's macromolecular theory was not merely the replacement of one theory by another; neither can it be seen simply as a revival of classical chemistry. The emergence of the macromolecular concept was accompanied by an epistemological shift in the chemical view of matter.

NOTES

[1]The best source on Staudinger's educational background, career, and scientific work is Hermann Staudinger, Arbeitserinnerungen (Heidelberg: Dr. Alfred Hüthig Verlag GmbH., 1961). This work has been translated into English under the title, From Organic Chemistry to Macromolecules: A Scientific Autobiography on My Original Papers, trans. Jerome Fock and Michael Fried (New York, London, Sydney, and Toronto: Wiley-Interscience, 1970). Staudinger's scientific papers were brought together in Das wissenschaftliche Werk von Hermann Staudinger, ed. Magda Staudinger, Heinrich Hopff, and Werner Kern, 7 vols. (Basel and Heidelberg: Hüthig & Wepf Verlag, 1969-1976). On Staudinger's life and work, see also Willem Quarles, "Hermann Staudinger: Thirty Years of Macromolecules," Journal of Chemical Education, 28 (1951): 120-122; Herman Francis Mark and Herman A. Bruson, "Hermann Staudinger," J. Poly. Sci., 19 (1956): 387-388; V. E. Yarsley, "Hermann Staudinger--His Life and Work: Memorial Lecture," Chemistry and Industry, no. 7 (February 18, 1967): 250-271; Dictionary of Scientific Biography, vol. 13 (1976), s.v. "Staudinger, Hermann," by Robert Olby; Claudia Krüll, "Hermann Staudinger --Aufbruch ins Zeitalter der Makromoleküle," Kultur und Technik, 2 (1978), no. 3: 44-49; and Yasu Furukawa, "Hermann Staudinger and the Emergence of the Macromolecular Concept," Historia Scientiarum, no. 22 (1982): 1-18.

[2]A prolific writer, Franz Staudinger published more than fifteen books on culture, society, ethics, politics, and philosophy, including Franz Staudinger, Die Gesetze der Freiheit: Unterschungen über die wissenschaftlichen Grundlagen der Sittlichkeit, der Erkenntnis und der Gesellschaftsordnung (Darmstadt: L. Brill, 1887); Ethik und Politik (Berlin: F. Dümmler, 1899); WirtschaftlicheGrundlagen der Moral (Darmstadt: E. Roether, 1907); Die Konsumgenossenschaft (Leipzig: B. G. Teubner, 1908); and Kultur-Grundlagen der Politik, 2 vols. (Jena: E. Diederichs, 1914).

[3]Hermann Staudinger, "Anlagerung des Malonesters an ungesättigte Verbingungen," (Dissertation, Universität Halle, 1903).

[4]See Ch. I, pp. 25-26.

[5]Daniel Vörlander and Hermann Staudinger, "Über Zwischenprodukte bei Additions- und Kondensationsreaktionen des Malonesters," Zeitschrift für Naturwissenschaften (Halle), 75 (1903): 385-432, "Über die Anlagerung des Malonesters an das System CH=CH-CH=CH-C=O," ibid.: 433-454; Hermann Staudinger, "Einwirkung von Natriummalonester auf Äthoxybernsteinsäureester und Athoxybenzylmalonester," Liebigs Ann. Chem., 341 (1905): 99-117; and "Cinnamylidenacetophenon und Natriummalonester," ibid., 345 (1906): 217-226.

[6]See Claudia Krüll, "Historische Experimente (um 1905): 'Denk-Experimente' zum Benzolring--aus Manuskripten Hermann Staudingers," Chemie-Experiment und Didaktik, 2 (1976): 441-448.

[7]A complete list of these papers is in Staudinger, Arbeitserinnerungen, pp. 17-20. See also ibid., pp. 11-17. Ketene is a class of organic compounds with the general formula, R_2=C=C=O, where R symbols represent organic radicals or hydrogen atoms.

[8]Hermann Staudinger, Die Ketene (Stuttgart: Verlag Enke, 1912).

[9]See Staudinger, Arbeitserinnerungen, pp. 22-30 and 43-46.

[10]Quarles, "Hermann Staudinger," p. 120.

[11]Yarsley, "Hermann Staudinger," p. 250.

[12]George Stafford Whitby, "Hermann Staudinger (1881-1965)," Rubber Chem. Tech., 40 (June 1967): xvi-xxiii, on p. xx.

[13]See Staudinger, Arbeitserinnerungen, pp. 59-63.

[14]"Those [colleagues] who knew my publications in the field of low molecular chemistry asked me why I was neglecting this interesting field and instead was working on very unpleasant and poorly defined compounds, like rubber and synthetic polymers. At that time the chemistry of these compounds often was designated, in view of their properties, as Schmierenchemie ("grease chemistry")." Staudinger, Arbeitserinnerungen, p. 77; Staudinger, From Organic Chemistry to Macromolecules, p. 77.

[15]See below pp. 50-53.

[16]Hermann Staudinger and Helmut W. Klever, "Über die Darstellung von Isopren aus Terpenkohlenwasserstoffen," Ber., 44 (1911): 2212-2215.

[17]"These differences in a number of properties [between synthetic rubber and natural rubber], in particular, stimulated my research in this field, especially investigations on the colloidal solutions of these materials." Staudinger, Arbeitserinnerungen, p. 77; From Organic Chemistry to Macromolecules, p. 77.

[18]Staudinger and Klever, "Darstellung von Isopren," p. 2215.

[19]"In his important work on the influence of ozone on organic substances, Harries in 1904 and 1905 was able to pave the way for the understanding as to how the iosprene molecules form rubber. I will not go into details here on his initial wrong assumption that rubber is composed of a carbohydrate of cyclooctadiene series. I adopt afterwards the work by Pickles that in the rubber formation the isoprene molecules get together at the ends, namely, 1,4-position, and that hundreds of isoprene molecules build up the large rubber molecules which could be made

observable through the ultramicroscope, and which determine the colloidal properties of rubber." Hermann Staudinger, "Über Isoprene und Kautschuk: Kautschuk-Synthese," (read at the 36th general meeting of the Schweizerischen Gesellschaft für chemische Industrie, October 7, 1917) in Staudinger, Wissenschaftliche Werk, vol. 1: Arbeiten über Isopren, Kautschuk und Balata (1969): 22-39 on pp. 24-25.

[20]Samuel Shrowder Pickles, "The Constitution and Synthesis of Cautchouc," J. Chem. Soc.,97 (1910): 1084-1090. On Pickles' career, see, e.g., Who's Who in British Science, 1953 (London: Leonard Hill, 1953), s.v. "Pickles, Samuel Shrowder."

[21]Ibid., pp. 1088-1090. C.f., Ch. I, pp. 26-28.

[22]Staudinger, "Über Isoprene und Kautschuk," pp. 25 and 27.

[23]Hermann Staudinger, "Über Polymerisation," Ber., 53 (1920): 1073-1085.

[24]"And therefore I believe that from the available observation material, such assumptions [of molecular compounds which are held together by secondary valences] as to the origin of polymerization products do not have to be made; it is much more likely that different types of polymerization porducts, as I hope to show in what follows, can be explained satisfactorily by normal valences, and as far as possible the properties of the compounds can continue to be expressed straightforwardly in organic chemistry by normal valence formulas." ibid., pp. 1073-1074; Hermann Staudinger, "On Polymerization," in Source Book in Chemistry, 1900-1950, ed. and trans. Henry M. Leicester (Cambridge, Massachusetts: Harvard University Press, 1968): 260-264, on p. 260. In this context, Staudinger criticized George Schroeter's interpretation of ketene polymerization as a molecular aggregation. Cf., Ch. 1, p. 28.

[25]Staudinger, "Über Polymerisation," p. 1074.

[26]Ibid., p. 1082.

[27]"Take, for example, hundreds of formaldehyde molecules, and we have twice the molecules in the unpolymerized condition. If we accept that these hundreds of molecules themselves polymerize to form a paraformaldehyde molecule, then we have there only two unsaturated positions; the reactivity is thus many hundred times less. This more or less agrees with the observation that high-molecular compounds are far less reactive than monomolecular end-products, and that they however still to some extent exhibit the reactions of monomolecular substances." ibid., p. 1083.

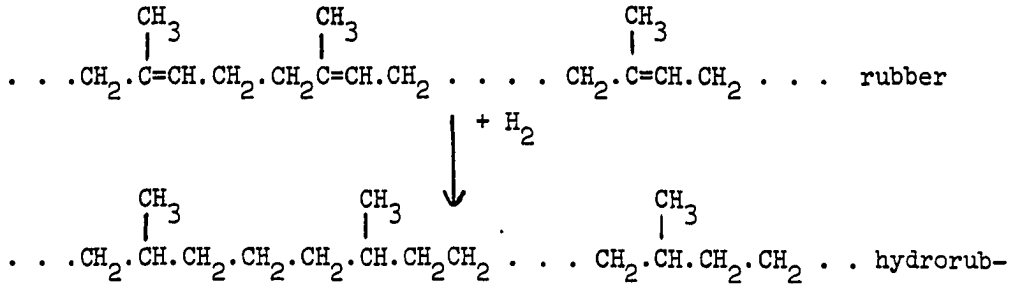
[28]See Ch. I, pp. 17-19.

[29]Staudinger, "Über Polymerisation," p. 1081.

[30]Staudinger, Arbeitserinnerungen, p. 83.

[31]Herman F. Mark, "Polymer Chemistry: The Past 100 Years," Chem. Eng. News, 54 (April 6, 1976): 176-189, on p. 180.

[32]Hermann Staudinger and Jakob Fritschi, "Über Isopren und Kautschuks: Über die Hydrierung des Kautschuks und über seine Konstitution," Helv. Chim. Acta, 5 (1922): 785-806, especially p. 788. Staudinger considered the hydrogenation of natural rubber as the following reaction in which the saturation of double bonds occurs without changing the size of the large molecule:



ber. See ibid., p. 790.

[33]"For those colloidal particles in which the molecule is identical with the primary particle and in which the individual atoms of the colloidal molecule are linked together by normal valences, we propose the term macromolecules. Such colloidal particles form true colloidal materials, which, in accordance to the bonding power of carbon, occur particularly in organic chemistry and in organic natural substances. Here the colloidal properties are determined by the structure and size of the molecule. . . ." Hermann Staudinger, "Über die Konstitution des Kautschuks," Ber., 57 (1924): 1203-1208, on p. 1206.

[34]According to Staudinger, the primary colloidal particles represent the macromolecules in most cases. But he admitted a few exceptions to this; for example, he thought that soaps form colloidal particles which consist of small molecules. He suggested calling this group of colloids "Pseudo-Kolloide," as distinguished from "Eu-Kolloide" in which colloidal particles are macromolecules. Hermann Staudinger, "Zur Chemie des Kautschuk und der Guttapercha," Kautschuk (August 1925): 5-6, and (September 1925): 8-10. See also Staudinger, Arbeitserinnerungen, pp. 108-115.

[35]Hermann Staudinger, "Die Chemie der hochmolekularen organischen Stoffe im Sinne der Kekuléschen Strukturlehre," Ber., 59 (1926): 3019-3043.

[36]"The essential proof for the existence of macromolecules was adduced by classical organic chemical methods via polymer analogous reactions; thus, polymers were converted into their derivatives without their degree of polymerization being changed. This is proved further when such polymer analogous reactions are carried out on the high and low molecular parts of a polymer homologous series, as in many cases was done. The argument for the existence of macromolecules is based on the same consideration as that for the existence of small molecules in

organic chemistry one century earlier. Thus Wöhler and Liebig in their research on the radicals ethyl and benzoyl in 1832 . . . were able to convert organic compounds into derivatives with other properties, whereas a large part of the molecule--the radical--remained unchanged in size. This discovery was very surprising at that time. In the same manner it can be demonstrated that under suitable conditions macromolecules leave their 'macroradicals' unchanged with respect to size when they are converted into their derivatives." Staudinger, Arbeitserinnerungen, pp. 115-116; From Organic Chemistry to Macromolecules, pp. 104-105.

[37]"Dear colleague, drop the idea of large molecules; organic molecules with a molecular weight higher than 5000 do not exist. Purify your products, then it will crystallize and prove to be a low molecular compound!" Staudinger, Arbeitserinnerungen, p. 79; From Organic Chemistry to Macromolecules, p. 79.

[38]Carl Harries, "Über Aggregation und Desaggregation: Hydrolyse des Schellackharzes. Hydrierung des Kautschuks," Ber., 56 (1923): 1048-1051, on p. 1050.

[39]Johann R. Katz, "X-ray Spectrography of Polymers and in Particular those having a rubber-like Extensibility," Trans. Faraday Soc., 32 (1936): 77-94, on p. 77.

[40]"During a lecture given in 1925 I thought I had given good evidence for the existence of macromolecular structures, using as examples rubber, polystyrene, and polyoxymethelene; then, however, the well-known mineralogist Paul Niggli rose and his only discussion remark was, "Such a thing does not exist!" Staudinger, Arbeitserinnerungen, p. 86; From Organic Chemistry to Macromolecules, pp. 84-85.

[41]During this period, it was generally assumed by crystallographers that the molecule could not be larger than the unit cell (or elementary cell). Since it was reported that the unit cells of cellulose, rubber, silk, and other polymers were small, many scientists believed that their molecular size is small. See Ch. pp. 29-30.

[42]"All the great men present: the organic chemist, Karrer, the mineralogist, Niggli, the colloid chemist, Wiegner, the physicist, Scherrer and the X-ray crystallographer (later cellulose chemist), Ott, tried in vain to convince Staudinger the impossibility of his concept because it conflicted with exact scientific data. The stormy meeting ended with Staudinger's shout [quoting Luther's words], 'Here I stand, I cannot do otherwise!'" A. F. Frey-Wyssling, "Frühgeschifte und Ergebnisse der submikroskopischen Morphologie," Mikroskopie, 19 (1964): 2-12, on p. 5.

[43]These doctoral students are: Max Brunner, Herman A. Bruson, Friedrich Felix, Karl Frey, Jakob Fritschi, Ernst Geiger, Hugo Harder, Ernst Huber, Hans W. Johner, Max Lüthy, Eric W. Reuss, Alfred Rheiner,

Rudolf Signer, Emil Suter, Ernst Urech, Siegfried Wehrli, and Willy Widmer. On their dissertations and Staudinger's scientific activity in Zürich, see Hermann Staudinger, "Über die Entwicklung der makromolekularen Chemie in den Jahren 1920 bis 1926," in Festgabe der GEP zur Hundertjahrfeier der Eidgenössischen Technischen Hochschule Zürich (1955): 399-411. This article has been reprinted in his Wissenschaftlich Werk, vol. 5: Arbeiten allgemeiner Richtung von Hermann Staudinger (1975): 3-15.

[44]Max Bergmann, "Allgeneine Strukturchemie der komplexen Kohlenhydrate und der Proteine," Ber., 59 (1926): 2973-2981. Hans Pringsheim, "Abbau und Aufbau der Polysaccharide," ibid.: 3008-3018. See Ch. I, pp. 26 and 36, n. 43.

[45]"The possibility of the existence of macromolecules can be deduced from wholly universal considerations." Staudinger, "Chemie," (see n. 35), p. 3041.

[46]"The world of organic compounds lies between the simplest carbon compounds such as methane, carbon monoxide, cyanogen, and the largest molecules, the high polymeric carbon compounds. . . . Despite the large number of organic substances which we already know today, we are only standing at the beginning of the chemistry of true organic compounds and have not reached anywhere near a conclusion." Staudinger, "Chemie," (1926) (see n. 35), pp. 3041-3043.

[47]Cf., Ch. I, pp. 29-30. See Herman F. Mark, "Polymer Chemistry in Europe and America--How It All Began," J. Chem. Educ., 58 (1981): 527-534, on pp. 529-530; and G. Allan Stahl, "Herman F. Mark: The Geheimrat," in Polymer Science Overview: A Tribute to Herman F. Mark, ed. G. Allan Stahl, ACS Symposium Series 175 (Washington, D.C.: American Chemical Society, 1981): 62-88.

[48]A. J. Reis, "Zur Kenntnis der Kristallgitter," Z. Physik, 1 (1920): 204-220.
K. Weissenberg, "Kristallbau und chemische Konstitution, 1-3," Z. Physik, 34 (1925): 406-419, 420-432, and 433-452.

[49]Herman F. Mark, "Über die röntgenographische Ermittlung der Struktur organischer besonders hochmolekularer Substanzen," Ber., 59 (1926): 2982-3000. Cf., Mark, "Polymer Chemistry in Europe and America," pp. 529-530.

[50]Ibid., p. 530

[51]Staudinger, Arbeitserinnerungen, p. 87.

[52]Herman F. Mark, "Coming to an Age of Polymers in Science and Technology," in History of Polymer Science and Technology, ed. Raymond B. Seymour (New York and Basel: Marcel Dekker, Inc., 1982): 1-9, on p. 2.

[53]Katz, "X-ray Spectrography of Polymers," p. 77.

[54]O. L. Sponsler and W. H. Dore, "The Structure of Ramie Cellulose as Derived from X-ray Data," Colloid Symp. Monogr., 4 (1926): 174-202. This paper was read in the American Colloid Symposium, held in June 1926 at the Massachusetts Institute of Technology at Cambridge, Massachusetts. Its German translation appeared in 1930 in the Cellulosechemie, 11 (1930): 186.

[55]"The molecular size of high molecular compounds cannot be determined by X-ray measurements." Hermann Staudinger, H. Johner, and R. Signer, G. Mie and J. Hengstenberg, "Der polymere Formaldehyd, ein Modell der Cellulose," Z. physik. Chem., 126 (1927): 425-448, on p. 448. Although this paper was co-authored by Staudinger, the X-ray measurements were carried out practically by the two physicists, Mie and Hengstenberg. See also J. Hengstenberg, "Röntgengenuntesuchungen die Struktur der Polymerisationsproduckte des Formaldehyds," Annalen der Physik, Folge 4, 84 (1927): 245-278.

[56]Katz, "X-ray Spectrography of Polymers," p. 79.

[57]See Staudinger, Arbeitserinnerungen, p. 86.

[58]"About two years after my call to the chemistry chair at the University of Freiburg, one of my older colleagues from the Freiburg faculty told me that he had heard from Erlangen that through Pummerer's work the question of the structure of rubber was solved, and that my concept therefore was untenable. I asked him if he and the faculty were now of the opinion that they had made a mistake by offering me the chair!" Ibid., p. 247. Rudolf Pummerer was an influential supporter of Harries' theory of rubber structure; in 1928 he claimed that his molecular weight measurements confirmed the aggregate structure of rubber with the formula $(C_5H_8)_8$. R. Pummerer and W. Gündel, "Über Darstellung and Molekulargrösse des Isokautschuk-nitrons," Ber., 61 (1928): 1591-1596.

[59]See Herman F. Mark to Hermann Staudinger, January 5, 1927, cited in Claus Priesner, H. Staudinger, H. Mark und H. Meyer: Thesen zur Grösse und Struktur der Makromoleküle (Weinheim; Deerfield Beach, Florida; and Basel: Verlag Chemie, GmbH, 1980), pp. 65-66.

[60]Carl W. Nägeli, Das Mikroskop: Theorie und Anwendung desselben 2nd ed. (Leipzig: W. Engelmann, 1877), p. 424 ff.

[61]E.g., Kurt H. Meyer and Herman F. Mark, "Über den Bau des kristallisierten Anteils der Cellulose," Ber., 61 (1928): 593-614, especially p. 609; "Über den Kautschuk," ibid.: 1939-1949.

[62]Kurt H. Meyer, "Räumliche Vorstellungen über den Bau der Kohlenstoffverbindungen und ihre Verwendeng in der Chemie der Hochpolymeren," Kolloid-Z., 53 (1930): 8-17, on p. 13.

[63]Hermann Staudinger, "Die Chemie der hochmolekularen Stoffe im Sinne der Kekuléschen Strukturlehre," Z. angew. Chem., 42 (1929): 37-40, 67-73; "Schlusswort (zu den Bemerkungen von K. H. Meyer)," ibid., p. 77.

[64]Herman F. Mark, "Interview with Herman F. Mark," J. Chem. Educ., 56 (1979): 83-86, on p. 84.

[65]The debate between Staudinger and Meyer-Mark has been extensively documented in Priesner's H. Staudinger, H. Mark und K. H. Meyer, pp. 65-216.

[66]"I cannot agree with him [Meyer] on two points. First, in my opinion, the statements of K. H. Meyer are not new, but coincide with the views that I have held for years and established experimentally; secondly, I do not believe that the introduction of 'primary valence chains', instead of macromolecules, serves for the clarification of the problem." Hermann Staudinger to Herman F. Mark, October 31, 1981; cited in ibid., p. 87.

[67]"I believe that we should put forward the viewpoint of this inquiry [the concept of long-chain molecules] and not emphasize the differences in our own conceptions. Otherwise, the high polymer camp could easily fall into error, which is merely well known from politics. Because of slight differences in neighboring opinions, a larger point of view does not get sufficient attention, nor does it find any vigorous expression." Herman F. Mark to Hermann Staudinger, November 2, 1928; cited in ibid., p. 92.

[68]Kurt H. Meyer, "Bemerkungen zu den Arbeiten von H. Staudinger," Z. angew. Chem., 42 (1929): 76-77. This article was followed by Staudinger's "Schlusswort" or final word (see n. 63).

[69]The debate over the same issues between Staudinger and Meyer continued at the Faraday Society meeting, held in Cambridge in September 1935. At this meeting, Meyer claimed that the problem as to whether substances such as cellulose are built up from macromolecules or from micelles had not been settled yet. Staudinger responded, "I regret Professor Kurt Meyer once more brings forward a question which I consider to have been answered long ago by the discussions of recent years." See Trans. Faraday Soc., 32 (1936), pp. 115-116 and 120-121. According to Staudinger, the controversy between Staudinger and Meyer-Mark ended after 1935 when the latter accepted Staudinger's conception of macromolecules. See Staudinger, Arbeitserinnerungen, p.93. Cf., Priesner, H. Staudinger, H. Mark und K. H. Meyer, pp. 191-216.

[70]Hermann Staudinger, "Über hochpolymere Vergindungen: Organische Chemie und Kolloidchemie," Kolloid-Z., 53 (1930): 19-30.

[71]These results were published in Hermann Staudinger and Ryuichiro Nodzu, "Viskositätsuntersuchungen an Paraffin-Lösungen," Ber., 63 (1930): 721-724; Hermann Staudinger and Eiji Ochiai, "Viskositätsmessungen an

Lösungen von Fadenmolekülen," Z. physik. Chem., (A), 158 (1932): 35-55. See also, Ryozo Goto and Kazuhiro Maruyama, "Nodzu sensei to Staudinger kyoju " (Master Nodzu and Professor Staudinger), Kobunshi (High Polymers, Japan), 32 (January 1983): 48-51.

[72]Staudinger, "Über hochpolymere Verbindungen," p. 28 ff. See also Hermann Staudinger and Werner Heuer, "Beziehungen zwischen Viskosität und Molekulargewicht bei Polystyrolen," Ber., 63 (1930): 222-234. Staudinger's Law was expressed by the following equation:

$$\eta_{sp}/C = Km \times M$$

where η_{sp} = specific velocity; C = concentration; Km = constant; and M = molecular weight. Staudinger had developed this formula as early as the fall of 1929. Robert Olby explains the context in which Staudinger conceived this viscosity formula:

> What Staudinger now required in order to establish this relationship [a proportionality between viscosity and molecular weight] was an independent method of molecular weight estimation. The obvious choice was Svedburg's ultracentrifuge [see Ch.II, p. 28]. . . . But the Nothgemeinschaft der deutsche Wissenschaft refused Staudinger's request for a grant to purchase this instrument. Magda Staudinger [his wife who was a plant physiologist] can recall a beautiful Sunday walk she took with her husband in the autumn of 1929 on the nearby Schönberg. Staudinger had just learnt the decision of the authorities. Evidently they considered work on the size of polymers, using this new-fangled and expensive instrument, a waste of time. He was very angry. On the walk their conversation turned to viscosity, end-group analysis and osmometry. When they returned home around 6 p.m. Staudinger "sat at his table and started to write and think. It was at two o'clock in the morning that the viscosity formula was on the table in front of him" (M. Staudinger, RS). This was the well-known Staudinger Law expressing the relationship between molecular weight and specific viscosity η_{sp} which represented the relative increase in the viscosity of a liquid due to the addition of the solute molecules per unit of concentration.

Robert Olby, The Path to the Double Helix (Seattle: University of Washington Press, 1974), pp. 14-15. Instead of the ultracentrifuge which was not available to him, Staudinger had to use conventional methods of molecular weight measurement. He had known that those available methods presented some difficulty in determining molecular weights of high polymers. For this reason, Staudinger chose as samples the so-called "Hemikolloide" with molecular weight only 2000-5000 which could be measured relatively easily. On the basis of these data, he was able to confirm the validity of his formula, and he thought that it could be applied to compounds with larger molecular weight.

[73]See Staudinger's discussion remarks in Kolloid-Z., 53 (1930), p. 42.

[74]Kurt H. Meyer, "Räumliche Vorstellungen" (see n. 62). Herman Mark, "Über das Verhalten der Hochpolymeren in Lösung," Kolloid-Z. 53 (1930): 32-41.

[75]Reginald O. Herzog, "Zur Deformation hochmolekularer Verbindungen," ibid.: 46-51; Kurt Hess, "Über alte und neue Auffassungen der Zellulosekonstitution und ihre experimentellen Grundlagen," ibid.: 61-75; and Rudolf Pummerer, "Zur Konstitution des Kautschuks," ibid.: 75-78.

[76]"My discussion does not intend to refute the view that the number of the C_6-group in the cellulose molecule can be very large. The intention in my presentation is to illuminate only experimental facts a little more sharply than before. One can hardly avoid the impression that the phenomena are more complicated than they appeared at the beginning, and that in order to elucidate them further we need new experimental data.

"In this sense, if it provokes new investigations, I am a friend of the old view of Emil Fischer and Bernard Tollen, revived by the work of Meyer and Mark in a new form. Even if this view must be abandoned or revised some day, it will not lose its great value; because the expression, 'the truth is what is fruitful!' would hold good in this difficult field more than for many others." Hess, "Über alte und neue Aufassungen," pp. 74-75.

[77]Ichiro Sakurada, Kobunshi-kagaku to tomo ni (Along with Macromolecular Chemistry) (Tokyo: Kinokuniya Shoten, 1969), p. 50.

