

The Science and Technology of Polymer Films

**Edited by
ORVILLE J. SWEETING**

Yale University

VOLUME I

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***The Science and Technology
of Polymer Films***

VOLUME I

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ADDITIONAL VOLUMES IN PREPARATION

*To my parents who
put up with me then*

*Rose E. Bailey, 1876-1935
Burton C. Sweeting, 1876-1939*

*and to Mary, Janet, Richard, and Barbara
who put up with me now*

PREFACE

It is the hope of the authors that this book will be of value to a wide audience. An attempt has been made to correlate the recent past in polymer chemistry with current theories in such a way as to be comprehensible to a newcomer in the field of polymer films, yet not insult the more sophisticated. The subject is a growing and rapidly changing field of chemistry, and the kaleidoscope which chemists amuse themselves by calling "the literature" makes it difficult to present a basis for understanding the structure and properties of thin self-supported polymeric films. This is a field in which the crystal ball gets cloudy fast. To paraphrase a remark made long ago by Mr. Justice Pound, with reference to the law, polymer chemistry should strive to be stable, yet not stand still.

This first volume presents the scientific basis for polymer films, with special, though not exclusive, emphasis upon packaging films. The chemistry and physics involved are complicated and in many respects are in need of further study and refinement. In some instances, basic explanations are lacking. Nonetheless, we have tried to present as much theoretical material as is consistent with an understanding of packaging film principles and applications, without the inclusion of highly abstruse material or speculative theories which must in future rest or fall on experiments not yet done.

It had been originally planned that one additional basic chapter entitled "Barrier Properties of Polymer Films" would appear in Volume I, but because of extraordinary delays in putting this chapter into final form, it will appear in Volume II.

Volume II, now in active preparation, will bring together the packaging-film facts and *raison d'être* for many of the important films in use today. Though much of this material may be found scattered in commercial brochures, books on polymer chemistry, and monographs on certain individual films, a modern comprehensive treatment of salient facts may be of value both to students and to specialists in the field.

I wish to express my thanks to all of the authors who have contributed, many of them former colleagues in the Film Division at Olin. Thanks are due also to the late Edward L. Lynn, then General Manager of Olin's Film Division, who encouraged the initial effort, and to Philip C. Brownell and Dr. Linton E. Simerl who approved the project. To all of these three who enthusiastically gave the idea life, I am grateful.

The editor welcomes comments and criticism. In a book as complex as this, in a field as rapidly changing as this, errors must certainly have infiltrated. I take full responsibility for them—and hope that they are small ones.

ORVILLE J. SWEETING

New Haven, Connecticut
May, 1968

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CHAPTER 1

INTRODUCTION

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I. General Aspects

The journal articles of 20 or 30 years ago occasionally reported the failure of an organic synthesis with a discouraging comment that failure was signified by formation of an intractable tar (usually black) from which no useful compound could be extracted. Who knows what gold was discarded by graduate students of yesteryear,

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always in search of simple, crystalline, easily characterized solids, melting preferably in the range 75–200°C?

In my day, the word *polymer* was a polite synonym for the gunks toward which many highly reactive compounds seemed to trend when heated at reduced pressure; the accursed polymers reduced the yields of useful compounds and resulted in the irretrievable loss of time and money. Today chemists in industrial laboratories (and even a few in academic posts) are attracted by reports in the journals that a “worthless tar insoluble in all common solvents was formed in large amount.” Such a comment is a challenge to the chemist working with synthetic polymers, for here may be the clue to a stable, insoluble, nonhydrolyzable, high-melting polymer of value as a structural material. It needs only to be made in quantitative yield and freed of the impurities that discolor it!