[78] "In the spring of 1931 when I was leaving Hess' laboratory [at Kaiser Wilhelm-Institut für Chemie], he told me: 'If I now give up this research, the public would think that the macromolecular theory of cellulose has been established by the German scientists. But the truth is not so simple as they have claimed. There are still many tasks to be done and many problems to be solved. Unlike Karrer and Bergmann, I will not give up this problem and I will continue thoroughly my research from the point of view which I have maintained for years." ibid., p. 51.

[79]Doctoral students who wrote their dissertations under Staudinger between 1928 and 1935 include: Werner Stark, Diomidis Russidis, Heinrich Thron (1928); Werner Heuer, Herbert F. Bondy (1929); Otto Schweiter, August Schwalbach, Walter Feist (1930); Willi Schaal (1931); Ernst Trommsdorff, Werner Kern, Heinrich Lohmann, E. O. Leopold (1932); Adorf Steiner (1933); Emil Dreher, Hajo Eilers, Heinz Schwalenstöcker (1934); Hans von Becker, Hubert Frey, Hans-Peter Mojen, Bernhard Ritzenthaler, Karl Rössler, and Friz Staiger (1935). Their dissertations are listed in the bibliography in Staudinger, Arbeitserinnerungen, Pt. 2. See also Ch. IV, p. 151.

[80]Hermann Staudinger, Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose (Berlin: Verlag von Julius Springer, 1932).

[81]On Svedberg's ultracentrifuge, see T. Svedberg and K. O. Pederson, The Ultracentrifuge (Oxford: Oxford University Press, 1940); Olby, The Path to Double Helix, pp. 11-21; and J. W. Williams. "The Development of the Ultracentrifuge and Its Contributions," in Annals of the New York Academy of Sciences, 325 (1979), The Origins of Modern Biochemistry: A Retrospect on Proteins, ed. P. R. Srinivasan, Joseph S. Fruton, and John T. Edsall: 77-91. Staudinger's 1932 textbook refers briefly to Svedberg's work on the ultracentrifuge in support of his arguments. See Staudinger, Die hochmolekularen organischen Verbindungen, pp. 38 and 101.

[82]Mark and Bruson, "Hermann Staudinger," p. 388.

[83]Quarles, "Hermann Staudinger," p. 120.

[84]Emil Ott, quoted in "Nobel Prize to German, Hollander," Chem. Eng. News, 31 (1953): 4760-4761, on p. 4761.

[85]"There is an essential difference between a simple and uniform material and a high molecular substance, the neglect of which prevented application of the molecule concept. All molecules have the same size in simple uniform compounds. On the contrary, high molecular compounds are mixtures of molecules of similar structure but different size. A separation into uniform products is not possible due to the small differences in their physical and chemical properties. If a molecular weight for high polymers is given, it can only be an average value." Staudinger, "Chemie," (n. 35), pp. 3021-3022.

[86]Hermann Staudinger, Makromolekulare Chemie und Biologie (Basel: Verlag Wepf & Co., 1947), especially on p. 134 ff; "Macromolecular Chemistry: Nobel Lecture, December 11, 1953," in Nobel Lectures: Chemistry, 1942-1962., ed. Nobel Foundation (Amsterdam, London, and New York: Elsevier, 1964): 397-419, on pp. 415-416. On the biological significance of Staudinger's macromolecular theory, see Robert Olby, "The Macromolecular Concept and the Origins of Molecular Biology," J. Chem. Educ., 47 (1970): 168-174; Olby, The Path to Double Helix, Chs. 2 and 3; Robert Olby, "The Significance of the Macromolecules in the Historiography of Molecular Biology," History and Philosophy of the Life Sciences, 1 (1979): 185-198; and John T. Edsall, "Proteins as Macromolecules: An Essay on the Development of the Macromolecule Concept and Some of Its Vicissitudes," Archives of Biochemistry and Biophysics, Supplement 1 (1962): 12-20.

[87]Hermann Staudinger, "Über die Einteilung der Kolloide," Ber., 68 (1935): 1682-1691; "Über Cellulose, Stärke und Glycogen," Naturwiss., 25 (1937): 673-681, on p. 681; and Staudinger, "Nobel Lecture," p. 404 ff.

[88]Staudinger, "Nobel Lecture," p. 404 ff.

[89]The concept of a flexibility of polymer chains, developed since

1932 by Mark, Werner Kuhn (1899-1963) and others, also provided an account of some physical properties of high polymers. Staudinger did not pursue this notion, maintaining that most of the macromolecules are stiff like a thin glass thread. In 1932 he explained that his viscosity law, ". . . can only be understood on the assumption that the molecules possess a rigid fiber shape. . . . In order to demonstrate my opinion about these molecules by a comparison, I would compare such a molecule with a thin flexible glass fiber, and not with a wool fiber, which is capable of assuming any shape. Of course, these molecules cannot be compared with absolutely rigid rods. But a rigid shape of the molecules seems to me to be necessary from very general experiences in organic chemistry. The large number of organic compounds is only to be understood if their molecules are rigid." Staudinger, a discussion remark, in Trans. Faraday Soc., 29 (1933), pt. 2, p. 44. This view of rigid molecules was however later revised. See further discussion on this issue in Ch. IV, pp. 146-148.

[90]"Molecules as well as macromolecules can be compared with buildings which are built essentially from a few types of building stones: carbon, hydrogen, oxygen, and nitrogen atoms. If only 12 or 100 building units are available, then only small molecules or relatively primitive buildings can be constructed. With 10,000 or 100,000 building units an infinite variety of buildings can be made: apartment houses, factories, skyscrapers, palaces, and so on. Constructions, the possibilities of which cannot even be imagined, can be realized. The same holds for macromolecules. It is understandable that new properties will therefore be found which are not possible in low molecular materials." Staudinger, Arbeitserinnerungen, pp.94-95;From Organic Chemistry to Macromolecules, p. 92. See also Staudinger, "Nobel Lecture," p. 414.

[91]As the American polymer chemist Carl S. Marvel (1894-) observed, in Staudinger's time many chemists "did not realize that macromolecules could have some properties which were determined by the size and shape of these big molecules." Carl S. Marvel, "The Development of Polymer Chemistry in America--The Early Days," J. Chem. Educ., 58 (1981): 535-539, on p. 536.

[92]In this context it is interesting to note that Staudinger held some holistic conception of life as well as matter. In reference to the minimum size of organisms, he stated, "The known facts of macromolecular chemistry show further that an individual macromolecule is still not living, however large it is and however complex its structure. On the contrary, the term is relevant to a certain amount of substance comprising numerous macromolecules with the constituent small molecules combined together by strictly prescribed order, an 'atomos' of living matter which is indivisible without losing its livingness." Thus, the living nature cannot be correctly understood by reducing the ordered whole of the "atomos" to its small parts. See Staudinger, "Nobel Lecture," p. 416 ff. Cf., Olby, "Significance of Macromolecules," p. 194. On physiological holism in the early twentieth century, see, e.g., Garland E. Allen, Life Science in the Twentieth Century (New York, London, Sydney, and Toronto: John Wiley Sons, Inc., 1975), pp. xix-xxiii and 103ff; Joseph S.

Fruton, Molecules and Life: Historical Essays on the Interplay of Chemistry and Biology (New York, London, Sydney, and Toronto: Wiley-Interscience, 1972), especially pp. 485-503; and Marcel Florkin, A History of Biochemistry (Comprehensive Biochemistry, 30) (Amsterdam, London, and New York: Elsevier, 1972), especially pp. [1]-[6].

[93]"Amidst the quantitative methods of modern chemistry, your attention was attracted by a zone in the chemical structure of our material world--and this seems very notable to me in which the quantum, the number of building units and elements of the material substances, are not anymore only a quantum but go over to quality, to cite a thought from Hegel's logic. You became aware of configurations and formations in which law, order, and shape--e.g., the shape of chains and rings of various types--are more important than the mere number of building units or the elementary active forces. Perhaps I may illustrate the point, where the quantum changes to quality by an allegory. Let us go with you and your science in the way you first went, thinking and exploring the way from classical quantitative chemistry to macromolecular chemistry. On this way it seems that we first walked over a big construction area, filled with a lot of valuable raw material, stones, iron bars, woods, and more things of this sort, and then we stepped in front of a building, a big house, perhaps a cathedral. A cathedral which certainly is more than the sum of the many single working units and building materials from which it is built up. It is more because the multitude of single building units are combined in it to a formed unity of higher level and of higher range. The quantum became a quality." Bernhard Welte, quoted in Staudinger, Arbeitserinnerungen, pp. 305-306; From Organic Chemistry to Macromolecules, pp. 240-241.

[94]Staudinger, "Nobel Lecture," p. 414.

[95]Staudinger, Arbeitserinnerungen, pp. 94-101.

CHAPTER III

WALLACE HUME CAROTHERS AND THE MACROMOLECULAR SYNTHESIS

I went into another room [at the Grand Academy of Lagado], where the walls and ceiling were all hung round with cobwebs, except a narrow passage for the artist to go in and out. At my entrance he called aloud to me not to disturb his webs. He lamented the fatal mistake the world had been so long in of using silk-worms, while we had such plenty of domestic insects, who infinitely excelled the former, because they understood how to weave as well as spin. And he proposed farther that by employing spiders the charge of dyeing silks should be wholly saved, whereof I was fully convinced when he showed me a vast number of flies most beautifully colored, wherewith he fed spiders, assuring us that the webs would take a tincture from them; and as he had them of all hues, he hoped to fit everybody's fancy, as soon as he could find proper food for the flies, of certain gums, oils, and other glutinous matter to give a strength and consistence to the threads.

--Jonathan Swift,
Gulliver's Travels (1726).

Our studies of polymerization were first initiated at a time when a great deal of scepticism prevailed concerning the possibility of applying the usually accepted ideas of structural organic chemistry to such naturally occurring materials as cellulose; and its primary object was to synthesize giant molecules of known structure by strictly rational methods.

--Wallace Hume Carothers,
"Artificial Fibers from Synthetic Linear Condensation Superpolymers," 1932.

A half century later Mark said two developments prevented his "more active" involvement. One was his and Meyer's belief that Staudinger had completely established his priority in proposing long chains. The second was the work of W. H. Carothers' which convinced him in 1929 that the long chain connection of natural and synthetic polymers would soon be irrevocably resolved.

--G. Allan Stahl,
"The Geheimrat," 1981.

While Hermann Staudinger's chemistry was under attack in German academic circles, Wallace Hume Carothers (1896-1937) in the United States embarked on a series of investigations on the mechanism of polymerization in the late 1920s. His systematic study strongly supported Staudinger's view of the macromolecularity of polymers and had immediate impact on his contemporaries. Although he belonged to the organic-structural tradition of Staudinger, his scientific style and career were sharply in contrast to those of his German counterpart. Trained as an organic chemist without the background of German chemical training from which earlier generations of American chemists often had benefitted, Carothers was a product of American pragmatic education after World War I. He was a research chemist in industry, unlike the university man Staudinger who was imbued with the ideal of German Wissenschaft. All of his work on polymers and polymerization was carried out with a number of his co-workers in the fundamental research program at the Du Pont Company during the period between 1928 and 1937. His approach to polymers was characteristically synthetic; with his theory of polymerization, he built up artificial macromolecules, the existence of which was then still controversial in scientific circles. Within the industrial framework, Carothers' theoretical work on the macromolecular synthesis led directly to practical applications such as the production of the first synthetic fiber, nylon. The way in which he pursued his research on polymers exhibits a remarkable character inherent in the tradition of American science as a whole, which we must take into consideration.

Young Carothers: Background

Wallace Hume Carothers, born in Burlington, Iowa, on April 27, 1896, was the eldest son of a middle-class, High Presbyterian family of Scottish descent.[1] His ancestors were farmers and artisans, and he was the first scientist in the family. His father, Ira Hume Carothers, a teacher, was later a vice president of the Capital City Commercial College, Des Moines, Iowa. His mother, Mary Evalina McMullin Carothers, a sensitive woman, instilled a love of music in her son. His intensive interest in and appreciation of music, especially classical music, continued throughout his life. He later remarked, on occasion, that were he to start over he would devote his life to music. As a young boy, Wallace displayed a deep love for books, finding special amusement in Gulliver's Travels, Mark Twain's books, and the Life of Thomas Edison. He also displayed a marked mechanical aptitude and spent much time in boyhood experiments. A moody perfectionist, the shy and modest young Carothers possessed a habit of leaving no work unfinished; to begin a task meant to him to accomplish and complete it. His restless devotion to work, later exhibited in his scientific work, was a characteristic shaped by the stern Protestant ethic of his Midwestern upbringing.[2]

Carothers began his college education by studying business. After graduating from North High School in Des Moines, he spent the 1914-1915 academic year mastering the accounting and secretarial curriculum at his father's commercial college. In 1915 Carothers enrolled in Tarkio College, a Presbyterian liberal arts college in northwestern Missouri, where he began his scientific studies. Thanks to his prior experience he was immediately made an assistant in Tarkio's commercial department;

he earned his educational expenses by teaching accounting for two years until he assumed a teaching position in the English department.

It was during this period, at the encouragement of his chemistry teacher, Arthur McCay Pardee (1885-1962), that Carothers decided on chemistry as his career. The young instructor, Pardee, who had just completed his own doctoral thesis on the conductivity of organic compounds under Harry Clary Jones (1865-1916) of the Johns Hopkins University,[3] taught Carothers organic chemistry and physical chemistry in his sophomore and junior years. In Pardee's recollection of Carothers,

> His interest in chemistry and the physical sciences was immediate and lasting, and he rapidly outdistanced his classmates in accomplishment. Throughout this entire time he helped his chemistry instructor [i.e., Pardee] in sustaining interest in the work of the department.[4]

Elsewhere, Pardee wrote, "I had a number of talks with him in which I showed that the sky was the limit in what he could accomplish."[5] During World War I when Pardee was called to Washington and Jefferson College, Washington, Pennsylvania, Carothers was appointed to take the teaching responsibility in chemistry. Exempted from military service on account of "a slight physical defect,"[6] the student thus served in the joint capacity as undergraduate and instructor until his graduation.

Leaving Tarkio College in 1920 with his bachelor's degree, he began graduate study at the chemistry department of the University of Illinois in Urbana, receiving the master of arts degree in the summer of 1921.[7] He spent the following academic year as instructor at the University of South Dakota, Vermillion, where his former teacher, Pardee, moved to head the chemistry department. During this year, Carothers developed his idea of the application of the electronic theory of valence to organic compounds.

Inspired by recently proposed theories in physical chemistry, particularly Gilbert Newton Lewis' theory of the shared-pair electron bond and Irving Langmuir's octet theory of valency, Carothers investigated their implications in his major field, organic chemistry.[8] The result was his first independent paper, "The Isosterism of Phenyl Isocyanate and Diazobenzene-Imide," which appeared in 1923 in the Journal of the American Chemical Society. Here he attempted to demonstrate that the two compounds, phenyl isocyanate and diazobenzene-imide, have identical atomic and electron arrangements.[9] His theoretical paper of 1924, "The Double Bond," extended his views to a general argument for reaction mechanisms (such as addition processes) of the double bond on the basis of the electronic theory.[10]

Despite his ambitious effort to combine the Lewis-Langmuir theory and organic reactions, this early work remained an isolated phenomenon at that time. American organic chemists in general rather resented the intrusion of these physical concepts of the sub-atomic structure into the realm of organic chemistry.[11] As his close friend John Raven Johnson (1900-) testified, his paper on the double bond was then considered "too fanciful" by many of his contemporaries. Indeed, "it barely escaped the editor's wastebasket in 1924."[12] Apparently, the electronic interpretation of organic reactions captured Carothers' mind for several years. However, after his later paper on this subject met a referee's strong criticism that "the author seems to attach an unwarranted measure of sanctity to the 'octet rule,'" Carothers no longer pressed the issue publicly.[13]

Returning to the University of Illinois in 1922, Carothers turned

to the more traditional mode of research in organic chemistry. Under the direction of the influential teacher, Roger Adams (1889-1971), he worked on his doctoral thesis on the catalytic reduction (hydrogenation) of aldehydes over the "Adams catalyst," a platinum oxide.[14] Adams had been educated at Harvard University, receiving the Ph.D. in 1912 under Charles Loring Jackson (1847-1935).[15] In 1912-13 he had studied in Germany under Otto Diels (1876-1954), then Privatdozent in Emil Fischer's laboratory at the University of Berlin, and later under Richard Willstätter, the rising star in German organic chemistry at the Kaiser Wilhelm Institut für Chemie.[16] At Berlin, Adams also attended lectures by Fischer, who was then sixty years old but still active in his study of proteins. After returning to the United States, Adams' interests continued along traditional lines of organic structural chemistry and organic syntheses, little influenced by the emerging trends of the physico-chemical applications to organic chemistry. Adams joined the faculty of chemistry at the University of Illinois in 1916 with this background.

Especially significant was the emphasis on synthetic chemistry in his research and education. During World War I, when the German sources of organic chemicals were cut off, Adams turned a summer project for the preparation of organic chemicals for classroom and research use (an enterprise called "Organic Chemical Manufactures") into a pilot-plant production of chemicals for war and industrial use. The Illinois venture was continued after the war, to introduce students to industrial operations. Bulletins were soon issued on the synthetic methods developed at Illinois, and in 1921 they were transformed into the monograph

series, Organic Syntheses.[17] During the next forty nine years, Adams served as a chief member of the Advisory Board for this series.

Adams' adherence to synthetic chemistry much reflected his pragmatic approach to chemistry. Although trained in German Wissenschaft, he was a "Yankee scientist" who vigorously challenged the tradition of "pure" chemistry for its own sake--an ideal which William Albert Noyes (1857-1947) had maintained as the department director at Illinois between 1907-1926. At a time of dramatic expansion of industrial research in this country, following World War I, Adams held the view that one of the primary responsibilities of universities ought to be to train chemists for industry. Chemistry must exist for and serve society. Through his close contacts with the chemical industry, he found positions for many of his students, while he himself served as consultant for several large chemical firms, including the Du Pont Company.[18] The synthetic approach and pragmatic orientation of the Adams school no doubt exerted a profound influence upon Carothers' career and style in chemistry, culminating in his study at Du Pont.

Carothers received his Ph.D. degree in 1924. The friendship between Carothers and his young teacher, Adams, lasted throughout the rest of the student's brief but productive life. According to Adams, at graduation Carothers "was considered by the staff as one of the most brilliant students who had ever been awarded the doctor's degree" in the department of chemistry at the University of Illinois.[19] Impressed by Carothers' ability and promise, Adams arranged his student's appointment as an instructor in organic chemistry at Illinois. In 1926 Carothers moved to Adams' alma mater, Harvard University, where he taught organic

and structural chemistry until he accepted a position as research chemist at Du Pont in early 1928.

Du Pont had set up a new program for fundamental research in its Chemical Department as early as 1927, following the suggestion of Charles Milton Altland Stine (1882-1954), the Chemical Director and later a Vice President of the Company. Modeled on precedents such as the research laboratory at the General Electric Company where Irving Langmuir (1881-1957) was successfully working on the incandescent light bulb, the Du Pont program however went even further. The function of the program was to discover and establish new scientific facts without regard to practical problems or immediate practical use. Stine intended to separate fundamental research from applied research concerned with existing processes and products. In this way, he tried to create a research environment which closely approximated conditions of the university laboratory, but with better facilities and more funds. Yet, obviously, Stine hoped that this type of research would eventually yield new products without depending on university science or outside technology, and that it would thus benefit the Company in the long run. Du Pont was willing to risk a few thousand dollars on this venture. In starting the program, the Company President, Lammot du Pont, requested only that it be carried out in fields relating to the Company's interest. Following this policy, colloid chemistry, physical chemistry, organic chemistry, and physics became the subjects of the first program.[20]

The thirty-one-year old Harvard instructor, Carothers, was hired to head the organic chemistry group, highly recommended by his teacher, Roger Adams, and by his colleague at Harvard, James Bryant Conant (1893-1978). The job appeared sufficiently attractive to cause him to leave

Harvard's academic life. The position demanded only research; he was promised a staff of trained scientists as assistants to work on any problems of his own selection. On February 6, 1928, Carothers began work in the new laboratory of the Du Pont Experimental Station in Wilmington, Delaware--a building dubbed "Purity Hall" by the other Du Pont chemists in reference to its devotion to pure research. Eight days after he came to the Company, Carothers wrote his friend, John Raven Johnson, about his new life as a Du Pont research chemist:

> Regarding the funds, the sky is the limit. I can spend as much as I please. Nobody asks any questions as to how I am spending my time or what my plans are for the future. Apparently it is all up to me. So even though it was somewhat of a wrench to leave Harvard when the time finally came, the new job looks just as good from this side as it did from the other. According to any orthodox standards, making the move was certainly the correct thing.[21]

At Purity Hall Carothers chose polymers for his research problems, a field in which he had neither published a paper nor performed any experiment, but in which he had developed an interest at Harvard.

Polymer Research in the American Scene: Reactions to the Macromolecular Concept

Carothers' decision to start the study of polymers was understandable not only because of his own interest, but also because of the Du Pont Company's background. Soon after the First World War, Du Pont had been transformed from a traditional explosives manufacturer into a maker of chemicals. By the middle of the 1920s, Du Pont's chemical products included artificial leather, nitrocellulose plastics, rayon, and cellophane, the products recognized as polymers by chemists. Elmer Keiser Bolton (1886-1968), Adams' friend and the director of the Chemical Section of the Du Pont Dyestuff Department, also initiated a small project on synthetic rubber

just before Carothers came to the Company.[22] Thus, Du Pont was primarily a polymer company. Carothers' fundamental research on polymers appeared to fit Du Pont's interests perfectly. Perhaps, what was significant in this context was not his selection of the field, but his acceptance of the macromolecular theory of polymeric substances from the outset of his research.

Between 1920 (the year in which Hermann Staudinger proposed his theory of large molecules) and 1928 (the year when Carothers embarked on his study of polymerization), a number of Americans were working on the problems of polymers such as rubber, cellulose, and proteins. However, Staudinger's theory drew little attention from the American investigators, especially in the first half of the decade. To examine the American reactions to the macromolecular concept before 1928, we must consider first the outlook of the chemical communities following World War I, and secondly, the internal or theoretical background in which American chemists were concerned with polymeric materials.

In the early 1920s, German scientific circles were isolated from those in America, Britain, and France. An unsettled political situation in Germany, amounting almost to civil war, and a devastating inflation around 1920 increased greatly the difficulties of travel and exchange of information between Germany and the Allies. A postwar nationalistic mood on both sides extended to science. In early 1920 an American protein chemist, Jacques Loeb (1859-1924), stated, "From all I hear the Germans are still on the whole in a very hostile attitude towards scientific work done in this country."[23] This is further illustrated by the fact that the International Union of Pure and Applied Chemistry was organized officially by the war victors in 1920. The Germans and Austrians were excluded from its conferences, since their scientists were

considered to be tainted with war-guilt and not fit to attend international meetings. The antipathy to the Germans among American chemists, as among British and French chemists, continued even in the mid-1920s. The attitude of Theodore William Richards (1868-1928) of Harvard, as reported by his colleague Conant, illustrates the widening breach in scientific communications between the wartime allies and Germany:

> His [i.e., Richards'] condemnation of the Germans [around 1925] was as total as it had been in August 1914. He had made no move to re-establish communications with his former scientific friends in what he now considered to be a hopelessly barbaric land.[24]

Given this historical context, it is not surprising that the allied chemical community was uninformed about the advances in the German community during the postwar period. Consequently, the upheaval in German chemistry in the early 1920s, namely, the emergence of the macromolecular theory, did not raise immediate reactions in Britain, France, and the United States; instead, the heated debate over Staudinger's theory remained a German phenomenon for the time being. In the 1920s, Staudinger's ideas were discussed on several important occasions in Austria, Switzerland, and Germany: in 1924 at the Innsbruck meeting of the Deutsche Naturforscher und Ärzte; in 1925 at a meeting of the Züricher Chemischen Gesellschaft; and in 1926 at the Düsseldorf meeting of Deutsche Naturforscher und Ärzte. The macromolecular debate reached its peak on the occasion in Düsseldorf. But it was not until the early 1930s that Staudinger and other German scientists brought up this issue at scientific meetings outside the German chemical circles.[25] Although Staudinger's views were available to Americans in such journals as the Berichte der Deutschen Chemischen Gesellschaft, Chemical Abstracts, and the Journal of the Chemical Society, Abstracts of Papers,

they were seldom cited in American articles. Thus, one suspects that the infrequency of reaction to the macromolecular concept in the United States between 1920 and 1928 was in part the result of postwar Germany's intellectual isolation.

Staudinger remained Professor at the Eidgenössische Technische Hoschschule in Zürich, where a number of German chemists occupied teaching positions, until he accepted a position in Freiburg im Breisgau in 1926. In Zürich he introduced the study of macromolecules to seventeen doctoral students, most of them Swiss or German.[27] During this period, there were two Americans who studied this field under Staudinger. Herman Alexander Bruson (b. 1901), a native of Ohio, wrote his dissertation, "Die Polymerisation von Cyclopentadien und Inden," under Staudinger's direction in 1925. He published three papers on this subject in German and Swiss journals in 1926 and 1929. After graduation, Bruson went to U.S. industrial firms and worked on practical fields.[28] Another American, Avery Allen Ashdown (b. 1891), a graduate of the Massachusetts Institute of Technology, received his postdoctoral education as a Moore fellow in Staudinger's laboratory between 1924 and 1925. He worked with Staudinger on the constitution of synthetic polymers such as polyindenes and poly-α-phenyl butadiene. The results of this study were published later in 1929 in a German journal (together with Bruson as well as Staudinger) and in 1930 in a Swiss journal. After returning to the United States in 1925, Ashdown, however, did not pursue this field further. He remained a faculty member at the Massachusetts Institute of Technology where his interests turned to the problems of organic reactions of normal low-molecular substances.[29] Aside from their German papers, the two American

students of Staudinger did not exert any visible influence upon polymer research in this country in the 1920s.

In the late 1920s, Staudinger's work was mentioned by some English-speaking chemists. An English cellulose chemist, Walter N. Haworth (1883-1950), for example, began citing Staudinger's theory of macromolecules in 1928 in the Annual Reports on the Progress of Chemistry, published by the Chemical Society of London.[30] The English-born rubber chemist, George Stafford Whitby (1887-1972) of McGill University in Montreal, made remarks in favor of Staudinger's views on occasion.[31] But despite this information available to American readers, the macromolecular concept still was largely ignored in American scientific circles.

There were good reasons that American chemists were, by and large, not receptive to the ideas of very large polymer molecules in the 1920s. Ironically this "chemical Zeitgeist" had been to a large extent determined by prewar German influence. Emil Fischer's elaborate study of proteins through the syntheses of artificial polypeptides was widely recognized by many American organic chemists. His famous 1913 lecture before the Naturforscher Versammlung in Vienna was translated into English and appeared in the next year in the Journal of the American Chemical Society. It was in this lecture that Fischer declared the molecular weight 4021 of his synthetic compound to be the highest of all synthetic substances of known structure and even of all natural proteins. This statement turned out to be an influential dictum convincing American chemists that compounds of molecular weight greater than approximately 5000 do not exist.[32]

The influence of the Ostwaldian tradition on American colloid

chemists also played a part in the American rejection of the concept of large molecules. Prior to 1910 few systematic studies of colloid chemistry had been carried out in the United States. In late 1913 to 1914, the son of Wilhelm Ostwald, Wolfgang Ostwald, the German leader of colloid chemistry, came to America to give his series of lectures in this field. His successful lectures drew considerable attention from the American audience. "Originally invited by five universities," Ostwald noted, "I found the interest in the science [in this country] . . . so great that their number grew to sixteen while the actual number of lectures demanded of me during some seventy-four days was fifty-six."[33] He evangelistically spread his colloid doctrine at many universities, including the University of Cincinnati, the University of Illinois, Columbia University, Johns Hopkins University, the University of Chicago, Ohio State University, the University of Pittsburgh, the University of Nebraska, and the University of Kansas; and he lectured before the National Academy of Sciences and the American Chemical Society as well. As Ralph Edward Oesper (1886-1977) of the University of Cincinnati reported, "Those who heard his wonderfully interesting and well illustrated talks were infected with enthusiasm and went away with a fuller comprehension of what colloid chemistry was and could become."[34] From these lectures resulted his book, Die Welt der vernachlassigten Dimensionen (1914), the English translation of which appeared in 1917, amidst the war, but won wide readership in this country well into the next decade.[35] Through his lectures and publications, a number of Americans were inspired to go into colloid chemistry, a branch of science both of theoretical and practical significance.[36] As American colloid chemistry

arose, the Ostwaldian doctrine, which viewed colloids as a physical state of matter, penetrated the chemical community.

Among the leading schools of colloid chemistry in this country in the 1920s was one founded by the physical chemist, Wilder Dwight Bancroft (1867-1953) at Cornell University.[37] Bancroft, a student of Wilhelm Ostwald, was an advocate of his teacher's ideal of allgemeine Chemie that would serve to unify the various branches of chemistry. Physical chemistry in Bancroft's view, was not merely a branch of chemistry but covered the whole of chemical science. Furthermore, he claimed that other sciences, such as biology, medicine, and even physics, are "all subdivisions of chemistry." "It should be the aim of all chemists to have chemistry take its place as the fundamental science and that can only be done by and through the physical chemist."[38] At Cornell he founded the Journal of Physical Chemistry (1896-), the first English-language periodical to cover physical chemistry. During the 1910s and 1920s, Bancroft's interest increasingly centered on colloid chemistry, a field which he considered as a significant part of physical chemistry and as still being in the early stages of development. By the end of World War I, almost half of the contents of his journal were concerned with topics in colloid chemistry.[39]

In 1921 Bancroft published a popular textbook, Applied Colloid Chemistry, of which two further editions appeared in 1926 and 1932.[40] In this book, he strongly supported the view, like Wolfgang Ostwald in Germany, that colloids are not true chemical compounds but matter in a state into which any substance might be brought. As he stated,

Graham believed that the distinction between a crystalloid and a

> colloid was fundamental and was due to some molecular condition. Though modern colloid chemistry begins with Graham, his distinction between crystalloids and colloids has been dropped. A colloidal substance is not necessarily amorphous. . . . We now speak of a colloidal state instead of a colloidal substance, and we call any phase colloidal when it is sufficiently finely divided dispersed, without committing ourselves definitely as to what degree of subdivision is necessary in any particular case.[41]

Like Max Bergmann, Bancroft vigorously upheld the view that proteins are composed of the aggregates of small molecules.[42] Rejecting reported high molecular weights for proteins, Bancroft asserted that protein solutions form colloidal suspensions which consist of two phases rather than one; for this reason, they do not obey van't Hoff's laws of osmotic pressure, since van't Hoff's laws are to be applied to a true chemical solution. He stated that,

> In general the apparent osmotic pressures of colloidal solutions are very small and this has led to absurd molecular weights. Such values as 30,000 for albumin, 700,000 for glycogen, over 48,000 for silica and "enormous" for Fe_2O_3 mean nothing whatsoever.[43]

For example, he did not accept the results of the Danish chemist, Søren Peter Lauritz Sørensen (1868-1939), who in 1917 calculated a molecular weight of 34,000 for egg albumin, an egg protein, on the basis of his measurement of the osmotic pressures.[44] Sørensen's study became known to Americans after the first world war, especially through his American student, Edwin Joseph Cohn (1892-1953). According to John Tileston Edsall (1902-) who worked in Cohn's laboratory at Harvard Medical School during the 1920s,

> At a scientific meeting shortly after 1920, Cohn had an exchange of remarks with Wilder D. Bancroft, the well-known colloid chemist, which went somewhat as follows:
>
> Cohn: Sørensen has measured the osmotic pressure of egg albumin, and finds a molecular weight of 34,000.
>
> Bancroft: Yes, yes. I understand. He is measuring a system of molecular aggregates. That is the molecular weight of the aggregate.

> Cohn: But the tryptophan content and sulfur content of ovalbumin have also been determined, and they give a minimum molecular weight of 34,000.
> Bancroft: Ah! Then in that case I would say that the aggregation factor is unity![45]

In Bancroft's view, any effort to treat proteins as chemical individuals of definitive structure was a waste of time, since the solutions of a protein or any other colloid represent merely a physical state of matter, and they are not substances of particular chemical structures. So staunch was his belief in proteins as molecular aggregates, that molecular weight measurements of proteins with Svedberg's new instrument, the ultracentrifuge, did not convince him of proteins as large molecules.[46] In 1932 Bancroft pointed out that the ultracentrifuge method,

> has proved a most effective instrument in determining particle size from the rate of sedimentation. Unfortunately Svedberg . . . has preferred to give his results on proteins in terms of molecular weights instead of particle sizes and he speaks of proteins having molecular weights of 35,000-210,000 or even millions.[47]

In Bancroft's eyes, Svedberg was only confusing the particle size with the molecular weight. What appeared to others to be a decisive step toward the establishment of the macromolecularity of proteins did not convince him at all.

Despite the opposition of the Bancroft school, Cohn continued Sørensen's lines of research on the molecular weights of proteins. One of the arguments for the aggregate structure of proteins, made by Reginald O. Herzog and others in the mid-1920s, was that proteins, when dissolved in phenol, fell apart into units with molecular weights of only between 200 and 600. They suggested that proteins were therefore aggregates of these small units held together by secondary valences.[48] In 1926 Cohn

and his colleague, James Bryant Conant of the Department of Chemistry at Harvard, demonstrated, by measuring freezing points of proteins in phenol, that the low values previously obtained are due to the presence of water as an impurity in the phenol. When the water content of the phenol was eliminated, the freezing point depressions produced by the addition of proteins were extremely small, which indicated that proteins have very large molecular weights.[49] In this way, they supported Sørensen's position and rejected a prevailing argument for the aggregate theory.

While working with Cohn on proteins, however, the organic chemist Conant maintained a cautious and rather skeptical attitude to Staudinger's view that polymeric compounds with a colloidal nature are made up of macromolecules. As early as 1925 when antipathy to German chemists was still strong among his colleagues, Conant had taken a private trip to Germany to visit postwar German laboratories and to meet a number of chemists.[50] In Switzerland, he met Staudinger, then Professor of Chemistry at the Eidgenossische Technische Hochschule in Zürich. It was during the time when Staudinger's theory was under strong attack from many of his contemporaries in the Swiss-German chemical community. Staudinger later remarked:

> Als Professor James B. Conant, der spätere amerikanische Botschafter in der Bundesrepublik Deutschland, mich im Jahre 1925 im Zürcher Laboratorium besuchte, haben meine Mitarbeiter und ich ihm die Argumente für den makromolekularen Bau dieser Stoffe vorgetragen mit dem Erfolg, dass ihm bei einem anschliessenden Besuch in Deutschland erklärt wurde, er möge kein Wort von den Anschauungen Staudingers glauben![51]

Conant confessed this story later in his congratulatory letter to Staudinger in 1953 when Staudinger received the Nobel Prize in chemistry. The climate of opinion of the time, one might well suspect, led Conant to his reluctance to accept the macromolecular view of polymers.

Although he admitted the apparent high molecular weights for proteins, he did not immediately conclude that proteins are composed of long-chain molecules held together by normal valences. In his textbook, Organic Chemistry, published in 1928, he wrote:

> The question arises, are the polypeptide units in the protein molecule held together by amid-like linkages or some other way? There is at present no conclusive answer to this question. Many believe that cyclic systems are involved and even the forces which unite the polypeptide residues are different from the usual valences which hold atoms together in the simple organic compounds. This is one of the important questions now facing the chemist.[52]

Concerning the structure of rubber, he expressed more explicitly a view in favor of the aggregate theory:

> If one obtains as pure a sample as possible of crude rubber and examines it in the laboratory, one finds that its analysis corresponds to the formula C_5H_8. The material dissolves in only a few organic solvents, forming a colloidal solution. It is not possible to determine the molecular weight because the substance cannot be vaporized without decomposition, and the freezing point and boiling point methods are not applicable to colloidal solution. The formula $(C_5H_8)_n$ is often written for it. It is probable that n has a value of 10 to 15.[53]

The polymerization of isoprene molecules would yield rubber-like materials $(C_5H_8)_n$. "But we are," he continued, "still uncertain how the isoprene molecules are united in the polymer; it is possible that the ten or more molecules combine in one or several large rings."[54] Thus, Conant, like many other chemists of the time, was inclined toward the aggregate theory developed by Carl Harries and Rudolf Pummerer, although he was well acquainted with Staudinger's ideas.[55]

It was at Harvard about this period that Conant's colleague, Carothers, developed his interest in the field of polymers. As Conant observed, Carothers' "first thinking about polymerization and the structure of substances of high molecular weight began while he was at Harvard

[i.e., sometime between 1926 and early 1928.]"[56] However, he departed from Conant's interpretation of the polymer structure. "He was never content," recalled Conant, "to follow the beaten track or to accept the usual interpretation of organic reactions."[57] Carothers accepted Staudinger's concept of macromolecules and developed it into his own research project on polymerization. Despite the scepticism of Conant and other colleagues, he came to Du Pont with a research program based on this idea.

The Macromolecular Synthesis

Apparently, Carothers adopted the macromolecular view through his reading and review of Staudinger's German papers published since 1920, as is indicated by his frequent citations of Staudinger in his entire work on polymerization.[58] As an organic structural chemist, he was able to share with Staudinger the belief in the molecularity of polymers on the basis of the classical structural theory. As he later recalled, his study was "first initiated at a time when a great deal of scepticism prevailed concerning the possibility of applying the usually accepted ideas of structural organic chemistry to such naturally occurring materials as cellulose. . . ."[59] He found that the tendency to evade or ignore the molecular concept in dealing with polymers is the source of such scepticism and confusion among chemists.[60] Like Staudinger, Carothers maintained that the chemical molecule is the entity from which stemmed all physical and chemical properties of the substance. Polymers were not an exception. Hence, the unique properties of polymeric substances, such as colloidal phenomena, should be explained only by the large molecules themselves, and not by physical forces of uncertain

origin. In this way, he followed the traditional mode of organic-structural approach on which Staudinger based his arguments as opposed to the prevailing physicalist views of polymers.[61]

In demonstrating the macromolecularity of polymers and in examining their properties, Carothers, however, took a step different from Staudinger's methods from the outset of his research. In his letter to Johnson (February 14, 1928), mentioned above, Carothers went on to explain his research plan at Du Pont:

> One of the problems which I am going to start work on has to do with substances of high molecular weight. I want to attack this problem from the synthetic side. One part would be to synthesize compounds of high molecular weight and known constitition. It would seem quite possible to beat Fischer's record of 4200. It would be a satisfaction to do this. . . .[62]

In a sense, Carothers intended to extend the synthetic approach emphasized by Emil Fischer, who had attempted to elucidate the protein structure by attaining the synthesis of artificial polypeptides of known structure.[63] The object of Carothers' research was to synthesize macromolecules of definitive structure by the use of established classical organic reactions, and to examine the relation between the properties of polymers and their chemical structures. Whereas Fischer's structural scheme turned out to limit the size of the Riesenmoleküle to about 4000 in molecular weight, Carothers had no doubt about the possibility of making exceedingly large molecules from his perspectives. He continued:

> Another phase of the problems will be to study the action of substances xAx on yBy where A and B are divalent radicals and x and y are functional groups capable of reacting with each other. Where A and B are quite short, such reactions lead to simple rings of which many have been synthesized by this method. Where they are long formation of small rings is not possible. Hence reaction must result either in large rings or endless chains. It may be possible to find out which reaction occurs. In any event the reactions will

> lead to the formation of substances of high molecular weight and containing known linkages.[64]

The reaction of compounds xAx with yBy, later called a "bifunctional reaction," remained substantial for his study of polymerization. It was an application of a classical organic reaction, condensation. For example, as was long known, an alcohol (R-OH, where R is an organic radical) reacts with a carboxylic acid (R'-COOH, where R' is another organic radical) to form an ester (R'-COO-R) by the elimination of water (H_2O). Likewise, a bifunctional alcohol (HO-R-OH) and a bifunctional carboxylic acid (HOOC-R'-COOH) would yield an ester (HOOC-R'-COO-R-OH) through the condensation process. Carothers had studied a particular case of this type of reaction at Adams' synthetic school in Illinois around 1925. "Before leaving the University of Illinois," Johnson remarked, "he [Carothers] had started an investigation of the reaction of ethylene glycol [HO-C_2H_4-OH] with succinic acid [HOOC-C_2H_4-COOH]."[65] Carothers was now extending this reaction mechanism to the building up of giant molecules. He realized that a continuous condensation reaction of these low molecules would produce long chain molecules of known structure (HOOC-R' . . . COO-R-OOC-R'-COO-R-OOC-R'-COO . . . R-OH) so far as the reaction does not end with the formation of large rings.

In 1929 Carothers presented a general theory based on these views in his landmark paper, "An Introduction to the General Theory of Condensation Polymers," published in the Journal of the American Chemical Society.[66] In this paper he classified polymers into two groups: addition polymers (or A-polymers) and condensation polymers (or C-polymers), according to the type of polymerization. Addition polymers are those produced by self-addition reaction of monomers. The molecular formula

of the monomer is therefore identical with that of the recurring structural unit of the polymer. Polystyrene and polyoxymethylenes, which Staudinger studied, belong to this group. On the other hand, condensation polymers are those formed by a polyintermolecular condensation reaction of the polyfunctional monomers through the elimination of simple molecules such as water (H_2O).[67] The formula of the monomer of this type differs from that of the structural unit of the polymer. Polyesters, polyanhyderides, and polyamides, represent the linear condensation polymer. "Polymerization then is," he wrote, "the chemical union of many similar molecules either (A) without or (C) with the elimination of simpler molecules. . . ."[68] Carothers' classification of polymers was thus made solely from the synthetic standpoint. Moreover, he applied this classification not only to synthetic polymers but also to naturally occurring polymeric substances: for example, from the structural analogy he identified rubber with linear addition polymers, and silk and cellulose with linear condensation polymers (see Fig. 3.1).[69] To Carothers there was no breach between natural and artificial processes. As he put it later,

> The idea that natural high polymers involve some principles of molecular structures peculiar to themselves and not capable of being simulated by synthetic materials is too strongly suggestive of the vital hypothesis, which preceded the dawn of organic chemistry, to be seriously considered.[70]

Carothers focussed his study on the synthesis of the condensation polymers--a subject which was largely neglected by Staudinger's school. Together with his co-workers, Carothers synthesized polyesters, polyanhydrides, and polyamides, from various possible starting materials.[71] Demonstrating analytically the presence of the end groups (e.g., hydroxyl

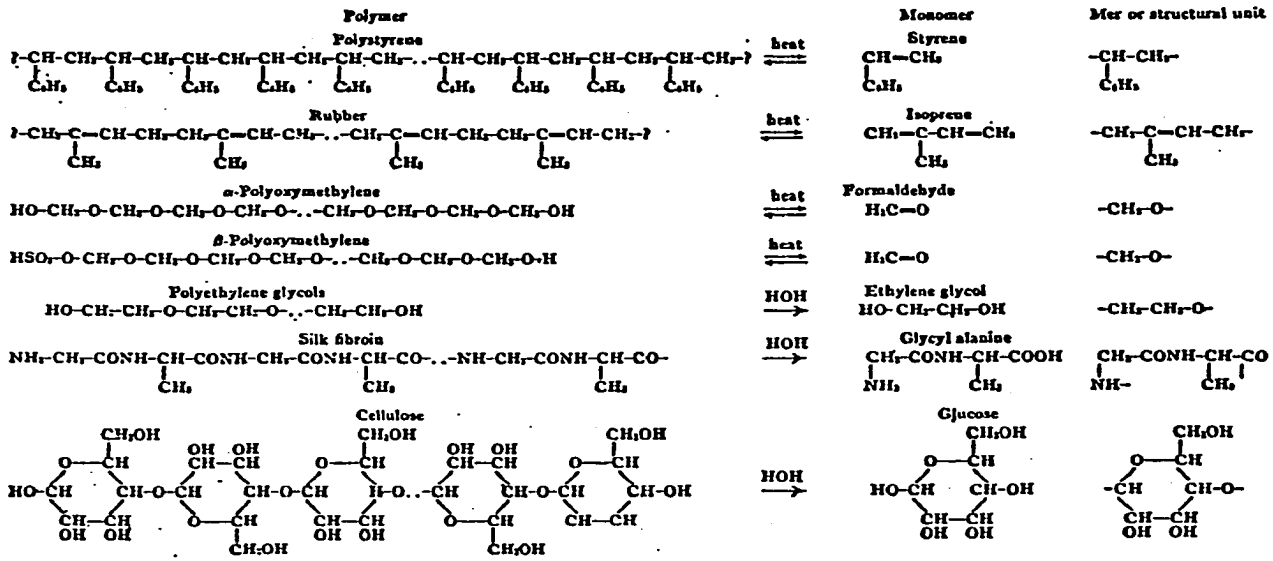


Fig. 3.1. Carothers' Chemical Formulas for Certain Macromolecules and their Structural Units.

and carboxyl groups) of the products, he showed that they consist not of molecular rings but of open-chain molecules. Their high molecular weights calculated from end-group determinations were in agreement with those determined by physical methods such as the boiling point method. In this way, he was able to conclude that these condensation polymers are indeed made up of linear macromolecules. The results were published in a series of articles, entitled, "Studies on Polymerization and Ring Formation," which resulted in a total of 29 papers by 1936.[72]

What Carothers' investigations continuously impressed upon his contemporaries was that polymerization is a normal organic reaction:

> . . . polymerization is chemical combination involving the operation of primary valence force, and . . . the term polymer should not be used (as it frequently is by physical and inorganic chemists) to name loose or vaguely defined molecular aggregation.[73]

On the same grounds, he did not accept the new micelle theory proposed by Kurt H. Meyer and Herman F. Mark, who assumed that cellulose is composed of micelles, i.e., the aggregates of long chain molecules held together by special micellar forces. Well aware of the debate between Staudinger and Meyer-Mark, Carothers was led to favor Staudinger's view that the "micelles" themselves are macromolecules, stating that "we can find no real objection to referring to primary valence chains as molecules."[74]

Carothers' synthetic approach to polymers was in contrast to Staudinger's analytical approach. Staudinger attempted to show the macromolecularity of polymers mainly by analyzing and examining products, such as natural rubber and cellulose. He converted such products into their derivatives through hydrogenation, methylation, and nitration, and showed the similarities in properties between the original products and

their derivatives, as exemplified by his 1922 experiment on the hydrogenation of rubber. This method formed Staudinger's important evidence for the long-chain structure of polymers, as discussed in the previous chapter.[75] Indeed, he did use a few synthetic models as a means of demonstration. But according to Carothers,

> . . . the products studied by him [Staudinger] (polyoxmethylene, polystyrene, polyacrylic acid, etc.) although unquestionably simpler than naturally occurring polymers, were produced by reactions of unknown mechanism, and their behavior, except in the case of polyoxymethylene, was not sufficiently simple to furnish an unequivocal demonstration of their structure. On the other hand, the development of the principles of condensation polymerization [proposed by Carothers] has led to strictly rational methods for the synthesis of linear polymers. . . .[76]

Time and again, Carothers distinguished his own approach from Staudinger's use of synthetic polymers as model substances, which clearly seemed to make the demonstration difficult.

> The obvious importance of simple synthetic models as an aid in studying macromolecular materials has been emphasized repeatedly by Staudinger. . . . Our own researches on condensation polymers were started with the idea that the fact of a proposed model's being synthetic is of little value unless the method of syntheiss is rational, i.e., unless it is sufficiently clear-cut to leave no doubt concerning the structure of the product. Polystyrene may, for example, serve as a simplified model of rubber, but it has the disadvantage that the method used in its synthesis . . . furnishes no certain clue to its structure. The independent demonstration of its structure presents the same difficulties as does rubber; in fact today the formula of rubber can be written with more assurance than that of polystyrene.[77]

In sum, Staudinger's synthetic models--addition polymers in Carothers' classification--were produced particularly by spontaneous polymerizations of unknown mechanism. Therefore, their structures had to be inferred only from the analysis of the final products and from the examination of their properties. They could hardly be inferred from the reaction mechanism. Staudinger then boldly used these synthetic polymers as models in

his demonstration of the macromolecular structure of natural polymers such as rubber and cellulose. Carothers was not convinced by this approach, since the structures of the synthetic models themselves appeared not to be vigorously proved. On the other hand, Carothers' method was simple and straightforward. Combine normal low molecules one by one by the use of the well-established organic reactions, and you will eventually obtain long-chain molecules of definitely known constitution. Thus, the structure of the polymerization product was predictable beforehand theoretically from the reaction mechanism and confirmable afterwards experimentally through, for instance, the demonstration of the presence and nature of end groups. This appeared to leave no doubt concerning the demonstration of the structure of the product. In this regard, Carothers considered his own synthetic method to be "strictly rational," as distinguished from Staudinger's approach.[78] From this "rational" construction of condensation polymers resulted a silk-like artificial fiber, nylon, to which we shall now turn.

The Discovery of Nylon

Although much of the literature on the discovery of nylon has endorsed the view that Carothers came to Du Pont to make synthetic fibers,[79] that claim cannot be substantiated. He did not intend to produce an artificial fiber when he started his study of polymerization in 1928, for he later remarked, "I do not think we had definitely in mind at all the idea of making a fiber, but we did want to make a molecule as large as we could get."[80]

The idea of the synthesis of artificial fibers occurred in 1930 incidentally to this study of the building up of giant molecules. During

the period between 1928 and early 1930, Carothers' group could not synthesize high polymers with a molecular weight of more than 5000. Polymers which they prepared were generally brittle, opaque solids which melted at a low temperature (100°C or less); they dissolved readily in certain solvents (e.g., chloroform) and could be crystallized in the form of white powder (see Fig. 2). Despite his conviction that they were built up from very large molecules, these polymers showed no signs of inherently colloidal behavior--a property peculiar to naturally occurring macromolecular compounds.[81] Carothers wished to make much larger molecules in order to examine further the relationship between the molecular size, molecule's chemical structure, and its properties. Since the experimental techniques used by his group thus far appeared to limit the polymerization reaction, he employed another means, the molecular still, which had been developed lately by several investigators for the separation of chemical mixtures.[83]

The molecular still is a distillation device in which the distance between the distilling and condensing surfaces is shorter than the mean free path--the mean distance traveled by a molecule between successive collisions with other molecules--at very low pressures (see Fig. 3.3). Under this condition the molecule escaping from the distilling surface usually reaches the condenser without colliding with another molecule; hence, the molecules of the evaporated substance can be promptly removed from the system of reaction. The reaction is therefore forced to completion in accordance with Le Chatelier's law of mobile equilibrium. Thus, this apparatus offered a method for displacing the equilibrium of the condensation of polymers toward a more complete reac-

Fig. 3.2.

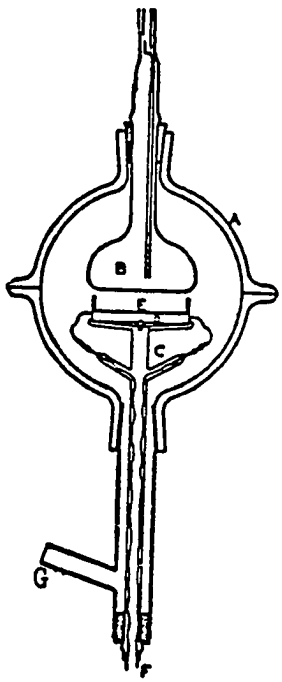
Polyesters from Glycols and DiBasic Acids[82]

Compound	Formula of structural unit	Atoms in chain of structural unit	Average observed molecular weight	Average number of structural units per molecule	Physical properties
Tetramethylene carbonate..	—O—$(CH_2)_4$—O—CO—	7	1400	11–12	Microcrystalline powder, m. p. 59°
Pentamethylene carbonate..	—O—$(CH_2)_5$—O—CO—	8	2700	20–22	Microcrystalline powder, m. p. 44–46°
Hexamethylene carbonate...	—O—$(CH_2)_6$—O—CO—	9	2800	18–21	Microcrystalline powder, m. p. 55–60°
Decamethylene carbonate...	—O—$(CH_2)_{10}$—O—CO—	13	1800	8–10	Microcrystalline powder, m. p. 55°
Ethylene succinate.....	—O—$(CH_2)_2$—O—CO—$(CH_2)_2$—CO—	8	3000	20	Microcrystalline powder, m. p. 108°
Ethylene adipate.....	—O—$(CH_2)_2$—O—CO—$(CH_2)_4$—CO—	10	2900	17	Microcrystalline powder, m. p. 50°
Hexamethylene succinate...	—O—$(CH_2)_6$—O—CO—$(CH_2)_2$—CO—	12	3400	14	Microcrystalline powder, m. p. 57°
Ethylene sebacate.....	—O—$(CH_2)_2$—O—CO—$(CH_2)_8$—CO—	14	4000	13	Microcrystalline powder, m. p. 79°
Trimethylene sebacate.....	—O—$(CH_2)_3$—O—CO—$(CH_2)_8$—CO—	15	3100	12	Microcrystalline powder, m. p. 56°
Decamethylene adipate.....	—O—$(CH_2)_{10}$—O—CO—$(CH_2)_4$—CO—	18	3000	10	Microcrystalline powder, m. p. 77°
Decamethylene sebacate....	—O—$(CH_2)_{10}$—O—CO—$(CH_2)_8$—CO—	22	3000	8	Microcrystalline powder, m. p. 74°
Ethylene phthalate.....	—O—$(CH_2)_2$—O—CO—C_6H_4—CO—	8	4800	25	Hard, transparent resin
Trimethylene phthalate.....	—O—$(CH_2)_3$—O—CO—C_6H_4—CO—	9	3100	14	Soft, transparent resin
Hexamethylene phthalate...	—O$(CH_2)_6$—O—CO—C_6H_4—CO—	12	1800	7	Soft, transparent gum
Decamethylene phthalate...	—O—$(CH_2)_{10}$—O—CO—C_6H_4—CO—	16	2100	7	Very viscous, transparent sirup
Trimethylene oxalate.....	—O—$(CH_2)_3$—O—CO—CO—	7	2000	15	Microcrystalline powder, m. p. 88°
Hexamethylene oxalate.....	—O—$(CH_2)_6$—O—CO—CO—	10	1100	7	Microcrystalline powder, m. p. 66°
Decamethylene oxalate.....	—O—$(CH_2)_{10}$—O—CO—CO—	14	1200	6	Microcrystalline powder, m. p. 79°
Polyester from hydroxydecanoic acid.....	—O—$(CH_2)_9$—CO—	11	5000	20	Microcrystalline powder, m. p. 76° (30)

Fig. 3.3.

Molecular Still[85]

(1/7 actual size)



A. Glass vessel.
B. Condenser provided with water leads.
C. Glass support.
D. Heater.
E. Distilling pan.
F. Heater leads.
G. Tube for application to a source of vacuum.

tion and towards higher molecular weight by distilling off simple reaction products, such as water, as soon as it is formed.[84] In April 1930, Carothers' team was able to synthesize "superpolymers" by this means. A superpolymer, an exceedingly long polymeric chain having a molecular weight of 10,000 or more, exhibited physical properties different from those of the polymer of lower molecular weight, although it closely resembled the initial polymer in its analytical composition and chemical property. The product was a tough, horny, and elastic mass, and it exhibited colloidal behavior in solution.[86]

The synthesis of superpolymers was immediately followed by a discovery of a phenomenon peculiar to these materials. Within a few weeks after the superpolymer synthesis, Carothers' co-worker, Julian Werner Hill (1904-), observed that the superpolymers could be mechanically drawn out from a molt or dry-spun from a solution into fibers or threads.[87] Moreover, this mechanical operation profoundly changed the physical properties of the original superpolymers. The drawn filaments exhibited properties (such as tensile strength, pliability, elastic recovery, transparency, and luster) similar to those of natural fibers such as cellulose and silk. X-ray diffraction patterns indicated that superpolymers in the undrawn state were crystalline, but that the crystals had a random orientation. Drawn filaments, on the other hand, gave a fiber pattern in which the long-chain molecules seemed to be in an ordered array with the fiber axis. The character of this pattern was similar to that obtained from natural silk fibers or rayon filaments under tention. The condensation polymers also resembled cellulose and silk in their basic chemical structures. All these analogies stemming

from this so-called "cold-drawing" phenomenon led Carothers to realize the possibility of making artificial fibers from linear-condensation superpolymers.

Carothers had thought that the strength and elasticity of natural fibers depended on their macromolecular structure. From a chemical standpoint, it had been reasonable to assume that sooner or later a way would be discovered to prepare artificial fibers from synthetic macromolecular compounds. Carothers' study now disclosed that although a particular macromolecular structure is a necessary condition, it is not a sufficient condition to account for the physical properties of fibers. Since properties depend not only on the chemical constitution but also on the physical treatment (or what he called "physical history") of high polymers, the action of the mechanical stress, namely the cold-drawing was the essential step to construct fibers. The phenomenon had never been observed with a synthetic material of any kind. Hill recalled, "The only effect known at the time that at all resembled it was the 'cold-drawing' of the silk glands of silk worms."[88] After questioning why this mechanical operation yielded a permanent high strength of the substance, Carothers concluded that it was due to the great size of the linear condensation polymer. He observed that "the property of cold-drawing does not appear until its molecular weight reaches about 9000 . . . a useful degree of strength and pliability in a fiber requires a molecular weight of at least 12,000 and a molecular length not less than 1000 Å." When the superpolymer receives an external mechanical tension, the long molecular chains are arranged in a highly ordered array parallel with one another. In this state, the mutual cohesive



Figure 3.4. The cold-drawing of the superpolymer, reenacted by Julian W. Hill, n.d., Du Pont Company.

force of the very long chain would act fully; hence, the drawn fibers exhibit the maximum possible strength.[89]

Carothers claimed that addition polymers, especially those produced from vinyl compounds, are less suitable for the fiber. In order to form oriented fibers, a compound must be capable of crystallizing, for crystallization makes possible the parallel arrangement of molecules. Unlike condensation polymers, addition polymers are often amorphous and rarely crystalline. According to Carothers, the presence of side chains (such as methyl or phenyl groups in the structural units) in the addition polymers diminishes the tendency of crystallinity. However large, the macromolecules of such addition polymers are less subject to the formation of oriented fibers.[90] For the same reason, "three-dimensional polymers are obviously unsuited for fiber orientation, and synthetic materials of this class are besides invariably amorphous."[91] By contrast, condensation superpolymers (such as polyesters and polyamides) are usually crystalline because of a high degree of linear symmetry of their molecular shape. Thus, they can easily be drawn out into strong, oriented fibers.[92]

After establishing the theoretical basis for making synthetic fibers, Carothers first publicly announced his findings at the Buffalo meeting of the American Chemical Society, held on September 1, 1931:

> While the method of preparation and the raw materials of the compounds so far studied are too costly to make them of any immediate practical application, the results clearly demonstrate for the first time the possibility of obtaining useful fibers from strictly synthetic materials.[93]

On the next day, the New York Times covered Carothers' presentation at the meeting with a headline, "Chemists Produce Synthetic 'Silk'."[94]

His study evoked the dream of the seventeenth-century microscopist, Robert Hooke (1635-1703), who had conceived a man-made silk in the Micrographia (1665). In the manuscript of his paper on artificial fibers, published in 1932, Carothers quoted a passage from Hooke, although it was deleted on publication:

> And I have often thought, that probably there might be a way found out, to make an artificial glutinous composition, much resembling, if not full as good, nay better, than that Excrement, or whatever other substance it be out of which, the Silk-worm wire-draws his clew. If such a composition were found, it were certainly an easie matter to find very quick ways of drawing it out into small wires for use.[95]

With Carothers' superpolymers and Hill's cold-drawing method, realization of this long-cherished Baconian dream seemed near at hand.

From then on Carothers' basic research group radically shifted its aim to the more practical goal, that is, the search for polymers which can be drawn into fibers of commercial use. One reason for this shift may be his own practical taste which he inherited from the Adams school. As Hill testified, Carothers was the pure researcher par excellence, but "at the same time he was a practical man."[96] Yet, more importantly, he was working within the industrial framework of Du Pont. His group was encouraged by the Company staff, notably the new Chemical Director, Elmer K. Bolton who had taken over Stine's position in 1930, to aim at commercial textile fibers. In 1931 Carothers filed two patents on synthetic fibers from condensation superpolymers, which were to become the basic patents of nylon.[97] From Bolton's point of view, Carothers' fibers then were still only of theoretical interest. Besides the high cost of raw materials, they were deficient in certain properties. For example, the melting points of the polyester fibers were too low for

textile purposes and their solubilities were too great. They had little utility as commercial fibers.[98] During the period between 1930 and 1933, Carothers systematically investigated various types of linear condensation superpolymers, including polyesters, polyanhyderides, polyacetals, polyamides, and polyester-polyamide mixtures, which were synthesized by his co-workers from hundreds of possible combinations of starting materials. As Thomas Edison had done in search of a filament for the light bulb from thousands of materials, his group examined the properties of drawn polymers by the cut-and-try method. But each was found to be deficient in one or more textile properties. "At one stage of the work," Bolton wrote, "the outlook was so dark that investigations along this line were actually halted for a time."[99]

Under the Company's pressure, however, Carothers continued his search. In 1934, after a survey of his work, he decided to resume work on the superpolyamides. In addition to their structural similarity to silk, the polyamides, prepared from amino acids and also from dibasic acids and diamines, appeared to have high melting points and high tensile strength. Subsequently, in February 1935, his collaborator, Gerard Jean Berchet (1902-) synthesized the "polymer 66," a superpolyamide prepared from hexamethylendiamine (with 6 carbons: $NH_2(CH_2)_6NH_2$) and adipic acid (with 6 carbons: $HOOC(CH_2)_4COOH$).[100] The polymer 66 melted at a high temperature (263°C), and its cold-drawn fibers exhibited a high strength and an elasticity greater than any natural fibers. Among other candidates, this polyamide was selected for initial manufacture "because it had the best balance of properties and manufacturing cost of the polyamide then known."[101] Once the decision was made by the Du Pont staff,

2/28/35 Adipate of hexamethylene diamine

7 g. diamine, 8.8 g. acid and 20 c.c. m. cresol heated 215° for 3 hours. Water came off during the first half hour. The temp. was then raised to 255-60° and the cresol distilled off in vacuum. The residue solidified at one time but melted again at 265°. It was heated under 1 mm at 265° for 3 hours. On cooling (overnight) the polymer broke the flask by contracting and showed a tenacious adherence to glass.

It was a very hard, horny solid melting at 252-254°. It was very readily spinnable. Sample turned over to S.N. Coffman.

There was obtained 12.5 g. of polymer, yield 90%.

3/1/35 GJB 3/21/35 HM Lightbown

Fig. 3.5. The record of the first synthesis of polyhexamethylenediamine adipate. From Gerard J. Berchet's Du Pont Company notebook, dated February 28, 1935.

the development of the processes for manufacturing intermediates and for fiber spinning and processing was launched in the various divisions of the Company. In order to reduce to a minimum "the time between the test tube and the counter," some 230 chemists and engineers were at one time or another engaged in this project.[102] The production of the textile yarn from the polymer 66 started in a new plant at Seaford, Delaware, in 1938. In October of this year, the Vice President, Stine, representing the Company, announced the first synthetic fiber, now christened with the generic name, "nylon:"

> Though wholly fabricated from such common raw materials as coal, water, and air, nylon can be fashioned into filaments as strong as steel, as fine as the spider's web, yet more elastic than any of the common natural fibers and possessing a beautiful luster.[103]

The new product promised a wide variety of uses ranging from hosiery to military parachutes. Within the Company framework, Carothers' theoretical work was thus deliberately diverted to practical application, the commerical production of nylon, which had an enormous impact on industry and culture. There followed what has been called the fourth textile revolution in the wake of the earlier inventions of mercerized cotton, synthetic dyes, and rayon. In 1940 a leading American magazine wrote:

> On the U.S. FRONTIER The Giant Molecule is a greater fact of history than Adolf Hitler, although it may take vision to believe it. Nylon, a product of the Giant Molecule and the fourth basic revolution in textile chemistry in four thousand years, is less a substance than a group of substances, all unlike anything found in nature. They didn't just happen--they were made to happen. . . .[104]

What the story of nylon discovery reveals us may be summed up as follows. Nylon was an unforeseen consequence of Carothers' intitial basic research. In an attempt to build up molecules as large as possible, he came to gain an insight into the possibility of making artificial fibers.

Realizing its practical significance, Du Pont immediately led his basic research group to a conversion from theory to practice. It was the Company's ensuing, deliberate efforts that created the industrialization of macromolecular science in a remarkably short period. The nylon adventure coincidentally turned out to be a large-scale test that proved the validity of Carothers' theory of condensation polymers.

In retrospect, April of 1930 was a good month for the industrial researcher Carothers and his group. Two years had passed since he started his study of condensation polymers. In this month, parallel to the synthesis of the first superpolymer, his team discovered a new addition polymer which became another important Du Pont commercial product, neoprene rubber. Again, the discovery was an unexpected event. Nylon was a direct application of his work on polymerization. But, unlike nylon's case, the initial discovery of neoprene took place from a different line of his investigations.[105]

In the late 1920s, a group at Du Pont's Jackson Laboratory in Pennsville, New Jersey, had been working on a conversion of acetylene to its dimer (monovinyl acetylene) and trimer (divinyl acetylene) by use of a cuprous chloride catalyst, on the basis of the recent study by Father Julius Arther Nieuland (1878-1936) at the University of Notre Dame. This research was carried out as a part of Bolton's synthetic rubber project, inaugurated in the middle of the 1920s. Bolton had hoped that this study on acetylene chemistry would provide a basis for synthetic rubber, since monovinyl acetylene had a similar chemical structure to that of butadiene, a possible alternative for isoprene. Despite Du Pont chemists' efforts over several years, the study yielded no rubbery material.[106]

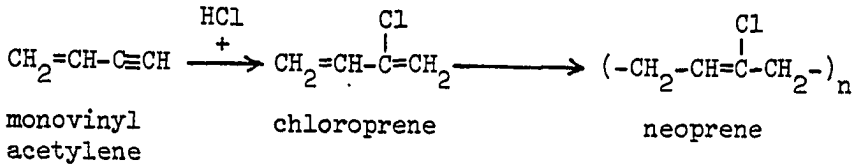
Carothers' study at the Experimental Station involved reviewing the chemistry of these low polymers of acetylene. Here his original goal was not synthetic rubber but a fundamental study of the reactions of these compounds. Since his emphasis was placed on the purity of chemicals in any polymer experiment, Carothers first assigned his co-worker, Arnold Miller Collins (1899-), to purify crude divinyl acetylene which was prepared from acetylene in the presence of cuprous chloride. Collins carried out a fractional distillation of this substance for this purpose. To quote Collins' recollection,

> A constant boiling main fraction [i.e., pure divinyl acetylene] was obtained, along with a definite lower boiling fraction. The main fraction was stabilized and stored in a refrigerator while the still was filled with nitrogen and left. This was on a Friday afternoon. By the following Monday, strange things had happened. The low boiling liquid fraction which had been collected in an attached test tube, had solidified, not to a resin but to that that had never been seen before in this work--a ball with a lively bounce and other characteristic physical properties of natural rubber. This was on April 10, 1930.[107]

Thus, the rubber-like material was obtained from the lower boiling fraction that Collins removed from pure divinyl acetylene.

Carothers soon interpreted this phenomenon in terms of his macromolecular concept. He had known that rubber belongs to the class of addition polymers, and that this type of polymer can be obtained by spontaneous polymerization, unlike condensation polymers. Chemical analysis of this rubbery material showed that it contained chlorine atoms, obviously derived from the cuprous chloride catalyst. From this, it was reasonable to assume that, with the exception of the presence of chlorine, the rubber-like product has a structure similar to natural rubber, and that the original fractional liquid is analogous to isoprene. Subsequent experiments supported this analogy: the addition of hydrogen chloride to

monovinyl acetylene directly yielded the same liquid, which was in turn transformed into the elastic solid spontaneously. In this way, Carothers identified the new liquid as 2-chloro-1,3-butadiene, or what he named "chloroprene". The rubbery material was its high addition polymer, the long-chain structure polychloroprene, later called neoprene.[108]

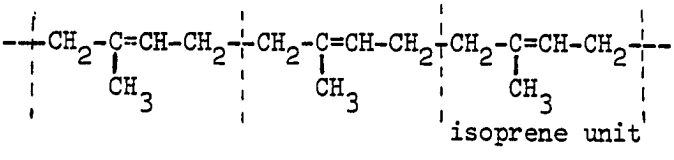


The Company recognized neoprene as a synthetic rubber with a great potential for commercial use, since it exhibited some physical properties far superior to those of vulcanized natural rubber (e.g., resistance to oxidation, to heat, and to many chemicals).

The results were reported at a Rubber Division Meeting of the American Chemical Society, held in Akron in November 1932, and were published in the same year in the Journal of the American Chemical Society.[109] After establishing a practical method for the polymerization of chroloprene, Du Pont started the commercial production of neoprene, under the trademark "Du Prene" in June, 1932.[110] The discovery of neoprene led Carothers to cultivate the field of the acetylene polymers, which formed his second major field. Between 1931 and 1934, along with his co-workers, he published 19 scientific papers on the synthesis and formation mechanism of acetylene polymers in a series entitled, "Acetylene Polymers and their Derivatives."[111] Thus, his achievement in this area illustrates a reciprocal approach in the industrial framework--from a basic study of the chemistry of monovinyl and divinyl acetylene

to synthetic rubber, and from the rubber product back down to the theoretical work on acetylene polymers.

The public image of Carothers as the inventor of nylon and neoprene has often overshadowed the role of his theoretical work on macromolecules. His macromolecular syntheiss convinced many of his American contemporaries of the macromolecularity of polymers. Carl Shipp Marvel (1894-), a faculty member at the University of Illinois, was impressed particularly by Carothers' long review article, "Polymerization," published in 1931: "After that article, the mystery of polymer chemistry was pretty well cleared up, and it was possible for less talented people to make good contributions in the field."[112] Carothers' former colleague at Harvard, James B. Conant, now came to accept Carothers' view. In a revised edition of his textbook on organic chemistry (published in 1933), Conant quietly altered his earlier description of the aggregate theory of synthetic rubber:

> . . . it seems probable that they [isoprene molecules] are united in a very long chain thus:
>
> 
>
>
> This chain must be imagined as extended until the molecular weight is at least a hundred thousand. . .[113]

In Germany, Staudinger was well acquainted with Carothers' activity, and his 1932 book, Die hochmolekulare organischen Vergindunger, gave several favorable references to Carothers' work on condensation polymers.[114] He welcomed this study, for with the work of his American counterpart, "die neuen Vorstellungen über den Bau der makromolekularen Verbindungen in Amerika . . . rasch Eingang gefunden haben."[115] Carothers' study had a fresh

and new impact on German chemists not only because of his cultivation of condensation polymers, but also because of his synthetic approach which contrasted with Staudinger's analytic approach. He thoroughly demonstrated the macromolecular structure of polymers through the formation mechanism of giant molecules. Mark, for example, considered Carothers' synthetic work as crucial for the fall of the aggregate theory in the early 1930s. As he stated later, ". . . probably more than any other single factor did the work of W. H. Carothers and his associates contribute to the ultimate breakthrough in favor of the long chain concept."[116]

Carothers' splendid career ended with his suicide in 1937. He neither lived to hear the name nylon nor lived to see its commercial production. He had suffered from chronic depression since his early days, and this grew more pronounced later on, especially after late 1935. He took leave of absence during most of 1936. He was hospitalized in an institution in Philadelphia for treatment. In the summer of that year the Company sent him on a trip to Europe for relaxation in an effort to improve his mental condition. After a brief respite on the tour with his former teacher Roger Adams, he returned to Wilmington to resume his work, searching for new research subjects. But, whatever his direct motives were, mentally ill, the forty-one-year-old scientist closed his life by taking cyanide in a Philadelphia hotel in late April, 1937. Thus, Carothers' fundamental research group was finally dissolved.[117]

One and a half years before his death, Carothers went to Cambridge, England, to give a paper at a Faraday Society meeting, where he was a principal speaker together with Staudinger, Mark, and Meyer. His outstanding presentation at the meeting rounded off his short but productive career as a founder of macromolecular chemistry, as will be discussed in the next chapter.

NOTES

[1]On Carothers' scientific career and work, see Roger Adams, "Biographical Memoir of Wallace Hume Carothers, 1896-1937," National Academy of Sciences, Biographical Memoirs, 20 (1939): 293-309; John Raven Johnson, "Wallace Hume Carothers, 1896-1937," J. Chem. Soc., 143 (1940): 100-102; Elmer K. Bolton, "Speech at the Dedication of 'The Carothers Research Laboratory' on Tuesday, September 17, 1946," Acc. 1497, Box 18, Eleutherian Mills Historical Library (hereinafter referred to as EMHL), Wilmington, Delaware; Dictionary of American Biography, Supplement 2 (1958), s.v. "Carothers, Wallace Hume," by John R. Johnson; Dictionary of Scientific Biography, vol. 3 (1971), s.v. "Carothers, Wallace Hume," by Julian Werner Hill; and Julian W. Hill, "Wallace Hume Carothers," in American Chemistry--Bicentennial (Proceedings of the Robert Welch Foundation Conferences on Chemical Research, XX), ed. W. O. Milligan (Houston, Texas: The Robert Welch Foundation, 1977): 232-251. For Carother's early education, see A. Truman Schwartz, "Made in the Midwest: The Undergraduate Education of Wallace H. Carothers and Ernest O. Lawrence," Paper delivered for the Midwest Junto for the History of Science at the University of Wisconsin, April 10, 1980; and "Importance of Good Teaching: The Influence of Arthur Pardee on Wallace Carothers," Journal of College Science Teaching, 10 (1981): 218-221. All of Carothers' papers on polymer chemistry were brought together in Wallace H. Carothers, Collected Papers of Wallace Hume Carothers on High Polymeric Substances, ed. Herman Francis Mark and George Stafford Whitby (New York: Interscience Publishers, Inc., 1940).

[2]Schwartz, "Made in the Midwest," p. 1. Cf., Kenneth R. Hardy, "Social Origins of American Scientists and Scholars," Science, 185 (1974): 497-506.

[3]Arthur M. Pardee, "A Study of the Conductivity of Certain Organic Salts in Absolute Alcohol at 15°, 25°, and 35°C," (Ph.D. dissertation, Johns Hopkins University, 1916.) This was published with H. H. Lloyd in Carnegie Institute of Washington, Publication,260 (1917): 99-118.

[4]Arthur M. Pardee, "Contribution to the Biographical Memoir of Wallace Carothers," February 19, 1938; cited in Schwartz, "Made in the Midwest," p. 5.

[5]Arthur M. Pardee to Betty Jo Travis, February 12, 1947; cited in ibid.

[6]Adams, "Biographical Memoir," p. 294.

[7]For the information on the Department of Chemistry at the University of Illinois during this period, see The University of Illinois, Department of Chemistry (Urbana, Illinois: The University of Illinois, 1927 and 1941).

[8]Gilbert Newton Lewis, "The Atom and the Molecule," J. Amer. Chem. Soc., 38 (1916): 762-785; Irving Langmuir, "The Arrangement of Electrons in Atoms and Molecules," ibid., 41 (1919): 868-934; "Isomorphism, Isosterism, and Covalence," ibid.; 1543-1559; "The Octet Theory of Valence and Its Applications with Special Reference to Organic Compounds," ibid., 42 (1920): 274-292.

[9]Wallace H. Carothers, "The Isosterism of Phenylisocyanate and Diazobenzene-imide," J. Amer. Chem. Soc., 45 (1923): 1734-1738.

[10]Wallace H. Carothers, "The Double Bond," ibid., 46 (1924): 2226-2236.

[11]See Robert E. Kohler, Jr., "The Lewis-Langmuir Theory of Valence and the Chemical Community, 1920-1928," Historical Studies in Physical Sciences, 6 (1975): 431-468, on pp. 436-445.

[12]John R. Johnson, ". . . This Uncommon Man," Du Pont Magazine, n.d., A. B. C. Strange Personal Collection (hereinafter referred to as SC).

[13]In 1928 Carothers submitted his paper, "The Ethyl Anion and the Structure of the Grignard Reagents," which included an application of the octet theory, to the Journal of the American Chemical Society. Although criticized by the referee, this paper was approved for publication but never appeared in the Journal. Wallace H. Carothers, "The Ethyl Anion and the Structure of the Grignard Reagents," unpublished MS, 1928; and "Comments of the Referee," October 1928, p. 2,

[14]This study was published with Roger Adams under the title, "Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. II. Reduction of Aldehydes. Activation of the Catalyst by the Salts of Certain Metals," in J. Amer. Chem. Soc., 45 (1923): 1071-1086.

[15]For Roger Adams, see Nelson J. Leonard, "Roger Adams," J. Amer. Chem. Soc., 91(1969): a-d; Dictionary of Scientific Biography, Supplement I (1978), s.v. "Adams, Roger," by Robert E. Kohler, Jr.; E. J. Corey, "Roger Adams," American Chemistry-Bicentennial. (Proceedings of Robert A. Welch Foundation Conferences on Chemical Research, XX), e.d. W. O. Milligan (Houston, Texas: The Robert Welch Foundation, 1977): 204-228; D. Stanley Tarbell and Ann Tracy Tarbell, Roger Adams: Scientist and Statesman (Washington, D.C.: Amercain Chemical Society, 1981).

[16]In Jackson's opinion, Willstätter was then the only German organic chemist comparable to Emil Fischer. See Tarbell and Tarbell, Roger Adams, p. 27 ff.

[17]Organic Syntheses: An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals (New York: John Wiley and Sons, Inc., 1921-), vol. 1- . Carothers edited the thirteenth volume of this series in 1933.

[18]See, e.g., Roger Adams, "Universities and Industry in Science," Ind. Eng. Chem., 46 (1954): 506-510. Adams took over Noyes' position as the department head in 1926. Between 1918-1958 (his retirement), Adams trained 184 Ph.D.'s, of whom 132 students went to industry immediately after graduation or later. The Adams-Du Pont connection was particularly tight; 25 doctoral students of Adams went to the Du Pont Company, including Carothers. See Tarbell and Tarbell, Roger Adams, pp. 95-100, and 221-228.

[19]Adams, "Biographical Memoir," p. 296.

[20]In a memorandum dated December 18, 1926, to the Executive Committee at the Du Pont Company, Stine stated, "We are including in the central Chemical Department's budget for 1927 an item of $20,000 to cover what may be called for want of a better name, pure science or fundamental research work. The purpose for which this sum is requested represents a sufficiently radical departure from previous policy so that it seems advisable to present the matter in this special letter. The prosecution of fundamental or pioneer research work by industrial laboratories is not an untried experiment. Not only is it fostered to a considerable extent by foreign industries, particularly in Germany, but also by certain concerns in this country, notably the General Electric Company. The sort of work we refer to is work undertaken with the object of establishing or discovering new scientific facts. It is thus distinguished from what may be called applied research, which applied previously established practical problems." Charles M. A. Stine to Executive Committee, December 18, 1926, Acc. 1497, Box 2, EMHL. For the Du Pont fundamental research program, see also Charles M. A. Stine, "The Place of the Fundamental Research in an Industrial Research Organization," Trans. Amer. Inst. Chem. Eng., 32 (1936): 127-137; Elmer K. Bolton, "Du Pont Research," 1961, Du Pont Company, Acc. 1689, EMHL; C. B. McCoybyline, "Moment of Decision," 1969, Du Pont Company, Acc. 1497, Box 24, EMHL; and Jeffrey Louis Sturchio, "Chemists and Industry in Modern America: Studies in the Historical Application of Science Indicators," (Ph.D. dissertation at the University of Pennsylvania, 1981), especially p. 144ff. In establishing the fundamental research program, Du Pont also made an inspection of Bell Laboratories: Interview with Elmer K. Bolton by Alfred D. Chandler, Richard D. Williams, and Norman B. Wilkinson, September 14, 1961, Acc. 1689, EMHL. Various aspects of American industrial research and its strategy have been discussed in Bernard Barber, Science and the Social Order (Glencoe, Illinois: The Free Press, Publishers, 1952), especially Ch. 7; Alfred D. Chandler, Strategy and Structure: Chapters in the History of American Industrial Enterprise (Cambridge, Massachusetts: MIT Press, 1962); Kendall Birr, Pioneering in Industrial Research: The Story of the General Electric Research Laboratory (Washington, D.C.: Public Affairs Press, 1957); John J. Beer and W. David Lewis, "Aspects of the Professionalization of Science," The Professions in America, ed. Kenneth S. Lynn et al. (Boston: Houghton Mifflin, 1965): 110-130; David F. Noble, America by Design: Science, Technology, and the Rise of Corporate Capitalism (New York: A. A. Knopf, 1977); Kendall Birr, "Industrial Research Laboratories," in The Sci-

ences in the American Context: New Perspectives, ed. Nathan Reingold (Washington, D.C.: Smithsonian Institution Press, 1979); John Rae, "The Application of Science to Industry," in The Organization of Knowledge in Modern America, 1860-1920, ed. Alexandra Oleson and John Voss (Baltimore: Johns Hopkins University Press, 1979); Leonard Reich, "Industrial Research and the Pursuit of Corporate Security: The Early Years of Bell Labs," Business History Review, 54 (1980): 503-529; Lillian Hoddeson, "The Emergence of Basic Research in the Bell Telephone System," Technology and Culture, 22 (1981): 512-544; George Wise, "A New Role for Professional Scientists in Industry: Industrial Research at General Electric, 1900-1916," ibid., 21 (1980): 408-429; and "Ionists in Industry: Physical Chemistry at General Electric, 1900-1915," Isis, 74 (1983): 7-21.

[21]Wallace Hume Carothers to John R. Johnson, February 14, 1928, SC. Johnson received his Ph.D. in 1922 under Roger Adams at the University of Illinois. After staying as Instructor of Organic Chemistry in Illinois (1924-1927), he moved to Cornell University, Ithaca in 1928, where he taught until his retirement in 1965. He was Carothers' intimate friend since their Illinois days. The large part of their correspondence between 1926 and 1937 is collected in SC. The information on the Du Pont Experimental Station during this period is in the Company's pamphlet, The Central Chemical Department and Its Laboratory, Wilmington, Delaware (Wilmington, Delaware: E. I. Du Pont de Nemours & Company, 1928). Du Pont Company's research policy at the Experimental Station was summarized in A. P. Tanberg, "The Conduct of Research," 1931, Du Pont Company, Pam. EMHL.

[22]See p. 39 ff.

[23]Jacques Loeb to T. H. Morgan, February 17, 1920; cited in Kohler, "Lewis-Langmuir Theory," p. 446.

[24]James Bryant Conant, My Several Lives: Memoirs of a Social Inventor (New York, Evanston and London: Harper and Row, 1970), p. 67. Conant was Richards' son-in-law. For an American chemist's postwar efforts to create a bridge between the scientific communities of Germany and the wartime allies, see William Albert Noyes' Building For Peace: A Chemist's Summer in Europe (New York: The Chemical Catalog Co., 1923) and Building for Peace II: International Letters (Cambridge: W. Heffer and Sons Ltd.; New York: The Chemical Catalog Co., 1924).

[25]These meetings include the French Chemical Society (1931), the Faraday Society in Manchester (1932) and in Cambridge (1935), and the Madrid meeting of the International Union of Pure and Applied Chemistry (1934). See also Ch. IV, p. 142.

[26]Staudinger's 1920 paper was briefly summarized in Chem. Abstracts, 14 (1920), Part 3: 3423-3424; and in J. Chem. Soc., Abstracts of Papers, 143 (1920), Part I: 517-518.

[27]See Ch. II, 77-78, n. 43.

[28]Hermann Staudinger and Herman A. Bruson, "Über das Dicyclopentadien und weitere polymere Cyclopentadiene," Liebigs Ann. Chem., 447 (1926): 97-110; "Über die Polymerisation des Cyclopentadiens," ibid.: 110-122; and Hermann Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson, and S. Wehrli, "Über die Konstitution des Poly-indens," Helv. Chim. Acta, 12 (1929): 934-957. On Bruson, see American Men of Science, 11th ed. (1965), s.v. "Bruson, Dr. Herman A(lexander)."

[29]Hermann Staudinger and Avery A. Ashdown, "Über Poly-α-phenylbutadien," Ber., 63 (1930): 717-721. His paper, published in 1929 with Staudinger, Bruson, and others, is shown in n. 28. On Ashdown, see American Men of Science, 11th ed. (1965), s.v. "Ashdown, Prof. Avery A(llen)." It is not known whether Carothers met Ashdown at Cambridge in the period between 1925 and 1928. In any event, according to Carothers' colleague at Du Pont, Julian W. Hill (an MIT graduate who knew Ashdown personally), Ashdown did not play an important role in the introduction of Staudinger's theory in the United States. Indeed, Hill himself was not interested in polymer research until he joined Carothers' group in 1929. Interview with Julian W. Hill by the author, November 29, 1982.

[30]Walter N. Haworth, "Aliphatic Division," Annual Reports on the Progress of Chemistry for 1927, 24 (1928): 61-105; Walter N. Haworth and E. L. Hirst, "Aliphatic Division," Annual Reports on the Progress of Chemistry for 1929, 26 (1930): 105-110.

[31]G. Stafford Whitby and Morris Katz, "The Polymerization of Indene, Cinnamal Fluorence and Some Derivatives of Indene," J. Amer. Chem. Soc., 50 (1928): 1160-1171. Cf., G. Stafford Whitby, "Recent Work on Harries on Cauotchoc," India-Rubber J., 617 (February 12, 1921): 315-317, on p. 315.

[32]Emil Fischer, "Synthesis of Depsides, Lichen-Substances and Tannins," J. Amer. Chem. Soc., 36 (1914): 1170-1201. Cf., Ch. I, p. 22.

[33]Wolfgang Ostwald, An Introduction to Theoretical and Applied Colloid Chemistry: The World of Neglected Dimensions, trans. Martin H. Fischer (New York: John Wiley and Sons, Inc.: London: Chapman and Hall, Ltd., 1917), p. ix. Cf. Ch. I, n. 33.

[34]Ralph E. Oesper, "Wolfgang Ostwald (1883-1943)," J. Chem. Educ., 22 (1945): 263-264, on p. 264.

[35]This English translation (see n. 33) was reprinted repeatedly until 1925.

[36]See, e.g., Harry N. Holmes, "The Growth of Colloid Chemistry in the United States," J. Chem. Educ., 31 (1954): 600-602, on p. 600.

[37]On Bancroft, see Alexander Findlay, "Wilder Dwight Bancroft, 1867-1953," J. Chem. Soc., 56 (1953): 2506-2514; John W. Servos, "Phy-

sical Chemistry in America, 1890-1933: Origins, Growth, and Definition," (Ph.D. dissertation at Johns Hopkins University, 1979); and "A Disciplinary Program That Failed: Wilder D. Bancroft and the Journal of Physical Chemistry, 1896-1933," Isis, 73 (1982): 207-232.

[38]Wilder D. Bancroft, "Physical Chemistry," in A Half-Century of Chemistry in America, 1876-1926, ed. Charles A. Browne, published at the Golden Jubilee Number, J. Amer. Chem. Soc., 48 (1926): 89-110, on p. 110. See also Wilder D. Bancroft, "The Future in Chemistry," Science, 27 (1908): 978-980, especially pp. 979-980.

[39]See Servos, "A Disciplinary Program That Failed," p. 219.

[40]Wilder D. Bancroft, Applied Colloid Chemistry: General Theory (New York: McGraw-Hill, 1921).

[41]Ibid., p. 1.

[42]Cf., Ch. I, pp. 26 and 29.

[43]Bancroft, Applied Colloid Chemistry, p. 187.

[44]Søren P. L. Sørensen, "Proteinstudien," Compt. rend. trav. Lab. Carlsberg, 12 (1917): 1-364.

[45]John T. Edsall, "Proteins as Macromolecules: An Essay on the Development of the Macromolecule Concept and Some of Its Vicissitudes," Archives of Biochemistry and Biophysics, Supplement 1 (1962): 12-20, on p. 18.

[46]Cf., Ch. II, p. 66.

[47]Wilder D. Bancroft, Applied Colloid Chemistry, 3rd ed. (1932), p. 232.

[48]Reginard O. Herzog and M. Kobel, "Protein Studien. II. Versuche zur Molekulargewichtesbestimmung an Seidenfibroin," Z. physiol. Chem., 134 (1924): 269-299.

[49]Edwin J. Cohn and James B. Conant, "The Molecular Weights of Proteins in Phenol," J. Amer. Chem. Soc., 12 (1926): 433-438.

[50]See Conant, My Several Lives, pp. 67-73.

[51]"When Professor James B. Conant, later American ambassador to the Federal Republic of Germany, visited my laboratories in Zürich in 1925, my co-workers and I told him our arguments in favor of the macromolecular structure of these polymeric compounds. On his visit to Germany which immediately followed he was told not to believe a word of Staudinger!" Hermann Staudinger, Arbeitserinnerungen (Heidelberg: Dr. Alfred Hüthig Verlag GmbH, 1961), p. 85; From Organic Chemistry to Macromolecules: A Scientific Autobiography on My Original Papers, trans. Jerome Fock and

Michael Fried (New York, London, Sydney, and Toronto: Wiley-Interscience, 1970), p. 84.

[52]James B. Conant, Organic Chemistry: A Brief Introductory Course (New York: Macmillan, 1928), p. 279.

[53]Ibid., p. 54.

[54]Ibid., p. 55.

[55]Cf., Ch. I, pp. 26-28.

[56]James B. Conant, quoted in Adams, "Biographical Memoir," p. 297.

[57]Ibid.

[58]Carothers had an excellent reading ability of the German chemical literature. Interview with Julian W. Hill, February 23, 1982.

[59]Wallace H. Carothers and Julian W. Hill, "Artificial Fibers from Synthetic Linear Condensation Superpolymers," J. Amer. Chem. Soc., 54 (1932): 1579-1587; Carothers, Collected Papers: 179-189, on p. 186.

[60]Wallace H. Carothers, "Polymerization," Chem. Reviews, 8 (1931): 353-426; Carothers, Collected Papers: 81-140, on p. 129.

[61]Carothers explicitly supported Staudinger's organic-structural approach to polymers: "The view that the ordinary structural theory of organic chemistry is adequate to deal with high polymers has been now for several years ably defended by Staudinger and his collaborators . . ." Wallace H. Carothers and G. L. Dorough, "Ethylene Succianates," J. Amer. Chem. Soc., 52 (1930): 711-721; Carothers, Collected Papers: 42-53, on p. 52.

[62]Carothers to Johnson, February 14, 1928. The actual value that Fischer gave for his synthetic compound was 4021 and not 4200. Cf., Ch. I, p. 22 and Ch. III, p. 98.

[63]On Fischer's synthetic approach to proteins, see Ch. I, p. 20 ff.

[64]Carothers to Johnson, February 14, 1928.

[65]Johnson, "Carothers" (1940) (see n. 2), p. 102.

[66]Wallace H. Carothers, "An Introduction to the General Theory of Condensation Polymers," J. Amer. Chem. Soc., 51 (1929): 2548-2559; Carothers, Collected Papers: 4-17.

[67]The condensation reaction includes esterification, amid formation, ether formation, and anhydride formation.

[68]Carothers, "Introduction," in Collected Papers, p. 7.

[69] Ibid., pp. 6 and 9.

[70] Carothers, "Polymerization," in Collected Papers, p. 124.

[71] The formation of these condensation polymers are illustrated as follows:

Polyesters formed by the intermolecular self-esterification of hydroxy acids,

$$HC\text{-}R\text{-}COOH+HO\text{-}R\text{-}COOH \rightarrow HO\text{-}R\text{-}CO\text{-}O\text{-}R\text{-}COOH+H_2O$$

$$2HO\text{-}R\text{-}CO\text{-}O\text{-}R\text{-}COOH \rightarrow HO\text{-}R\text{-}CO\text{-}O\text{-}R\text{-}CO\text{-}O\text{-}R\text{-}CO\text{-}O\text{-}R\text{-}COOH+H_2O, \text{ etc.};$$

Polyesters formed by the action of dibasic acids on dihydric alcohols,

$$n\ HOOC\text{-}R\text{-}COOH+(n+1)HO\text{-}R'\text{-}OH \rightarrow HO\text{-}R'\text{-}O\text{-}(CO\text{-}R\text{-}CO\text{-}O\text{-}R'\text{-}O)nH+H_2O, \text{ etc.};$$

Polyethers formed by the intermolecular self-etherification of glycols,

$$HO\text{-}R\text{-}OH+HO\text{-}R\text{-}OH+HO\text{-}R\text{-}OH+\text{etc.}, \rightarrow HO\text{-}R\text{-}O\text{-}R\text{-}O\text{-}R\text{-}O\text{-}R\text{-}O\text{-}R\text{-}O\text{-}\text{etc.}, +H_2O$$

Polyanhydrides derived from dibasic acids,

$$HOOR\text{-}R\text{-}COOH+HOOC\text{-}R\text{-}COOH+\text{etc.} \rightarrow HOOC\text{-}R\text{-}CO\text{-}L\text{-}LC\text{-}R\text{-}CO\text{-}O\text{-}OC\text{-}R\text{-}CO\text{-}\text{etc.}, +H_2O,$$

where R and R' indicate organic radicals.

[72] See Carothers, Collected Papers, pp. 3-270.

[73] Carothers, "Polymerization," in Collected Papers, pp. 82-83.

[74] Carothers and Dorough, "Ethylene Succinates," in Carothers, Collected Papers, pp. 52-53. Cf., Ch. II, pp. 59-62.

[75] Cf., Ch. II, p. 51.

[76] Carothers and Hill, "Artificial Fibers," in Carothers, Collected Papers, p. 186.

[77] Wallace H. Carothers and F. J. van Natta, "Polyesters from ω-Hydroxydecanoic Acid," J. Amer. Chem. Soc.,55 (1933): 4714-4719; Carothers, Collected Papers: 195-202, on p. 196.

[78] As he put it, the primary object of his study was "to synthesize giant molecules of known structure by strictly rational methods" Carothers and Hill, "Artificial Fibers," in Carothers, Collected Papers, p. 186. Concerning the addition polymerization of unsaturated compounds, Carothers stated in 1931: "So far as the formation of materials of high molecular weight is concerned, such reactions are much less clear-cut than bifunctional condensations, for the latter involve only the application of

known reactions of typical functional groups, and the general structural plan of the product may be inferred directly from the structure of the starting materials. On the other hand, no clue to the intimate details of the mechanism of self-addition can be found in the reactions of the compound concerned with any compounds other than itself." Carothers, "Polymerization," in Collected Papers, pp. 113-114.

[79] E.g., "Nylon" (anon.), Fortune, vol. 22, no. 1 (1974): 57-60, 114, and 116, on p. 58; Leonard Mosley, Blood Relation: The Rise and Fall of the du Ponts of Delaware (New York: Atheneum, 1980), pp. 362-363.

[80] Quoted in Cole Coolidge to Robert N. Anthony, October 20, 1952, Acc. 1497, Box 18, EMHL.

[81] See e.g., Carothers, "Polymerization," in Collected Papers, pp. 88-89 and 129-136.

[82] Ibid., pp. 88-89.

[83] J. N. Brønsted and G. Hevesty, "On the Separation of the Isotopes of Mercury," Philosophical Magazine, 43 (1922): 31-49; and C. R. Burch, "Some Experiments on Vacuum Distillation," Proceedings of the Royal Society of London, 123 (1929): 271-284.

[84] W. H. Carothers and Julian W. Hill, "The Use of Molecular Evaporation as a Means for Propagating Chemical Reactions," J.Amer.Chem. Soc., 54 (1932): 1557-1559; in Collected Papers, pp. 154-156.

[85] Ibid., p. 155.

[86] W. H. Carothers and J. W. Hill, "Linear Superpolyesters," J. Amer. Chem. Soc., 54 (1932): 1559-1566; "Polyamides and Mixed Polyester-Polyamides," ibid.: 1566-1569; "A Linear Superpolyanhydride and a Cyclic Dimeric Anhydride from Sebastic Acid," ibid.: 1569-1579; Carothers, Collected Papers: 156-179. The first superpolymer was prepared on April 16.

[87] Hill initially found this phenomenon when he pulled threads of a molton superpolyester with a rod. See Hill's later demonstration, Figure 3.2. See also memorandum from J. W. Hill to W. H. Carothers, "Review of Work on Superpolymers," Du Pont Company, February 6, 1931, Acc. 903, Rutledge Scrapbook, vol. 598, EMHL.

[88] Julian W. Hill to Bettina Sargeant, November 17, 1960, Acc. 1497, Box 24, EMHL.

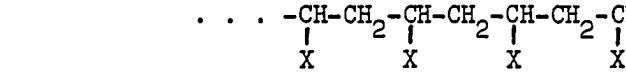
[89] Carothers and Hill, "Artificial Fibers," Collected Papers, p. 187. Although Carothers rejected the prevailing concept of the aggregate force of small molecules, he admitted the existence of the cohesive forces which exert between macromolecules. He stated:

> The cohesive forces which resist the separation of molecules from one another . . . increase continuously with increasing molecular

> weight in a given series, and in high polymers they reach values greatly in excess of the energy required to rupture a primary valence linkage in a chain. For this reason high polymers cannot be distilled without decomposition; indeed it appears that the upper limit of distillability may lie at as low a molecular weight as 1200 and 1500.

See Carothers, "Polymerization," Collected Papers, p. 130. Carothers' concept of the cohesive force reflects the idea of "micellar force" proposed around 1928 by Kurt H. Meyer and Herman Mark, who assumed that cellulose is composed of micelles or the bundles of long chain molecules held together by special micellar forces. While highly evaluating Meyer and Mark's work, however, Carothers did not adopt all aspects of the new micelle theory. Well aware of the dabate between Staudinger and Meyer-Mark, he was led to favor Staudinger's position that the micelles themselves are large molecules. See, e.g., Wallace H. Carothers and G. L. Dorough, "Ethylene Succinates," J. Amer. Chem. Soc., 52 (1930): 711-721, in Carothers, Collected Papers, 42-53, on pp. 52-53; and Carothers, "Polymerization," Collected Papers, p. 126. On the new micelle theory, see Ch. II, pp. 59-62.

[90]This type of polymers is exemplified by Staudinger's polystyrene:



where X represents phenyl group.

[91]Carothers and Hill, "Artificial Fibers," Collected Papers, p. 188.

[92]Ibid., pp. 187-188. Cf., Carothers, "Polymerization," Collected Papers, pp. 132-136. Staudinger and Rudolph Signer (1903-) had reported in 1929 photomicrographs of fibrous crystals of polyoxmethylene formed directly from formaldehyde vapors, and they claimed that these crystals were the first fibers to be prepared by synthesis. But these fibrous materials were only a few millimeters in length and too fragile for Carothers to consider as fibers. In his opinion, a useful fiber must satisfy certain mechanical requirements. Wallace H. Carothers, "Artificial Fibers from Synthetic Linear Condensation Superpolymers," a manuscript made around August, 1931, Carothers File, Lavoisier Library, Du Pont Company, p. 1. Cf., H. Staudinger and R. Signer, "Über den Kristallbau hochmolekularer Verbindungen," Zeitschrift für Kristallographie, 70 (1929): 193-210, on p. 208.

[93]W. H. Carothers and J. W. Hill, "Artificial Fibers from Synthetic Linear Condensation Superpolymers: Abstract of Paper to be given at the Buffalo Meeting of the American Chemical Society, September 1, 1931," Acc. 903, Rutledge Scrapbook, vol. 598, EMHL. Cf., Carothers and Hill, "Artificial Fibers," in Collected Papers, especially p. 180.

[94]New York Times, "Chemists Produce Synthetic 'Silk'," September 2, 1931.

[95]Carothers, "Artificial Fibers from Synthetic Linear Condensation Superpolymers," M S , 1931, Lavoisier Library, Du Pont Company, Wilmington, Delaware, p. 1. Robert Hooke, Micrographia: Or Some Physiological Descriptions of Minute Bodies Made by Magnifying Glasses with Observations and Inquiries Thereupon, (London, 1665), p. 7.

[96]Interview with Julian W. Hill by the author, February 22, 1982.

[97]W. H. Carothers, "Linear Condensation Polymers," U.S. 2,071,250 patented February 16, 1937; "Fiber and Method of Producing It," U.S. 2,071,251, patented February 16, 1937.

[98]Elmer K. Bolton, "Development of Nylon," Industrial and Engineering Chemistry, 34 (1942): 53-58, on pp. 54 ff. See also interview with Elmer K. Bolton by Alfred D. Chandler, Richmond D. Williams, and Norman B. Wilkinson, September 14, 1961, Acc. 1689, EMHL, pp. 20-21.

[99]Elmer K. Bolton, "Nylon," Chemical and Engineering News, 20 (1942): 1365-1366, on p. 1365.

[100]Gerard J. Berchet, "Adipate of Hexamethylene Diamine," (experimental record), Du Pont Company, February 28, 1935. The chemical structure of the polymer 66 is:

. . . -NH-R-NH-CO-R'-CO-NH-R-NH-CO-R'-CO- . . .

where R is $-(CH_2)_6-$ and R' is $-(CH_2)_4-$. Cf., the structure of silk:

. . . -NH-R-CO-NH-R'-CO-NH-R-CO-NH-R'-CO- . . .

where R is $-\underset{\displaystyle CH_3}{\overset{}{CH}}-$ and R' is $-CH_2-$.

[101]Bolton, "Development of Nylon," p. 55.

[102]See ibid., pp. 56-58; Ferdinand Schulze, The Technical Division of the Rayon Department 1920-1950, revised and enlarged from a manuscript prepared by Roy Soukup (Wilmington, Delaware: Textile Fibers Department, Patent Division, E. I. du Pont Nemours and Company, 1952), pp. 159-170.

[103]Charles M. A. Stine, "What Laboratories of Industry Are Doing for the World of Tomorrow: Chemicals and Textiles," an address delivered before New York Herald Tribune EighthAnnual Forum on Current Problems, October 27, 1938, Acc. 903, Rutledge Scrapbook, vol. 598, EMHL. Nylon was officially defined as "a man-made protein-like chemical product (polyamide) which may be formed into fibers, bristling filaments, sheets and other forms which are characterized when drawn by extreme toughness, elasticity, and strength." See e.g., "Some Facts About Nylon," Public Relations Department, Du Pont Company, November, 1939, Acc. 903, Rutledge Scrapbook, vol. 598, EMHL, pp. 4-5. On the naming of nylon, see Charles H. Rutledge, "The Name Nylon and Some of Its Adventures," Product Information Group, Textile Fibers Department, Du Pont Company, June 20, 1966, Acc 903, Rutledge Scrapbook, vol. 598, EMHL. The name was decided by the Company in 1938 through subscriptions of Du Pont workers.

[104]"Nylon" (anon.), Fortune, p. 86 (n. 79).

[105]On the discovery of neoprene, see Charles M. A. Stine, "The Approach to Chemical Research Based on a Specific Example," Journal of the Franklin Institute, 218 (1934): 397-410; Arnold M. Collins, "The Discovery of Polychloroprene: Charles Goodyear Medal Address--1973," Rubber Chem. Tech., 46 (1973), no. 2: G48-G52; Hill, "Carothers," (1976), pp. 245-249; and John K. Smith, "The Ten-Year Invension: Neoprene and Du Pont Research, 1930-1939," unpublished paper prepared at the University of Delaware for the fiftieth anniversary of neoprene, September, 1981.

[106]Collins, "Discovery of Polychloroprene," pp. G49-G50; and Smith, "Ten-Year Invension," pp. 4-5. The preparation of monovinyl acetylene and divinyl acetylene from acetylene molecule is shown as follows:

$$\underset{\text{(acetylene)}}{CH{\equiv}CH} \xrightarrow{CuCl} CH_2{=}C{-}C{\equiv}CH \quad \text{(monovnyl acetylene)}$$

$$+$$

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \quad \text{(divynyl acetylene)}$$

[107]Collins, "Discovery of Polychloroprene," p. G50.

[108]Cf. the chemical structure of isoprene,

$$CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

[109]Wallace H. Carothers, Ira Williams, Arnold M. Collins, and James E. Kirby, "A New Synthetic Rubber: Chloroprene and Its Polymers," J. Amer. Chem. Soc., 53 (1931): 4203-4225.

[110]On the development and commercial production of neoprene, see Smith, "Ten-Year Invention," pp. 10-24. G. S. Whitby and M. Katz's article "Synthetic Rubber," Ind. Eng. Chem., 25 (1933): 1204-1211 and 1338-1348, on pp. 1342-1347, includes an extensive account on the properties and industrial significance of neoprene rubber.

[111]See Carothers, Collected Papers, Pt. II and pp. 426-427.

[112]Carl S. Marvel, "The Development of Polymer Chemistry in America --Early Days," J. Chem. Educ., 58 (1981): 535-539, on p. 536. On Marvel see Ch. IV, pp. 168.

[113]James B. Conant , The Chemistry of Organic Compounds: A Year's Course of Organic Chemistry (New York:. MaCmillan, 1933), p. 78. Cf. his statement on the structure of synthetic rubber in the 1928 edition, Ch. III, p. 104, n. 54.

[114]Hermann Staudinger, Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose (Berlin: Verlag von Julius Springer, 1932), pp. 11, 40, 148, and 255.

[115]"The new ideas on the structure of macromolecular compounds were quickly introduced into America." Hermann Staudinger, Arbeitserinnerungen (Heiderberg: Dr. Alfred Hüthig Verlag GmbH., 1961), p. 226.

[116]Herman F. Mark, "Polymers--Past, Present, Future," in Polymers (Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research, X), ed. W. O. Milligan (Houston, Texas: The Robert A. Welch Foundation, 1967): 19-43, on p. 28. Cf., Ch.IV, pp. 168-171.

[117]Carothers appears to have suffered from periods of depression since his Illinois days. According to the diagnosis of Kenneth Appel, a Philadelphia psychiatrist who treated Carothers for some time before his death, Carothers had schizophrenia. On the other hand, Carothers' colleagues at Du Pont believed that it was a manic depressive phsychosis. JKH, "Dr. Wallace Hume Carothers," memorandom, dated September 30, 1954, Du Pont Company. Various conjectures have been reported about the motives of Carothers' suicide, referring to his sensitive personality, private and social life, the takeover of the nylon project by other departments (1935), his marriage (February, 1936), the death of his beloved sister, Isabel (January, 1937), his dilemma involving the conflict between academic and industrial values, Du Pont's organization, and society. But they are largely hindsight, and some of them even groundless.

CHAPTER IV

TOWARD THE CONSTRUCTION OF A NEW SCIENCE: THE GROWTH OF MACROMOLECULAR CHEMISTRY

By the middle of the 1930s, the significance of the issue of macromolecules had been well recognized in chemical communities outside Germany and the United States. The postwar intellectual isolation of Germany apparently disappeared in the opening of the new decade.[1] As a proselytizer for macromolecular theory, Hermann Staudinger wasted no time in spreading his macromolecular theory in Europe. In 1931 he gave lectures on the macromolecular structure of polymers at the International Solvay-Congress in Brussels and before the Société Chimique de France in Paris.[2] In the following year the Faraday Society in England organized a symposium, "The Colloid Aspects of Textile Materials and Related Topics," in Manchester, where Staudinger, Herman F. Mark, and other German chemists were invited to present papers.[3] The subject of high polymers was also discussed by Staudinger at the ninth Congress of the International Union of Pure and Applied Chemistry, held in Madrid in the spring of 1934.[4]

Around 1933 the political upheaval in Germany began to make a profound impact on its academic circles. The Weimar Republic ended in 1933 when Hitler came to power with his anti-Semitism campaign. In April of this year, the Nazis managed to pass the Civil Service Law

under which no employment was to be given to persons of non-Aryan descent.[5] The leading authorities on polymers, including Staudinger's redoubtable opponents, were forced to resign their positions at the Kaiser Wilhelm-Institute, which was then under State control. Max Bergmann, then the director of the Institut für Lederforschung in Dresden, moved to the United States in 1933. He later worked for the Rockefeller Institute for Medical Research in New York until his death in 1940. Reginald O. Herzog, the director of the Institut für Fasenstoffchemie Berlin-Dahlem, fled to Istanbul in 1934 and died a year later. Hans Pringsheim, ausserordentlicher Professor at the University of Berlin, left for Paris in 1933 and died in Genf in 1940. While Staudinger, non-Jewish and politically neutral, remained at Freiburg im Breisgau, the political conditions in Germany also caused the supporters of the large-molecular concept, Kurt H. Meyer and Mark at the I. G. Farbenindustrie, to leave the country in 1932. Meyer succeeded Amé Pictet (1857-1937) as head of the laboratories of organic and inorganic chemistry at the University of Geneva, Switzerland, where he continued his research on natural polymers. Half Jewish, Mark moved to Austria, accepting the position of Director of the first Chemical Laboratorium at the University of Vienna. There, together with a number of his young colleagues, he zealously injected polymer chemistry into the traditional chemical curriculum and put forward his investigations on polymerization.[6] The intellectual migration of these polymer chemists provided a renewed stimulus in this field to European scientific circles, and in the mid-1930s the arena of heated discussions on macromolecules moved almost entirely outside the walls of the Third Reich.

Faraday Society, 1935

The Faraday Society arranged an international symposium on "The Phenomena of Polymerization and Condensation" at the University of Cambridge in September 1935. This was the first international conference devoted exclusively to general studies of polymers. It was also at this meeting that the two champions of macromolecules, Staudinger (Freiburg) and Wallace H. Carothers (Wilmington, Delaware), met together for the first time. In addition, the overseas guests included Meyer (Geneva), Mark (Vienna), Pringsheim (Paris), Johann R. Katz (Amsterdam), and the cellulose chemist, Karl Freudenburg (b. 1886) (Heidelberg). Among the British speakers were Eric Keightley Rideal (b. 1890) and Harry Work Melville (b. 1908) both at Cambridge, who had embarked on their studies in this field. The large size of the program was indicated by the total of thirty-three papers presented during the three-day session.[7]

Mark remembers, "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"[8] Appearing before the European audience for the first time, Carothers gave a lecture, "Polymers and Polyfunctionality,"[8] which dealt mainly with his major field, condensation polymerization.[9] Staudinger, on the other hand, presented a paper, "The Formation of High Polymers of Unsaturated Substances," which was devoted to addition polymerization.[10]

Let us remember that, striking a blow against the physicalist conception of polymerization, Staudinger had brought back Berzelius' classical notions about polymers to this field. In his discussions at

the meeting, he again stressed that "a polymerisation is a process in which a substance of low molecular weight is transformed into a substance of equal composition but of higher multiple molecular weight."[11] In this process, a monomer and a polymer ought to have the same composition, namely, the polymer is simply made up of monomer units. This definition can be applied only to the addition polymerisation of unsaturated monomer molecules which tend to combine together without changing the composition. It followed that condensation polymers, such as polyesters and polyamides, are not "polymers" by definition, since they are formed by elimination of secondary compounds (such as water) and not by pure self-addition. Consequently, Staudinger's group directed chemists' attention exclusively to the "true" polymerization products, namely addition polymers. But in his lecture, Carothers suggested that the definition of polymerization is in need of alteration. He stressed:

> Professor Staudinger's point of view has considerable historical justification, but it presents certain logical and practical difficulties. Apparently it involves the necessity of making a distinction between polymers and "real polymers" and of admitting that polymers can be formed by reactions that are not polymerisation. . . .
>
> It is true that large molecules are in some cases built up from small ones by reactions that appear, at least, to consist in pure addition, while in other cases they are formed by reactions that are demonstrably condensations. Staudinger proposes to call the latter type of reaction polycondensation. . . . but I contend that we may as well give in to the logic of the situation and admit that such reactions constitute one type of polymerisation: the products are polymers . . .[12]

Although the issue was of wording, the clarification of the terminology was particularly important during this period, amidst the transition in chemists' concept of polymers and polymerization. Now that the old definition did not match the practical usage, the creation of a new definition involving both addition and condensation polymers seemed indispen-

sable. Carothers' claim demanded sufficient consideration among his contemporaries and an agreement was reached later when the Council of the International Union of Pure and Applied Chemistry made its "Report on Nomenclature in the Field of Macromolecules" in 1951. The general definitions were given as follows:

> Polymerization: the process of formation of polymer molecules from small molecules, with or without the production of other small molecules not entering into the composition of the polymer.
>
> High polymer: a macromolecular substance which . . . consists of molecules which are at least approximately, multiples of a low-molecular unit. In agreement of present-day usage, a high polymer need not consist of molecules which are all of the same size, nor is it necessary that they have exactly the same composition or chemical structure as each other or as the corresponding monomer.[13]

The issues under discussion at the 1935 Faraday Society meeting centered on the details of polymers and polymerization, including the mechanism of polymerization reactions, the determination of molecular weight, the viscosity law, the nature of polymers, the shape of macromolecules, and potential areas of application. As had happened at the previous Faraday Society conference in 1932, Staudinger defended his view against Mark that linear macromolecules have a rigid fiber shape just like a thin flexible glass fiber. His viscosity law, that viscosity is in direct proportion to molecular size, was only understandable on this assumption. Accordingly, long rigid rods of the macromolecule move across a flowing liquid, rotating as they move in a disc-like plane. A rigid shape of the molecules appeared to him in harmony with general experiences in organic chemistry.[14]

However, Mark continued to vigorously oppose Staudinger on this matter, taking the view that such a mechanism contradicts all requirements of physical chemistry:

> The chain-like macromolecules, which must be investigated in extremely diluted solution seem not to be compact, more or less sphere-like clusters (compare for instance, Fig. 1a). They are, moreover, not quite extended and stiff with elastic vibrations (as shown in Fig. 1b), but they are in a state, as it is shown in Fig. 1c, that is to say, they are bent but not rolled entirely together. If one assumes the form shown in Fig. 1c one gets in fairly good agreement with all experimental evidence . . . and remains at the same time in concordance with fundamental statistical considerations and with the principle of the free rotation round the single carbon bond. I think that the shape shown in Fig. 1c may be regarded as a close approximation to the real form of the long molecules in solution.[15]

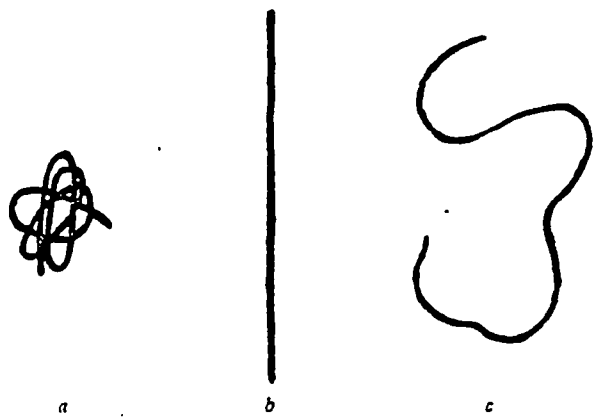


Fig. 4.1.

Supported by the latest statistical study by Werner Kuhn (1899-1963), which suggested that the separate links of the macromolecular chain can revolve in relation to each other, Mark's concept of flexible chains was to lead to an alteration of Staudinger's viscosity equation several years later.[16] The new formula showed that the empirical Staudinger relationship is valid only for a few specific systems but not for many important polymers such as rubber, polystyrene, and polyamides. The so-called linear macromolecules exhibit a considerable number of irregularly contorted configurations, which would well explain some physical properties of polymers including the very high viscosity of dilute polymer solutions,

double refractions of flow, and rubber elasticity. The contorted configurations were a possibility which the structural organic chemist Staudinger did not take into account. Ironically, the rise of Mark's and Kuhn's views indicated the great possibilities still left to the physicalist approach in the field of macromolecules which Staudinger had deliberately organized as a branch of organic chemistry.[17]

While there were conflicts of opinions between speakers, the scene of the 1935 Faraday Society was on the whole impressive enough to persuade Mark to call it one of the "milestones of modern chemical history."[18] What was absent from this symposium was the familiar debate between the macromolecular theory versus aggregate theory, which had been so dominant at previous scientific gatherings. The former exponent of the aggregate view, Pringsheim, now present at the Cambridge meeting, no longer invoked his initial theory against the macromolecularity of polymers. Referring to recent developments furthered by the work of Staudinger, Carothers, Meyer, himself, and others, Mark was able to declare in his lecture that "the chain-structure of the polymerization products can now be considered as a fairly well-established fact."[19] The large size and high level of this conference, Mark wrote,

> 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. . . .
>
> 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.[20]

The Cambridge international conference on polymerization thus vividly illustrated the end of the decade-long controversy over the fundamental principle, the macromolecular structure of high polymeric substances.

With the shift from the aggregate theory toward the macromolecular theory, polymer chemistry now became identical with the chemistry of macromolecules in scientists' conceptions.

Macromolecular Schools and the Emerging Discipline in Germany and America

The wide reception of the macromolecular theory followed a rapid expansion of investigations on polymers toward the early 1940s. Owing to the two initiators, Staudinger and Carothers, Germany and the United States won particularly early recognition for macromolecular chemistry as a growing new field of chemical science. Staudinger's Zürich and Freiburg schools and Carothers' Wilmington circle played key roles in the diffusion of knowledge and the training of younger generations of scientists and industrial chemists in this field. Yet a parallel development, in the two countries does not mean that exactly the same pattern in the rise of this field was followed. Rather, the different schools of macromolecular chemistry in Germany and the United States largely reflect the different institutional and social settings in which scientists interacted. This section attempts to examine and contrast some of the important characteristics of the two macromolecular schools in Germany and the United States in relation to the growth of macromolecular chemistry between the 1920s and 1940s.

Staudinger's impact is most clearly illustrated by the large number of his students and co-workers. Zürich and Freiburg, where he had been putting forward his macromolecular theory since the beginning of the 1920s, were called the "Highboroughs of High Polymers" from which emerged a generation of macromolecular chemists in universities,

Hochschules, and industrial laboratories.[21] Between 1920 and 1927, Staudinger trained 17 doctoral students in this field at the Eidgenösissche Technische Hochschule in Zürich. During the period between 1928 and his retirement in 1954, he directed 57 doctoral students in the study of macromolecules at the University of Freiburg. The sum total was 74 doctorates in thirty-five years of his academic career (see Fig. 4.2). During this period, as a prolific writer, Staudinger published over five hundred papers on macromolecular chemistry in various German scientific periodicals, although the papers often overlapped in content. He published these treatises alone and with approximately one-hundred co-workers who included his doctoral and postdoctoral students as well as his colleagues (see Fig. 4.3).

In many respects, Staudinger's macromolecular school, whether in Zürich or Freiberg, shared characteristics often found in other distinguished research schools of the time, such as Emil Fischer's Berlin school of organic chemistry, and Roger Adams' Illinois school of synthetic chemistry, although differing from them in that the Staudinger school emerged with views in conflict with current, well-established theory.[24] In contrast, the schools of Fischer and Adams carried out innovative research programs within existing and well-founded specialties. Here, we see that Staudinger's strong leadership persuaded his pupils to follow the master's foresight. He used all possible means at his disposal, through his students, his associates, his lectures and publications, to spread his views and to spur those interested in the field into action. From the start of his investigations on macromolecules, he was an organic chemist of high reputation in traditional lines of research

Fig. 4.2. Staudinger's Doctoral Students in Macromolecular Chemistry, 1920-1954.[22]

Eidgenössische Technische Hochschule, 1920-1927

Name	Thesis Completed	Name	Thesis Completed
E. Suter	1920	E. Geiger	1926
F. Felix	1923	E. Huber	1926
J. Fritschi	1923	E. W. Reuss	1926
M. Lüthy	1923	S. Wehrli	1926
A. Rheiner	1923	H. Harder	1927
H. A. Bruson	1925	H. W. Johner	1927
W. Widmer	1925	R. Signer	1927
M. Brunner	1926	E. Urech	1927
K. Frey	1926		

Universität Freiburg im Breisgau, 1928-1954

Name	Thesis Completed	Name	Thesis Completed
D. Russidis	1928	G. Daumiller	1937
W. Starck	1928	K. Fischer	1937
H. Thron	1928	I. Jurisch	1937
H. F. Bondy	1929	F. Reinecke	1937
W. Heuer	1929	H. Schmidt	1938
W. Reisst	1930	J. Schneiders	1938
A. Schwalbach	1930	A. W. Sohn	1938
O. Schweitzer	1930	K. F. Daemisch	1939
W. Schaal	1931	B. Lantzsch	1939
W. Kern	1932	O. Nuss	1939
E. O. Leupold	1932	F. Zapf	1939
H. Lohmann	1932	K. Eder	1940
E. Trommsdorf	1932	F. Finck	1940
A. Steinhofer	1933	Hj. Staudinger*	1940
E. Dreher	1934	O. Heick	1941
H. Eilers	1934	H. Jorder	1941
H. Schwalenstöcker	1934	E. Roos	1941
H. von Becker	1935	F. Berndt	1942
H. Frey	1935	W. Döhle	1942
H.-P. Mojen	1935	W. Keller	1942
B. Ritzenthaler	1935	G. Lorentz	1943
K. Rössler	1935	H. Hellfriz	1944
F. Staiger	1935	P. Herrbach	1944
M. Sorkin	1936		
A. E. Werner	1936		

Fig. 4.2, continued.

Name	Thesis Completed
H. Schnell	1944
H. Sattel	1945
H. Batzer	1946
K.-H. In den Birken	1949
M. Häberle	1952
W. Hahn	1952
T. Eicher	1953
G. Niessen	1954
K. Wagner	1954

*Hansjürgen Staudinger (1914-), Hermann Staudinger's son, an organic chemist.

Fig. 4.3. Co-authors of Staudinger's Papers on Macromolecular Chemistry, 1920-1955.[23]

M. Asano
A. A. Ashdown
R. C. Bauer
M. von Becker
G. Berger
F. Berndt
G. Bier
H. F. Bondy*
F. Breusch
M. Brunner*
H. A. Bruson*
K. F. Daemisch*
G. Daumiller*
W. Döhle
E. Dreher*
T. Eicher*
H. Eiler*
H. af Ekenstam
W. Feisst*
K. Feuerstein
K. Fischer*
T. Fleitmann
E. Franz
H. Fredenberger
K. Frey*
J. Fritschi*
W. Frost
P. Garbsch
E. Geiger
H. Haas
M. Häberle*
W. Hahn*
O. Heick*
H. Hellfriz*
J. Hengstenberg
J. J. Herrera
P. Herrbach*
W. Heuer*
E. Huber*
O. Huntwyler
E. Husemann*
K.-H. In den Birken*
H. Jöder
H. W. Johner*
H. Joseph
I. Jurisch*
W. Kern*
H. W. Klever
H. W. Kohlenschütter
B. Kupfer
B. Lantzsch
L. Lautenschläger
E. O. Leupold*
H. Lohmann*
G. Lorentz*
M. Lüthy*
H. Machemer
G. Mie
R. Mohr
H.-P. Mojen*
H. Moser
G. Niessen*
R. Nodzu
O. Nuss
E. Ochiai
F. Reinecke*
A. Rheiner*
B. Ritzenthaler*
K. Rössler*
D. Russidis*
E. Sauter
W. Schaal*
A. Schwalbach*
G. Schiemann
W. Schilt
H. Schmidt*
J. Schneiders*
H. Schnell*
H. Scholz
G. V. Schulz
H. Schwalenstöcker*
O. Schweitzer*
J. R. Senior
R. Signer*
A. W. Sohn*
M. Sorkin*
F. Staiger*
W. Starck*
Hj. Staudinger*
M. Staudinger
A. Steinhofer*
H. Stock
E. Trommsdorf*
E. Urech*
K. Wagner*
H. Warth
S. Wehrli*
K. W. Werner
G. Widmer
W. Widmer*
W. Widerscheim
E. Zapf*

*--Staudinger's doctoral students.

and thus able to exercise his institutional power. With a coherent method and program of macromolecular research, he maintained his charismatic leadership of dozens of advanced students.

At the same time, he did not neglect opportunities to pay his co-workers tributes for their collaboration. His students were encouraged to publish their work early under the joint names of their own and the master's. Although strict and rigorous in teaching, the educator's attitude toward his students no doubt consolidated the teacher-student relationship. Apparently, Staudinger's school was isolated during the 1920s when he was involved in stormy controversy with many scientists with high academic positions. His wife Magda Staudinger later recalled that this made his students cling together tightly: "the laboratory was [then] very much like a dedicated brotherhood . . ."[25]

A number of Staudinger's students remained as Privat Dozenten at his school for some years after graduation, continued their studies, and directed younger students along the lines of the Professor's program. One of Staudinger's outstanding students, Rudolph Signer (b. 1903), who received the doctoral degree in 1927, served as Privat Dozent at Freiburg for eight years before he accepted a position at the University of Bern in 1935. Staudinger assigned him investigations on the shape of macromolecules in solution. Signer completed this task by introducing an apparatus for flow birefringence, a simple device that measures optically the approximate length to breadth ratio of long-chain molecules. Signer, who also studied the ultracentrifuge at Sveberg's laboratory in Uppsala in his postdoctoral years, thus showed the influence of "physical"

method on Staudinger's school.[26] Among Staudinger's chief collaborators was Günther Viktor Schulz (1905-). He was not Staudinger's doctoral student but studied colloid chemistry under Herbert Freundlich (1880-1941) at the Kaiser Wilhelm-Institut für Physikalische und Elekrochemie in Berlin-Dahlem. Schulz fell under the influence of Staudinger when the macromolecular chemist invited this young colloid chemist to join the Freiburg school as Dozent in 1937. Of particular interest is the implication that Staudinger's intent was to extend the understanding of macromolecules on the basis of physico-chemical methods--a subject which Staudinger traditionally had left aside. Schulz fulfilled this request through his considerable study on molecular weight determinations and the kinetics of polymerization reactions. After moving to the University of Rostock in 1943 and then the University of Mainz, he further exerted powerful influence on academic circles in this field.[27]

Papers of the Staudinger school were published for two decades in various journals, including Berichte der deutschen chemischen Gesellschaft, Helvetica Chimica Acta, Angewandte Chemie, Justus Liebigs Annalen der Chemie, and Chemiker-Zeitung. In 1940 he took over the editorship of the Journal für praktische Chemie, published in Leipzig. Taking advantage of this position, he converted this old, established periodical into a new form with the sub-title Unter Berücksichtigung der makromolekularen Chemie. The revised issue started in February 1940 with his introductory essay, "Über niedermolekulare und makromolekulare Chemie."[28] Although the primary coverage was the field of large molecules, this journal still carried unrelated subjects in organic chemistry. The first volume of the revised edition (four issues) contained twenty papers of which only

eight articles dealt directly with macromolecular chemistry. Four years later, Staudinger ventured to change the whole title of the journal into Journal für makromolekulare Chemie. But it was not sufficiently distributed and ended with the publication of only two volumes as a result of the wartime conditions in Germany. After World War II, since journal publication at Leipzig became virtually impossible, he founded the new journal Die makromolekulare Chemie in Basel in 1947. From a practical point of view, this was the first German periodical devoted exclusively to macromolecular chemistry. Staudinger reigned over this journal as editor for the ensuing two decades until his death at the age of eighty-four.[29]

Throughout his long career, Staudinger's interest remained primarily in the realm of pure science and did not extend to its practical applications. This disinterest was a facet of his scientific personality. Magda Staudinger relates,

> he never was interested in industrial processes of production and applications; he preferred to work on the whole field of macromolecules . . . he was very interested to see what was going on in industry and to hear what his pupils were doing there--but not to work himself for such applications.[30]

In his most active research period (the 1920s and 1930s), he devoted his studies to demonstrating the macromolecular structure of natural polymers such as rubber and cellulose. As we have seen earlier, the synthetic polymers (such as polyoxymethylenes, polystyrenes, and polyvinyl alcohols) that he prepared in his laboratories were used for the models for those natural polymers. He had little intention to transform his synthetic polymers into industrial porducts. To be sure, he did realize the possibility of their practical utility in due course, since the structure of synthetic high polymers resembled that of natural polymers. While

Carothers' group was developing fiber synthesis from condensation superpolymers, Staudinger pointed out that "sooner or later a way will be discovered to prepare artificial fibers" from his addition polymers.[31] Nevertheless, in contrast to Carothers, he never pursued the practical problem of how, then, fibers could be drawn from the chemical materials. His work on addition polymers had drawn particular attention from the chemical industry and the electrochemical industry as early as the middle of the 1920s. I.G.-Farben Fabrik Höchst, for example, attempted to develop polyvinyl acetate in co-operation with the Freiburg laboratory in 1926.[32] But, with such few exceptions, Staudinger himself was not directly involved in industrial undertakings. Applied research was not within the scope of his own research program. Within the walls of universities, the German professor could retain the traditional values of academic scientists and pursue the ideal of German Wissenschaft. Apart from the fact that some of his students brought his science into industrial research, the impact of Staudinger's work on German industry was less direct than on academic circles. The firm establishment of practical foundations and subsequent industrialization of macromolecular science occurred in the United States earlier than in Germany. They took place, even at the time when the majority of American academic scientists was still not ready to enter this field.

Carothers' circle at Du Pont took the initiative in the emergence of American macromolecular chemistry academically as well as industrially. His group of fundamental research in organic chemistry was organized into Du Pont's Chemical Department and located in the Experimental Station, Wilmington (see Fig. 4.4). Although the group was small in size as compared

with Staudinger's German school, Carothers headed a number of well-trained, able research chemists. Between June 1928 and his premature death in April 1937, he had a total of 25 co-workers including 20 researchers with the Ph.D. degree and 5 non-Ph.D. chemists. While the group members changed from time to time, the number working together at any one time was usually about ten during his active period (see Figs. 4.5 and 4.6). Many of these co-workers were only slightly younger than the group leader.

In the short space of eight years (1929-1936), Carothers, alone and with a total of 14 collaborators, published 52 papers on polymers and polymerization mostly in the Journal of the American Chemical Society (see Fig. 4.7). He was granted sixty-nine U.S. patents in this field, most of which were equivalent in content to scientific papers.[37]

Unlike the German professor Staudinger, Carothers was not an authoritative leader in his group. Informal in the group, Carothers maintained an intellectual atmosphere in which the leader never "directed" but rather "guided" his co-workers in accordance with their own skills. The group leader constantly reminded his co-workers of working with him, and not for him. This team concept came not merely from the company structure but largely from Carothers' own personality.[38] According to his close friend John R. Johnson,

> His dominant quality was that of the research scholar. He was modest and unassuming in manner, shunned publicity, and, shy and sensitive by nature, was ill at ease in a large group, although within his small circle of close friends he was a witty conversationalist.[39]

In his Harvard days, he had not been a particularly successful lecturer in the classroom. He was not the type of scholar who would become a top professor with administrative power, but he was primarily a research man.

Fig. 4.4. The Organization of the Chemical Department, E. I. Du Pont de Nemours and Company, as of July, 1930.[33]

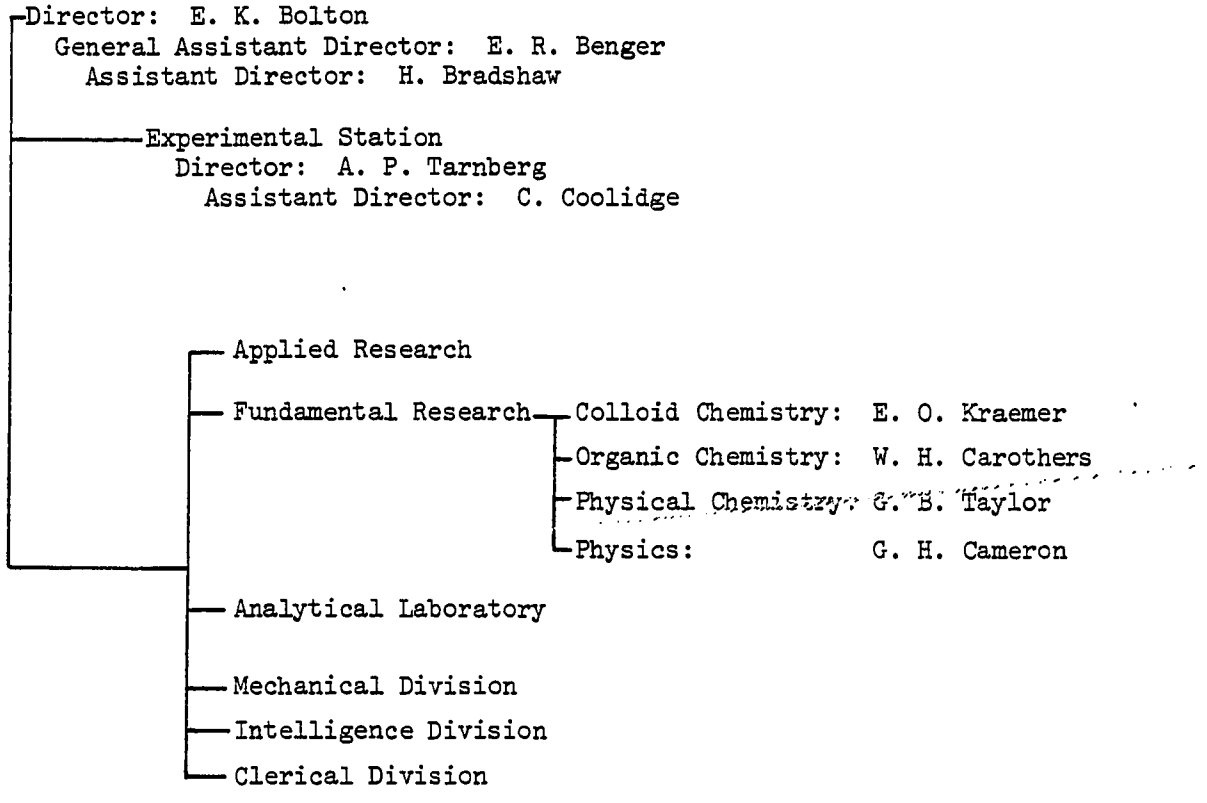


Fig. 4.5. Carothers' Co-workers in the Fundamental Research Group in Organic Chemistry at the Du Pont Company, 1928-1937.[34]

Name	University (Date of Ph.D.)	Research Period in Carothers' group at the Du Pont Company
J. A. Arvin	Illinois (1928)	1928
G. J. Berchet	Colorado (1930)	1929-1937
D. D. Coffman	Illinois (1930)	1931-1935
A. M. Collins	Columbia (1920)	1930-1934
. . Conner*		1934
M. E. Cupery	Illinois (1930)	1931-1933
G. L. Dorough	Johns Hopkins (1929)	1929-1932
H. B. Dykstra	Ohio State (1927)	1932
P. J. Flory	Ohio State (1934)	1934-1937
J. H. Hill	MIT (1928)	1929-1935
R. A. Jacobson	Illinois (1925)	1928-1931
G. A. Jones*		1929-1930
J. E. Kirby	Iowa State (1929)	1929-1934
O. R. Kreimeier*		1931-1932
S. B. Kuykendall*	Ohio State (1935)	1930
W. L. McEwen	Harvard (1928)	1929-1935
W. J. Merrill	Ohio State (1930)	1931-1932, 1935
W. R. Peterson	Illinois (1927)	1934-1936
G. W. Rigby	MIT (1930)	1934-1935
E. W. Spanagel	McGill (1933)	1933-1935
H. W. Starkweather	Harvard (1925)	1931-1934
W. F. Talbot	Iowa (1929)	1930
W. H. Taylor*		1928
F. J. van Natta	Michigan (1928)	1928-1935
F. C. Wagner	Johns Hopkins (1929)	1935

The asterisk indicates a then non-Ph.D. chemist.

Fig. 4.6. Number of Carothers' Co-workers, 1928-1937.[35]

Date	Ph.D. Workers	Non Ph.D. Workers	Total
1928	3	1	4
1929	7	1	8
1930	9	3	12
1931	11-12	1	12-13
1932	11-12	0-1	11-13
1933	10	0	10
1934	10-12	0-1	10-13
1935	9-10	0	9-10
Fall 1935-Spring 1936	3	0	3
Summer 1936	0	0	0
Fall 1936	1	0	1
1937	2	0	2

Fig. 4.7. Co-authors of Carothers' Papers on Polymer Chemistry, 1929-1936.[36]

J. A. Arvin*
G. J. Berchet*
D. D. Coffman*
A. M. Collins*
M. E. Cupery*
G. L. Dorough*
H. B. Dykstra*
J. H. Hill*
R. A. Jacobson*
J. E. Kirby*
J. A. Nieuland
E. W. Spanagel*
F. J. van Natta*
I. Williams

Asterisks are Carothers' co-workers at Du Pont.

Du Pont's fundamental research program was apparently well suited to his scientific personality, since it demanded only basic research in a small group of chemists to assist him with facilities that "would be difficult or impossible to duplicate in most university laboratories" (as James B. Conant put it).[40] The Company allowed him to select his own research subject and to publish scientific papers. This "academic freedom" was sustained by the Company staff, notably the directors of the Chemical Department who possessed strong administrative power at Du Pont. Carothers served as a thinker or a man of ideas in this framework. This role which Carothers played was much admired by Elmer K. Bolton, the Chemical Director who worked with him between 1930 and 1937:

> All of us who have had association with him were impressed by his broad and profound knowledge of chemistry. Not only his co-workers were inspired by his theoretical knowledge but all those who sought his adivce, which he gave generously. . . . He was a man of fine personality, modest, generous, uncomplaining, and a tireless worker. In short, he approached the ideal of a scientific investigator in personal characteristics and in relationships with his associates.[41]

This combination of the director with administrative power (Bolton) and the group leader with scientific originality (Carothers) shaped a successful organization character of the fundamental research program at Du Pont.

It is important to note that the contrast between Staudinger's and Carothers' research circles is not simply due to a difference between academic science, on the one hand, and industrial or applied research on the other. In the past decade, a number of historical studies have focussed attention on the problem of "research schools," including Liebig's Giessen school of analytical chemistry (J. B. Morrell), Michael Foster's Cambridge school of physiology (G. L. Geison), Ira Ramsen's Johns Hopkins

school of chemistry (O. Hannaway), and Bancroft's Cornell school of physical chemistry (J. W. Servos).[42] These studies have largely expounded various factors (in general terms) which might contribute to the success or failure of scientific research schools. The existing literature tends to consider the research school as a peculiar phenomenon closely associated with the institutionalization of science in the universities. Thus, Gerald L. Geison defines research schools as "small groups of mature scientists pursuing a reasonably coherent programme of research side-by-side with advanced students in the same institutional context and engaging in direct, continuous social and intellectual interaction." A common picture of successful or influential research schools is the image of a charismatic university professor with a distinguished research reputation and institutional power directing a host of faithful graduate students along the lines of his innovative research program, controlling publication outlets and exerting strong influence on the scientific community.[43] Indeed, such a picture does correspond with Staudinger's university-based school of macromolecular chemistry.

Yet Carothers' fundamental research group at Du Pont does not fit with this conventional image of research schools. Like others, it was a laboratory-based research school with a coherent new program. It did carry out basic research which pioneered American polymer chemistry. However, Carothers' mode of industrial research was by no means a mere copy of university practice. Let us consider why this is the case. In his recent study of industrial research at the General Electric Company between 1900 and 1916, George Wise has outlined some important characteristics accompanying the new type of industrial research that marked

early twentieth-century America. Previously, the movement of professional scientists into industry during this period was often interpreted as follows: the industrial scientist was molded into a worker on the production line; or on the contrary, the industrial research laboratory was a sort of "university-in-exile insulated from the demands of the factory." Regarding these oversimplified pictures as untenable, Wise has pointed out that the research laboratory created an entirely new role: "a blend of research freedom and practical usefulness not available before 1900." He has suggested that those who chose research careers in industry were "attracted to the content of the physical sciences, the identity of a researcher rather than a tester or engineer, the wish to attack practical problems, and the desire to share in the financial rewards offered by industry."[44] Carothers' basic research program at Du Pont, which was initially modeled on the GE experience, possessed a similar nature, namely a blend of research freedom and practical orientation. This dual character of academic and practical science becomes particularly clear when we see the remarkable flexibility with which the Carothers' circle converted his basic scientific theory into a program of applications in the Company's organization.

Under Carothers' guidance, his co-workers devoted full time to the basic research on polymers at Du Pont's "Purity Hall." This state of affairs presents a marked contrast to the case of Meyer and Mark, who worked together between 1927 and 1932 in this field at the I. G. Farbenindustrie in Germany. Mark wrote:

> K. H. Meyer was a member of the Board of Directors of I. G. Farben and the manager of the plant at Ludwigshafen. I was manager of a relatively large industrial research and development laboratory--

> almost 50 scientific collaborators--in which existing manufacturing processes were supervised and new commercially feasible products developed. Professor Meyer and I spent very little time on fundamental research usually only in occasional discussions, over weekends or during a joint visit to Frankfurt. My laboratory was essentailly occupied with the examination and testing of viscose and acetate fibers which were produced by the company, and with the synthesis and evaluation of new polymers . . .[45]

Du Pont expended approximately a total of 250,000 dollars on the basic research of the Carothers team for the first four years (1928-1931), amid the Great Depression.[46] In addition, the Company purchased for research purpose a Svedberg ultracentrifuge--a costly apparatus which even Staudinger could not obtain in Germany.[47] However, while starting with a purely scientific inquiry on the macromolecularity of polymers, Carothers' fundamental research group was destined to turn in the direction of practical application, once the Company recognized the prospects for the usefulness of their findings, as we have seen in the discovery of nylon. Here, the directors wasted no time in inducing Carothers to a conversion from theory to practice. This inducement was quickly followed, and the results were the industrialization of macromolecular science in a remarkably short period.

Undoubtedly, there existed more or less the familiar conflict between academic and industrial values in Carothers' mind, as pointed out in other similar case studies of American industrial researchers.[48] Apparently, his primary interest was in pure science. Like other academic scientists, he was always concerned with publication. Within the industrial organization, he was able to fullfil this desire by publishing an exceptionally large number of scientific papers, many of which were so open that the readers could realize what Du Pont research was up to. Yet the publications were made after the Company's meticulous

censorship and patent application whenever necessary.[49] To that extent, Carothers' "academic freedom" was restricted by the industrial framework. However, there are several indications that Carothers relatively smoothly accepted and endeavored to assimilate himself into the given industrial environment. A top student of the pragmatic chemist Roger Adams, he complemented his concern with pure science with a keen and active interest in practical aspects of his science, as a number of his associates reported.[50] Parallel to his scientific papers, he filed a large number of patents himself, with a hope that their "broad claims are likely to dominate any practical developments that are made in the future."[51] During his Wilmington days, he was offered attractive academic positions from several universities, including the University of Chicago. But he chose to remain to the end as an industrial scientist at the Du Pont Company.

Carothers' work on the macromolecular synthesis had immediate effects on industrial chemists. For example, inspired by Carothers' 1931 paper, "Polymerization," and his subsequent fiber patents (and not by Staudinger's work), Paul Schulack (1897-) of the I.G. Farbenindustrie in 1938 synthesized nylon 6, a nylon formed by the polymerization of a carboxyl amine with ring structure, caprolactam. Given the trade name "Perlon," the fiber was produced at the I.G. plants during the second world war; its manufacture was adopted after the war by Japan, Italy, Holland, and other countries which could not obtain Du Pont's patent of nylon 66. The English industrial chemists, John Rex. Whinfield (1901-1966) and James Tennent Dickson, working in the laboratories of the Calico Printers' Associations, snythesized in 1941 a polyester fiber of high quality, later called "Terilen." Almost simultaneously with the British

development, Du Pont independently discovered the same fiber, named "Dacron." This concurrence was by no means an accident, for both works were based on Carothers' studies on condensation polymers in the 1930s. As Whinfield wrote, their investigations were "a logical extension" of Carothers' series of papers, "Studies on Polymerization and Ring Formation."[52]

Unlike the university professor Staudinger, Carothers did not train students. Yet, under his influence, there emerged the first generation of polymer chemists in American universities. Through his series of papers, his work on the macromolecular synthesis was known in academic circles in his lifetime. He gave lectures on polymers and on his theory of polymerization before several chemical groups, including the American Chemical Society and the Johns Hopkins summer colloquium. After his untimely death in 1937, Paul Flory (1910-) and Carl Shipp Marvel were among those who followed up on the Carothers tradition of research.

Flory was introduced to the field of macromolecules when he joined Carothers' fundamental research group at Du Pont in 1934. Trained as a physical chemist at Ohio State University, Flory embarked on a program of support for Carothers' study from the mathematical side. At Du Pont he investigated molecular size distribution in linear condensation polymers on the basis of statistical methods. His study of the kinetics of addition reaction introduced the concept of chain transfer, whereby a growing chain molecule can be saturated with an atom from another molecule that might be a monomer, a polymer, or a solvent molecule.[53] In 1938, shortly after Carother's death, Flory left the Du Pont Company for the University of Cincinnati and later Cornell

University, where he continued his theoretical studies in the physical chemistry of macromolecules--the work which was to win him the Nobel Prize in chemistry in 1974. His textbook Principles of Polymer Chemistry (1953), which stemmed from his Baker Lectures at Cornell in 1948, played a definitive role in pedagogy in this growing field. The book served as the bible for generations of polymer scientists throughout the world.[54]

Marvel, Adams' colleague at the University of Illinois, was also ignited in his interest in polymer chemistry through close contact with Carothers, both as a friend and as a consultant for the Du Pont Company from 1928. Influenced by Carothers' work, Marvel devoted most of his research to this field from 1933 onwards. His investigation areas ranged from sulfur dioxide addition polymers, and the mechanism of vinyl polymerizations to the development of synthetic rubber. In Illinois he trained a large body of doctoral and postdoctoral students and published over four hundred papers in polymer chemistry.[55] Thus, Carothers' successors brought the study of macromolecules into the academic setting already in the 1930s. American polymer chemistry, which first arose from the basic research program in industry, gradually spread as an academic discipline in the universities by the late 1940s. Carothers' basic research led to the production of nylon and contributed to the doubling of Du Pont's expectations, this mode of organizing research played a crucial role in the emergence of a new science in this country.

Further, in 1940, the American chemical community was to welcome a powerful organizer of macromolecular chemistry from Vienna, Herman F. Mark. In 1938, when Hitler's troops invaded Austria, Mark fled to Canada, where he

worked for the Canadian International Paper Company for two years. With the loss of Carothers, the Du Pont Company was eager to contact the best polymer chemists available and showed growing interest in establishing a connection with Mark who had personally corresponded with Carothers since 1934. Moving to the United States in 1940, he was appointed to a joint position as Du Pont consultant and Adjunct Professor at the Polytechnic Institute of Brooklyn, New York, with the financial backing of Du Pont.[56] In that year he started the publication of a monograph series on the chemistry of high polymers. Its first volume, edited with George S. Whitby, was Collected Papers of Wallace Hume Carothers on High Polymeric Substances. This "classical" work, the editors were convinced,

> will always remain an essential part of the foundation on which the high polymeric chemistry of the future will be erected. . . . there could be no better start for this series than to publish, as the first volume in it, a collection of the papers embodying Carothers' studies of high polymers and closely related matters."[57]

To this, three other volumes were added in this series by 1942, including works by Mark and his friend Kurt H. Meyer.[58] At Brooklyn, Mark taught his students an introductory course in polymer chemistry, and established a series of weekly symposia and intensive summer courses in this field, involving outside scholars and industrial researchers. By the middle of the decade the "Brooklyn Poly" had established a graduate program leading to M.S. and Ph.D. degrees with the major in polymer chemistry. A number of newly educated polymer chemists worked and helped to teach this field at the Institute under Mark's directorship. Specialized courses then offered included "Polymerization Kinetics" by Turner Alfrey (1918-), "Solution Properties of High Polymers," by Freder Roland Eirich (1905-), and "Organic Polymer Chemistry" by Charles Gilbert Overberger (1920-).

Developed into the independent "Polymer Research Institute" in 1946, Mark's Brooklyn school became a mecca for advanced students and polymer researchers, along with Marvel's Illinois school.[59]

World War II accelerated polymer research in American universities and industries. The government synthetic rubber research program, which started in 1941 in the face of Japan's occupation of the Pacific area, involved not only polymer chemists but also directed the attention of many leading academic and industrial scientists to the scientific problems involved in this field.[60] In the following year, Du Pont's entire production of nylon was allocated by the War Production Board for vital military uses such as parachutes, flak vests, and military tires. Shortly after the war, as the polymer industry grew to be one of the major industries in the United States, publications in polymer chemistry reached the point that the Journal of the American Chemical Society could hardly accept too many polymer manuscripts. Mark wasted no time in founding a separate journal in this field. The Journal of Polymer Science, the first English-language periodical devoted to the field of macromolecules, was inaugurated under the editorship of Mark in 1946, a year earlier than Staudinger's German journal, Die makromolekulare Chemie. Its first volume carried fifty-seven papers, and the journal became the leading vehicle for the growing number of polymer scientists in the postwar America. Building on the foundations that the researcher Carothers and his successors had firmly laid, Mark thus served as an important organizer and teacher in establishing the discipline of macromolecular chemistry in the United States, while Staudinger played the triple role as researcher, teacher, and organizer by his own efforts in the German academic circles. At the

same time, the growth of American macromolecular chemistry is a representative example of vital interactions between science, industry, and society.

NOTES

[1]Cf., Ch. III, pp. 95-97.

[2]Hermann Staudinger, "Sur la Structure des Composés à poids moléculaire élevé," (read at the ninth International Solvay-Congress, Brussels, April 1931); reprinted in Hermann Staudinger, Das Wissenschaftlichte Werk von Hermann Staudinger: Gesammelte Arbeiten nach Sachgebeiten geordnet, eds. Magda Staudinger, Heinrich Hopff, and Werner Kern, vol. 5: Arbeiten allgemeiner Richtung von Hermann Staudinger (Basel and Heidelberg: Hüthig & Weph Verlag, (1973): 55-125. Hermann Staudinger,"Sur la Constitution des Colloïdes moléculaires," (read at the Société chimique de France, June 12, 1921), Bull. Soc. chim., 49 (1931): 1267-1279.

[3]Papers at this meeting were published in Trans. Faraday Soc., 29 (1933), Pt. 1.

[4]Hermann Staudinger, "Die neuere Entwicklung der organischen Kolloidchemie," (lecture given on April 10, 1934, at the IXth International Congress for Pure and Applied Chemistry, Madrid, April 5-11, 1934), Trabajos del IX Congreso Internacional de Quimica Pura y Aplicada, Tomo IV: 9-47; reprinted in Staudinger, Wissenschaftlichte Werk, vol. 4: Physikalischchemische Untersuchungen an makromolekularen Stoffen (1975): 45-83.

[5]Cf., Edward Yarnall Hartshorne, The German Universities and National Socialism (Cambridge, Massachusetts: Harvard University Press, 1937); Fritz Ringer, The Decline of the German Mandarins: The German Academic Community, 1890-1933 (Cambridge, Massachusetts: Harvard University Press, 1969); Donald Fleming and Bernard Bailyn, eds., The Intellectual Migration: Europe and America, 1930-1960 (Cambridge, Massachusetts: Harvard University Press, 1969); and Alan D. Beyerchen, Scientists under Hitler: Politics and Physics Community in the Third Reich (New Haven and London: Yale University Press, 1977).

[6]For Meyer, see Herman F. Mark, "Kurt Heinrich Meyer, 1883-1952," Angew. Chem., 64 (1952): 521-523; L. E. R. Picken, "Prof. Kurt H. Meyer," Nature, 169 (1952), p. 820; A. J. A. van der Wyk, "Kurt Heinrich Meyer," Helv. Chim. Acta, 35 (1952): 1418-1422; and Dictionary of Scientific Biography, vol. 9 (1974), s.v. "Meyer, Kurt Heinrich," by W. V. Farrar. For Mark's activity during this period, see Herman F. Mark, "Polymer Chemistry in Europe and America--How It All Began," J. Chem. Educ., 58 (1981): 527-534, on pp. 531-532; Morton M. Hunt, "Profiles: Polymers

Everywhere--II," The New Yorker, (September 20, 1958): 46-79; and G. Allen Stahl, "Herman F. Mark: The Geheimrat," Polymer Science Overview: A Tribute to Herman F. Mark (Washington, D.C.: American Chemical Society, 1981): 61-88, on pp. 76-78.

[7]Papers at this meeting were published in Trans. Faraday Soc., 32 (1936), Pt. 1: 3-412.

[8]Herman F. Mark, "Coming to an Age of Polymers in Science and Technology," in History of Polymer Science and Technology, ed. Raymond B. Seymour (New York and Basel: Marcel Dekker, Inc., 1982): 1-9, on p. 5.

[9]Wallace Hume Carothers, "Polymers and Polyfunctionality," Trans. Faraday Soc., 32 (1936), Pt. 1: 39-49.

[10]Hermann Staudinger, "The Formation of High Polymers of Unsaturated Substances," ibid.: 97-115.

[11]Staudinger, discussion in Trans. Faraday Soc., 32 (1936), Pt. 1, p. 52. For this reason, Staudinger had called addition polymers "true polymerization products" (echte Polymerisationprodukte), as distinguished from "false polymerization products" (unechte Polymerisationprodukte), i.e., condensation polymers. Cf., Hermann Staudinger, "Über Polymerisation," Ber., 53 (1920): 1073-1085, on pp. 1074-1075.

[12]Wallace H. Carothers, discussion in Trans. Faraday Soc., 32 (1936), Pt. 1, p. 53. See also Carothers, "Polymers and Polyfunctionality," p. 39. Cf., Ch. III, pp. 107-108.

[13]International Union of Pure and Applied Chemistry, "Report on Nomenclature in the Field of Macromolecules," J. Poly. Sci., 8 (1952): 257-277, on pp. 258 and 261. The wording is slightly altered from the original text.

[14]Hermann Staudinger, discussion in Trans. Faraday Soc., 32 (1936), Pt. 1, pp. 311-313. See also Hermann Staudinger, "Viscosity Investigations for the Examination of the Constitution of Natural Products of High Molecular Weight and of Rubber and Cellulose," Trans. Faraday Soc., 29 (1933), Pt. 1: 18-32, p. 26 ff; and his discussion in ibid., pp. 43-44. Cf., Ch. II, pp. 83-84, n. 89.

[15]Herman F. Mark, discussion in Trans. Faraday Soc., 32 (1936), Pt. 1, p. 312. The number of the figure is mine. See also Herman F. Mark, discussion in Trans. Faraday Soc., 29 (1933), Pt. 1, pp. 40-43. At the 1932 Faraday Society meeting J. R. Katz had supported Staudinger's view of the rigid molecule, and N. K. Adam, E. K. Rideal, and W. Harrison argued in favor of Mark's concept of the flexible molecule. Ibid., pp. 44-53.

[16]Werner Kuhn, "Über die Gestalt fadenförmiger Moleküle in Lösungen," Kolloid-Z., 68 (1934): 2-15; and Eugen Guth and Herman F. Mark, "Zur innermolekularen Statistik, insbesondre bei Kettenmolekülen I," Monatsh.,

65 (1934): 93-121. In 1938 Mark proposed his general viscosity formula:

$$\eta_{sp} = \text{constant} \times M^{a}$$

where M = molecular weight, and "a" is a characteristic value for a given type of macromolecule, ranging between 0.5 and 2.0. If the exponent "a" is numerically large, then the chain is less folded; if it is small, the chain is highly folded and does not show strong influence on viscosity. Since the same formula was suggested simultaneously by Roelof Houwink (b. 1897) at Eindhoven, Holland, it has been called the Mark-Houwink Equation.

Cf., Staudinger's equation in Ch. II, p. 81, n. 72.

[17]The issue of molecular flexibility was briefly summarized in Herman F. Mark, Physical Chemistry of High Polymeric Systems (New York: Interscience Publishers, Inc., 1940), pp. 288-293. See also Mark, "Polymer Chemistry in Europe and America," p. 531 ff; and L. M. Pritykin, "The Role of Concepts of Structure in the Development of the Physical Chemistry of Polymers," Isis, 72 (1981): 446-456.

[18]Mark, "Coming to an Age of Polymers," p. 5.

[19]H. Dostal and Herman F. Mark, "The Mechanizm of Polymerisation," Trans. Faraday Soc., 32 (1936), Pt. 1: 54-69, on p. 54.

[20]Mark, "Coming to an Age of Polymers," p. 5.

[21]Herman F. Mark and Herman A. Bruson, "Hermann Staudinger," J. Poly. Sci., 19 (1956): 387-388, on p. 388.

[22]Based on the bibliography in Staudinger, Arbeitserinnerungen. Cf., Ch. II, pp. 77-78, n. 43, and p. 82, n. 79.

[23]Names drawn from the indices in Staudinger, Wissenschaftliche Werk, vols. 1-5, and from the bibliography in Staudinger, Arbeitserinnerungen (which lists 644 publications on polymer chemistry by Staudinger's group).

[24]For Fischer's characteristics and his Berlin school, see, e.g., Richard Willstätter, Aus meinem Leben: Von Arbeit, Musse und Freuden (Weinheim: Verlag Chemie, 1949) and Ch.I, pp. 9-12. On Adams' Illinois school, see D. Stanley Tarbell and Ann Tracy Tarbell, Roger Adams: Scientist and Statesman (Washington, D.C.: American Chemical Society, 1981) and Ch. III, p.91ff.in this essay. Cf., pp. 21-22 in this chapter.

[25]Cited in V. E. Yarsley, "Hermann Staudinger--His Life and Work: Memorial Lecture," Chemistry and Industry, no. 7 (February 18, 1967): 250-271, on p. 268.

[26]E.g., Rudolph Signer, "Über die Strömungsdoppelbrechung der

Molekülkolloide," Z. physik. Chem., (A) 150 (1930): 257-284.

[27]E.g., Günther V. Schulz, "Über die Beziehung zwischen Reaktionsgeschwindigkeit und Zusammensetzung des Reaktionsproduktes bei Makropolymerisationsvorgängen," ibid., (B) 30 (1935): 379-398; "Über die Verteilung der Molekulargewichte in hochpolymeren Gemischen und die Bestimmung des mittleren Molekulargewichtes," ibid., (B) 32(1936): 27-45; and "Osmotische Molekulargewichtsbestimmungen in polymerhomologen Reichen hochmolekularer Stoffe," ibid., (A) 176 (1936): 317-337.

[28]Hermann Staudinger, "Über niedermolekulare und makromolekular Chemie," J. prakt. Chem. 155 (1940): 1-12.

[29]See Staudinger, Arbeitserinnerungen, p. 100 ff.

[30]Quoted in Yarsley, "Hermann Staudinger," p. 263.

[31]Staudinger, "The Formations of High Polymers," p. 105.

[32]See Staudinger, Arbeitserinnerungen, p. 196 ff.

[33]Based on the organization chart of Chemical Department, E. I. Du Pont de Nemours & Company, July 11, 1930, in HD 9651.9, D 94 A13, EMHL.

[34]Based on the organization charts, "Experimental Station--Technical Staff," Oct. 23, 1928-May 14, 1937 (possession of Julian W. Hill); and American Men of Science, 7th ed. (1944) and 11th ed. (1967).

[35]Figures taken from "Experimental Station--Technical Staff."

[36]Names drawn from the publication list in Wallace Hume Carothers, Collected Papers of Wallace Hume Carothers on High Polymeric Substances (New York: Interscience Publishers, Inc., 1940), eds. Herman F. Mark and G. S. Whitby, pp. 424-427.

[37]See the patent list in Carothers, Collected Papers, pp. 429-432.

[38]Interview with Julian W. Hill, February 22, 1982; and interview with Martin E. Cupery by A. B. C. Strange, August 2, 1978, SC.

[39]Dictionary of American Biography, Supplement 2 (1958), s.v. "Carothers, Wallace Hume," by John Raven Johnson: 96-97, on p. 97.

[40]James Bryant Connant, quoted in Roger Adams, "Biographical Memoir of Wallace Hume Carothers, 1896-1937," National Academy of Sciences, Biographical Memoirs, 20 (1939): 293-309, on p. 297.

[41]Elmer Kaiser Bolton, "Speech at the Dedication to 'The Carothers Research Laboratory' on Tuesday, September 17, 1946," Acc. 147, Box 18, EMHL, pp. 1-2.

[42]For general discussions on this issue, see, e.g., Diana Crane,

Invisible Colleges: Diffusion of Knowledge in Scientific Communities (Chicago and London: The University of Chicago Press, 1972); and Gerald L. Geison, "Scientific Change, Emerging Specialties, and Research Schools," History of Science, 19 (1981): 20-40. Specific case studies of research schools and emerging specialties include Joseph Ben-David, "Scientific Productivity and Academic Organization in Nineteenth Century Medicine," American Sociological Review, 25 (1960): 828-843; J. B. Morrell, "The Chemist Breeders: The Research Schools of Liebig and Thomas Thomson," Ambix, 19 (1972): 1-46; Robert Fox, "The Rise and Fall of Laplacian Physics," Historical Studies in the Physical Sciences, 4 (1974): 89-136; Owen Hannaway, "The German Model of Chemical Education in America: Ira Remsen at Johns Hopkins (1876-1913)," Ambix, 23 (1976), 145-164; Gerard Lemaine, Roy MacLeod, Michael Mulkay, and Peter Weingart, eds., Perspectives on the Emergence of Scientific Disciplines (The Hague and Paris: Mouton; Chicago: Aldine, 1976); Gerald L. Geison, Michael Foster and the Cambridge School of Physiology: The Scientific Enterprise in Late Victorian Society (Princeton: Princeton University Press, 1978); R. G. A. Dolby, "The Transmission of Two New Scientific Disciplines from Europe to North America in the Late Nineteenth Century," Annals of Science, 34 (1977): 287-310; John W. Servos, "The Knowledge Corporation: A. A. Noyes and Chemistry at Cal-Tech," Ambix, 23 (1976): 1915-1930; "Physical Chemistry in America, 1890-1933: Origins, Growth, and Definition" (Ph.D. dissertation, Johns Hopkins University, 1979); and "A Disciplinary Program That Failed: Wilder D. Bancroft and the Journal of Physical Chemistry, 1896-1933," Isis, 73 (1982): 207-232.

[43] See Geison, "Scientific Change," pp. 23-27. The quotation is from p.23.

[44] George Wise, "A New Role for Professional Scientists in Industry: Industrial Research at General Electric, 1900-1916," Technology and Culture, 21 (1980): 408-429, quoted from pp. 410 and 429. See also George Wise, "Ionists in Industry: Physical Chemistry at General Electric, 1900-1915," Isis, 74 (1983): 7-21.

[45] Mark, "Polymer Chemistry in Europe and America," p. 530.

[46] Wallace Hume Carothers, memorandum to members of the group, Du Pont Company, July 28, 1932, Lavoisier Library, Du Pont Experimental Station, Wilmington, Delaware. This memorandum includes his review of the fundamental research between 1928 and July 1932, and lists annual expenditures of his group. Cf., Ch. III, pp. 93-94.

[47] Du Pont was the first company to obtain the ultracentrifuge in American industry. Together with the apparatus of the University of Wisconsin, there were only two ultracentrifuges in the United States during the mid-1930s. Cf. J. W. Williams, "The Development of the Ultracentrifuge and Its Contributions," in Annals of the New York Academy of Sciences, vol. 325 (1979): The Origins of Modern Biochemistry: A Retrospect on Proteins, eds. P. R. Srinivasan, Joseph S. Fruton, and John T. Edsall: 77-91.

[48] Scientists' dilemma involving the conflict between academic and

industrial values in early twentieth century America has been discussed in John W. Servos, "The Industrial Relations of Science: Chemistry at MIT, 1900-1939," Isis, 71 (1980): 531-549; George Wise, "A New Role for Professional Scientists" and "Ionists in Industry."

[49]For example, the manuscript of Carothers' 1932 paper, "Artificial Fibers from Synthetic Linear Condensation Superpolymers," was checked by the Company staff, chemists in other research groups, and the Publicity Department as early as August, 1931.

[50]Carothers' co-workers, Hill and Gerard J. Berchet both agree on this point. Interview with Hill, February 22, 1983; and interview with Gerard J. Berchet, March 13, 1982. Cf., Ch. III, p. 123.

[51]Carothers, memorandum to the group, July 28, 1932.

[52]John Rex Whinfield, "Chemistry of Terilen," Nature, 153 (1946): 930-931, on p. 931. For Perlon, see Basil G. Achilladelis, "A Study in Technological History: Part I. The Manufacture of 'Perlon' (Nylon 6) and Caprolactam by IG Farbenindustrie," Chemistry and Industry, (December, 1970): 1549-1554.

[53]Paul John Flory, "Molecular Size Distribution in Linear Condensation Polymers," J. Amer. Chem. Soc., 58 (1936): 1877-1885; and "The Mechanism of Vinyl Polymerizations," ibid., 59 (1937): 241-252. For Flory, see Walter H. Stockmayer, "The 1974 Nobel Prize," Science, 186 (1974): 724-726; David W. Ridgway, "Interview with Paul J. Flory," J. Chem. Educ., 54 (1977): 341-344; and Harold A. Scheraga, "Paul J. Flory on His 70th Birthday," Macromolecules, 13 (1980), no. 3: 8A-10A.

[54]Paul John Flory, Principles of Polymer Chemistry (Ithaca: Cornell University Press, 1953).

[55]For Marvel, see J. E. Mulvaney, "Interview with Carl S. Marvel," J. Chem. Educ., 53 (1976): 609-913; and Carl Shipp Marvel, "The Development of Polymer Chemistry in America--The Early Days," J. Chem. Educ., 58 (1981): 535-539.

[56]For Mark's activity in the United States, see Hunt, "Profiles," pp. 46-79; Mark, "Polymer Chemistry in Europe and America," pp. 533-534; Stahl, "Herman F. Mark," pp. 82-85; and interview with Herman F. Mark by the author, March 19, 1982.

[57]Carothers, Collected Papers, p. ix.

[58]Vol. 2: Herman F. Mark, Physical Chemistry of High Polymeric Systems (New York: Interscience Publishers, Inc., 1940); Vol. 3: Herman F. Mark and R. Raff, High Polymeric Reactions (1941); and Vol. 4: Kurt H. Meyer, Natural and Synthetic High Polymers (1942).

[59]See, e.g., Charles E. Carraher, "Polymer Education and the Mark

Connection," in Stahl, ed., Polymer Science Overview: 123-142, on p. 131 ff.

[60]See e.g., Maurice Morton, "History of Synthetic Rubber," in Syemour, History of Polymer Science and Technology: 225-238, on pp. 231-233 and 237-238.

CONCLUSION

The chemistry of macromolecular materials is still in its infancy . . .

--Wallace Hume Carothers,
"Review of Die hochmolekularen organischen Verbindungen," 1932.

Macromolecular chemistry is the youngest branch of organic chemistry . . .

--Hermann Staudinger,
"Nobel Lecture," 1953.

Macromolecular chemistry is a relatively young science.

--Giulio Natta,
"Nobel Lecture," 1963.

The field of polymer chemistry has already reached a high degree of excellence and a certain maturity. . . .

--B. C. Anderson, L. R. Bartron, and J. W. Collette,
"Trends in Polymer Development," 1980.

A scientific theory not only rests on certain historical facts and is verified or disproved by certain other historical facts; it is itself an historical fact, namely the fact that someone has propounded or accepted[,] verified or disproved, that theory. . . . [N]atural science as a form of thought exists and always has existed in a context of history, and depends on historical thought for its existence.

--R. G. Collingwood,
The Idea of Nature, 1945.

This study has expounded the emergence of macromolecular chemistry from its origins in the early decades of this century to its development toward the period of World War II. The macromolecular theory was fairly well accepted in scientific circles around the middle of the 1930s. By shortly after the war, the chemistry of macromolecules had recognizably

taken shape as a new scientific discipline in institutional settings, as indicated by the large number of academic and industrial researchers, the growth of university teaching in this area, and the creation of new journals devoted exclusively to investigation of macromolecules. This specialty was appreciated as an important and indispensable new field of organic chemistry, distinguished from classical organic chemistry which deals only with low molecular compounds of carbon. A large portion of organic substances, both natural and synthetic, have turned out to be high molecular compounds which required special understanding in the light of new concepts and methods regarding macromolecules. The rise of macromolecular chemistry also compelled colloid scientists to depart from their traditional scheme of colloids and to redefine their objects of inquiry and study. Because of its theoretical significance in the science of molecules, its profound biological implications, and its phenomenal industrial applications (such as synthetic fibers, synthetic rubbers, and plastic materials), macromolecular chemistry became a rapidly maturing science during the postwar period.

In this study, I have called particualr attention to the role of conceptual and epistemological reasoning in the emergence of this science, which is of some significance in the historiography of chemical science. The dominance of physics over other natural sciences is one of the general features of modern science. Conceptions and methods of physics have indeed exercised a wide influence on the way in which chemists, biologists, and scientists of other fields pursue their research areas. In chemical science, physical chemistry emerged as a boundary science in the late nineteenth century, and has provided a deeper

methodological insight into the study of inorganic, organic, and biological chemistry. Not surprisingly, this climate has increasingly created an impression that all chemistry follows deductively from the principles of physics. Modern textbooks of chemistry and even historical studies in some quarters have fallen under this influence, seeing the growth of modern chemistry merely as linked with the victory of the physicalist view of nature or the "mechanization of the world picture."

The story of the emergence of macromolecular chemistry, which the present study has examined, gives a counter-example for this conventional interpretation. Macromolecular chemistry as a new field of organic chemistry arose from a conceptual conflict between the physicalist and the organic-structural traditions. The physicalist approach to polymer-colloid sutstances, as represented by the colloid doctrine and the aggregate theory, flourished in the early part of this century, reflecting the rise of physical chemistry. Yet the success achieved by Hermann Staudinger and Wallace H. Carothers in the 1920s and 1930s, following the decade-long controversy over macromolecules from roughly 1925 and 1935, was a manifestation of the conceptual power of orthodox organic chemistry in the face of the popular physico-chemical trend. Conceptually and epistemologically, the macromolecular theory was deeply antiphysicalistic, dismissing concepts that reduced chemical phenomena to smallest parts of matter and interacting forces. The new theory was firmly grounded in the traditional molecular approach to organic compounds, which viewed the molecule as the unit from which stem physical and chemical properties of matter. The macromolecular view further carried a holistic or emergent conception that a whole is not a mere total sum of

its constituent parts, but something more than that. This was an epistemological ground essential to the macromolecule concept, which Staudinger stressed time and again in opposing the mechanical reductionism of upholders of the aggregate theory. Defining colloids as "physical compounds" and not as chemical ones, a physicalist noted in 1927:

> Simplicity and symmetry should be among the chief aims of a scientific theory. It is probable that the same laws which regulate the movement of electrons within the atom also determine the paths of planets in their orbits; a complete understanding of the simplest phenomenon may enable us to explain the Universe.[1]

In contrast, the following statement by Paul J. Flory, Carothers' successor, illustrates the viewpoint of the macromolecular chemist:

> The reductionist attitude has encouraged chemists to focus their investigative efforts on the simplest molecules to virtual exclusion of all else, as if full knowlege gained at the simplest level would suffice to explain the more complex by straightforward deduction. This is demonstrably false. . . .
>
> To be sure, a great deal can be learned by investigation of the simplest systems, but comprehension of those of higher complexity cannot be achieved through processes of deduction alone. . . . [F]ull knowlege concerning simple molecules did not pave the way for comprehension of macromolecules. Further creative effort, formation of new concepts with appropriate abstraction, and so forth, were required.[2]

Thus, the large molecule as a whole exhibits its own properties which cannot be deduced from those of smaller molecular or atomic units, and which cannot be predicted even by a thorough study of the low molecular substances. Hence, emphasis was placed by macromolecular chemistry on the superstructure of molecules, namely the molecular size and shape that determine unique properties of polymers, such as colloidal phenomena, elasticity, and fibrousness. These new conceptions associated with the organic-structural approach to macromolecules expanded the theoretical outlook of classical chemistry, that is, the science of molecules.

As we have seen in Chapter II, Staudinger's macromolecular theory

originated in his firm conviction of Kekulé's structural scheme and in his suspicion of the current interpretation that polymers were aggregates of small molecules held together by the non-Kekuléan secondary valence forces. Inspired by his own early study of ketenes and by Samuel S. Pickles' 1910 paper, which criticized Carl D. Harries' view of "physical bonding" of rubber molecules, he developed his organic-structural approach to polymeric compounds in the early 1920s. The ensuing macromolecular debate presents a clear picutre of the conceptual and methodological clash between Staudinger's organic-structural school and physicalist schools. Despite Staudinger's confidence, his early experimental evidence for the existence of macromolecules, based on purely organic-chemical techniques and methods (such as polymer analogous reactions), was not taken as persuasive or crucial by his physicalist opponents. The recognition process of the macromolecular theory before 1930 was manifold among scientists. The X-ray work on the cellulose structure by Olenus L. Sponsler and Walter H. Dore (1926) and on the polyoxmethylene structure by Gustav Mie and Josef Hengstenberg (1927) led some X-ray specialists and physical chemists, such as Johann R. Katz, to accept the view of long-chain structure for polymers, Some protein scientists saw as decisive the Svedberg's ultracentrifuge studies measuring the high molecular weight of proteins (1926-), whereas colloid chemists like Wilder D. Bancroft readily rejected Svedberg's results as a misinterpretation of experimental data. A compromise between the aggregate and the macromolecular views, the new micelle theory of Kurt H. Meyer and Herman F. Mark, proposed in 1928, moved several leading cellulose chemists, including Kurt Hess, to reconsider their aggregate point of views. Some scientists

were impressed by Staudinger's viscosity formula for macromolecular solutions at the turn of the decade, although it also met serious opposition. Conceptually bounded by the aggregate theory, the large majority of organic chemists considered the ideas of giant molecules as untenable still in the late 1920s.

As analyzed in Chapter II, Carothers was among the earliest organic chemists who found soundness in Staudinger's own argument that the polymer structure can be explained only in terms of the Kekulé covalent bond. Sharing the organic-structural approach to polymers with Staudinger, Carothers adopted the principle of macromolecules around 1927 mainly through reading Staudinger's early German papers. It is to be emphasized that Carothers' direct motives in his acceptance were neither interest in the recent studies of X-ray crystallography nor Svedberg's ultracentrifuge work on proteins, but rather in that belief in structural organic chemistry with which Staudinger started his study of polymers. By the mid-1930s, it became clear to his contemporaries that Carothers' systematic work on the mechanism of polymerization vigorously supported Staudinger's ideas from the synthetic side, and a large number of practioners in organic chemistry came to adopt the macromolecularity of polymeric compounds in place of the aggregate theory.

The confrontation between the physicalists and the organic-structuralists, at the same time, involved setting or establishing disciplinary boundaries in chemical science. Wolfgang Ostwald, the German physicalist, had declared in the mid-1910s that colloid chemistry is an independent division of physico-chemical science, cultivating the "World of Neglected Dimensions" that lies between the molecular level and the microscopic

level, a world ruled not by traditional organic chemistry but by the laws of colloid science. Likewise, Bancroft, the American advocate of this field, claimed that colloid studies are one of the most important branches to be explored only by physical chemists. From the outset, the organic chemists Staudinger and Carothers rejected these claims and criticized their fellow chemists' abandonment of the fundamental axioms of structural organic chemistry in dealing with colloid polymers. Polymers, such as rubber, cellulose, polysaccharides, and proteins, are organic compounds, namely compounds of carbon, which ought to be pursued by the principles of organic chemistry and not by physical doctrines. Staudinger thus reinterpreted Ostwald's world of colloidal dimensions by considering it to be a realm of giant organic molecules and to be a new field within organic chemistry. The Frankfurt meeting of the Kolloid-Gesellschaft on "Organische Chemie und Kolloidchemie," which Ostwald presided over in 1930, illustrates colloid scientists' concern about the problem of the disciplinary boundaries. Staudinger's 1940 book, Organiche Kolloidchemie, as its title suggests, intended to direct chemists' attention from traditional colloid doctrines to the principles of macromolecules in dealing with organic colloids.[3]

On another level, we have seen human factors associated with the emergence of macromolecular chemistry. Staudinger's uncompromising attitude and a personality intolerant of his opponents in scientific meetings aroused antipathy during the macromolecular debate. The polemic over the priority of the long-molecular concept between Staudinger and Meyer complicated the issue further around 1930. As a researcher, teacher, and proselytizer for macromolecular chemistry, Staudinger in effect

succeeded in establishing this field as a new specialty or organic chemistry. But the way in which the charismatic professor sternly pushed his working field ahead often was viewed by his contemporaries as too high-handed. Even Carothers and some of Staudinger's own students considered his scientific style and personality to be dogmatic and too intuitive. Yet, as Ryuzaburo Nodzu, a student of Staudinger at Freiburg, recalled, it was just this determined and strong characteristic in Staudinger that enabled him to challenge accepted views, to survive a decade-long controversy against leading scientists of his time, and eventually to reign over scientific circles. On the other hand, Nodzu believed, it was the same polemical nature in Staudinger that delayed his reception of the Nobel Prize.[4]

An introverted and logically minded perfectionist, Carothers criticized as speculative some of Staudinger's arguments that appeared to be based on scanty experimental evidence. Claiming his own approach to be "strictly rational," he distinguished his method of demonstration from Staudinger's method. This "rationality" was built upon Carothers' firm convictions about organic synthesis which he inherited from Roger Adams' Illinois school. While his German counterpart was primarily concerned with the elucidation of the structure of existing natural products such as rubber and cellulose, Carothers aimed to make giant molecules through stepwise, established organic reactions of smaller molecules. As I have suggested, the two strikingly contrasting approaches reflect the different intellectual milieux in which they attacked the problem of macromolecules. Staudinger's analytical approach reflects an aspect of German Wissenschaft, the pursuit of nature itself. While

adopting technically Emil Fischer's method of protein study, Carothers' synthetic approach embodied Adams' ideal of science, or more broadly, that facet of American pragmatism directed towards the artificial duplication or control of nature. The two distinct approaches in the organic-structural tradition turned out to play complementary roles for laying theoretical and practical foundations of the chemistry of macromolecules.

That an estrangement between the physical approach and the organic approach could not last long is perhaps not material to the argument. The rejection of the physicalist standpoint in establishing the basis for this discipline did not mean that its founders negated the applicability of physics and physical chemistry. What is significant here is the fact that the chemistry of macromolecules stemmed from organic chemistry's own principle, the molecular approach, and not from physical doctrines. Admittedly, the organic chemist Staudinger showed distaste for physical methods, and his scientific thought was to a large extent limited to the framework of non-physical organic chemistry. Facing the problems posed by physical concepts and methods (such as X-ray diffractions of polymers and the flexibility of linear macromolecules), he had to call for cooperation from able physicists and physical chemists, including Gustav Mie, Josef Hengstenberg, and Günther V. Schulz, and from his Dozenten such as Rudolph Signer. These co-workers then supported Staudinger's theory from the physical side. Carothers had ample knowledge of physical chemistry, as illustrated by his early ambitious study of the electronic theory of the double bond. Nevertheless, his mathematical capacities were reportedly very limited, and he requested from his co-worker, the physical chemist Paul Flory the statistical and mathematical

investigations of polymerization. Staudinger and Carothers thus perceived the applicability of mathematico-physical treatments in their field, although their initial studies had made little use of those methods. After accepting the fundamental concept of the macromolecular structure for polymeric compounds, then, Mark, Werner Kuhn, Schulz, Flory, Maurice L. Huggins (b. 1897), and young generations of physical chemists were able to apply securely the physico-chemical methods, such as kinetics, statistics, thermodynamics, and hydrodynamics, to the polymer field towards the second half of the 1930s. Certainly, the physical chemistry of macromolecules became a vital part in the study of polymers and polymerization during the postwar period.

While Carothers never lived to see the later spectacular growth of his science, Staudinger witnessed the success of his labours and the further development made by younger generations of scientists. In his later career, Staudinger turned his interest to biological aspects of macromolecules. Since 1926 he had pointed out the biological implications of macromolecules such as proteins. His thought was further inspired by his wife Magda Staudinger, a plant physiologist who helped to develop some new concepts relating macromolecules to physiological and philosophical questions. In 1946 he published a monograph, Makromolekulare Chemie und Biologie, in which he attempted to explain the life processes of the living cell from the point of view of macromolecular chemistry. Through macromolecules, he thus returned to his earliest field of interest, biology, dealing with living, truly organic matter. Although his own work on bio-macromolecules touched only upon the fringe of the subject, the macromolecular theory itself opened a door for a new approach

to biologists, chemists, and physicists in attacking the enigma of life. Symbolically, Staudinger received his "belated" but most coveted Nobel Prize in chemistry as the founder of macromolecular chemistry in 1953, the year in which the Watson-Crick double helix theory of the DNA giant molecule emerged as a landmark of the new science, molecular biology.

In Chapter IV, I have contrasted institutional settings of German and American macromolecular science, and I have indicated how the growth of macromolecular chemistry in these two settings illustrates some features of the relationships between science, industry, and society. In addition to its theoretical concerns, industrial success of macromolecules unquestionably played a key role for the legitimatization of this science in society. Americans achieved this success in the large-scale industrialization of macromolecular chemistry earlier than did Germans. Reflecting the master's own scientific style, Staudinger's research school in Germany, by and large, avoided direct involvement in industrial undertakings, and its impact on German industry was less direct than on academic research. In contrast, Carothers' basic research group in Wilmington took initiative in industrial application of this field. Yet, as we have seen, this application process presents a far more complicated picture than the mere conversion from scientific theory to practice would imply. Rather, the specific applications were an unforeseen consequence of Carothers' investigations, where his initial objective was to demonstrate the macromolecular theory of polymers from the standpoint of organic synthesis. As the story of nylon reveals, during the course of his fundamental study along this line, Carothers' group incidentally discovered the possibility of making synthetic fibers,

with Du Pont then immediately redirecting his research goals and deliberately attempting to develop his findings into a new commercial product. Du Pont's success in the synthetic fiber and rubber, as substitutes for natural products, had a profound influence on the course of chemical industry. Carothers' theoretical work on macromolecular design became a prototype for industrial research of polymer chemists, ushering in the plastic age or the epoch of synthetic polymers in the postwar period.

In 1936 Carothers was elected to the National Academy of Sciences --the first organic chemist associated with industry to be so honoured. If we look at Carothers' work as an outgrowth of Du Pont's new experiment, the industrial fundamental research program, his achievement occupies a remarkable position in the history of American science and industrial research. From the late nineteenth century, occasional contacts had existed between science and industry in the United States. University professors served as part-time consultants for industry. A small number of university-trained scientists found opportunities to work for companies on testing, chemical analysis, and engineering.

But the role of professional scientists in relation to American industries drastically changed in the early decades of this century, when a number of large corporations began establishing their own research laboratories, employing many Ph.D.'s who conducted science-based applied research. Du Pont's program, in which Carothers' group devoted full time to fundamental research in organic chemistry, was among the earliest of a newer movement still in American industry: the creation of the basic research program. Industry expected new products or processes from this type of pure science. And Du Pont's venture paid off with the new

successful commercial products, nylon and neoprene. Yet, far exceeding Du Pont's expectations, the new research yielded also a new science. Carothers' Wilmington circle turned out to be the cradle of American macromolecular chemistry, from which this new field spread into university teaching and research in the second half of the 1930s. Carothers' case thus reversed the traditional relationship between science and industry, in which industry only followed university science. His scientific activity at Du Pont showed his contemporaries that industry now might take the kind of initiatives traditionally expected of pure science.

Thus, we find that our comparative study of Hermann Staudinger and Wallace H. Carothers not only has illuminated the experimental and theoretical foundations of macromolecular, or polymer, chemistry, but it also has shed light on the academic and industrial milieux of twentieth-century chemical science. We have seen many contrasts, both psychological and social, between these two men and their research schools. These contrasts are not wholly idiosyncratic, but in some respects characteristic of contrasts between German and American university and industrial science in the 1920s and 1930s. Simultaneously, we have noted Staudinger's and Carothers' shared approach to fundamental chemical problems through a common commitment to the methods of molecular analysis and synthesis, rather than to the assumptions of physicalist reductionism. Whether through its biological significance, or industrial implications or the pure intellectual pleasure it gave, the new discipline of macromolecular chemistry was to become a major new field in twentieth-century science.

NOTES

[1]Victor Cofman, "Colloid Dynamics," Chem. Reviews, 4 (1927): 1-49, on p. 1.

[2]Paul J. Flory, "The Science of Molecules," Chem. Eng. News, 52 (1974), no. 30: 23-25, on pp. 24-25. See also Flory's "Macromolecules Vis-a-Vis the Traditions of Chemistry," J. Chem. Educ., 50 (1973): 732-735. On Staudinger's arguments for this matter, see Ch. II, pp. 69-72.

[3]Hermann Staudinger, Organische Kolloidchemie (Braunschweig: Verlag Vieweg & Sohn, 1940).

[4]Ryuzaburo Nodzu, "Staudinger hakase no insho," (My Impression of Dr. Staudinger), Kobunshi (High Polymers, Japan), 3 (1954): 375-377, on pp. 376-377.

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Abbreviations

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