Today it is not necessary to explain even to most school children what a polymer is (they have a feel for the word), but large books are required to explain what polymers are, how they behave, and what they can do. In a short historical introduction, Rowland Hill, writing in 1953 (1), commented that “high polymer chemistry, or macromolecular chemistry as it is sometimes called, can now very properly be accepted as a science in its own right.” Yet I can recall that in my own graduate school days, 10 years before, a faculty member of the department of chemistry where I was studying who wished to offer a graduate course in the chemistry of high polymers was, after due deliberation of the faculty, denied permission, on the grounds that polymer chemistry could be quite adequately taught within the subdivisions of chemistry then in vogue.

In this country, Herman Mark, formerly at Staudinger’s laboratory at Freiburg Breisgau where they had collaborated on fundamental research into the structure of cellulose, and afterwards a director of research at I. G. Farben and professor at the University of Vienna, helped to publicize the field of high polymers, as these intractable organic compounds began to be termed, and put the study of them on a scientific basis. He was audacious enough to entitle Volume I of a new series of abstracts *The Science of Plastics. A Comprehensive Source Book Based on the Original Literature for 1942–1946* (2). Thus was the subject dignified: a “science” of plastics drawn from the original “literature”! Now textbooks exist on the subject, eloquent testimony to the commercial worth of writing

for those who learn of polymers in schools, (3,3a). Although it is said (3) that the first chemists to define certain natural products as polymeric in the modern sense were H. Hlasiwetz and J. Habermann in 1871, Staudinger first introduced the term *macromolecule* (4) for these substances of high molecular weight, e.g., proteins, cellulose, and rubber. In the 20 years which followed, many chemists developed new methods such as the use of x-rays for investigation of the fundamental properties of high polymers. In the late 1920's, Wallace H. Carothers at the E. I. du Pont de Nemours & Co. Experimental Station in Wilmington, Del. began a series of brilliant researches on the synthesis of molecules of very high molecular weight. The results appeared in a steady flow of articles in the *Journal of the American Chemical Society*, the work duly protected by United States and foreign patents (5). One of the first patents in this field granted to Carothers (6) has rarely been equalled in its clarity of description of crucial experiments and the massive bulwark presented in basic coverage of an important scientific and commercial development. For the first time, synthetic condensation polymers of nearly all imaginable sorts had been made and shown to have a useful degree of pliability, strength, and elasticity. Carothers had reexamined the pioneering work of Staudinger and by a close look at fundamentals, he made for the first time materials with useful (not merely interesting) properties.

Carothers writes (6):

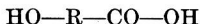
. . . The synthetic linear condensation superpolymers produced in accordance with the present invention are suitable for the production of artificial fibers which are pliable, strong, and elastic and which show a high degree of orientation along the fibre axis. In this respect they resemble cellulose and silk which, as recent researches have proved, are also linear superpolymers. So far as I am aware, no synthetic material has hitherto been prepared which is capable of being formed into fibres showing appreciable strength and pliability, definite orientation along the fibre axis, and high elastic recovery in the manner characteristic of the present invention. It is true that Staudinger has frequently emphasized the probable structural analogy between polyoxymethylene and cellulose, and he has shown that it is possible to obtain polyoxymethylene in the form of oriented fibres, but these fibres are only a few millimetres in length and they are very fragile. It is true also that threads or filaments can be drawn from any tough thermoplastic resin, and British Patent 303,867 discloses a process for making artificial silk in which a condensation product of a polyhydric alcohol and a polybasic acid or its anhydride is employed as a raw material. British Patent 305,468

discloses a process for making synthetic fibres from a urea-formaldehyde resin. But there is nothing in the disclosures of these references to indicate that the filaments or fibres are sufficiently strong or pliable to have any utility, and insofar as I am able to ascertain, filaments or fibres produced in accordance with the disclosures of these patents do not have any useful degree of pliability, strength, or elasticity.

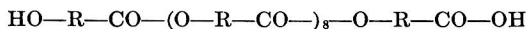
After defining the terms, condensation ["new bonds between atoms not already joined . . . with the elimination of elements (H_2 , N_2 , etc.) or of simple molecules (H_2O , C_2H_5OH , HCl , etc.)"], linear polymer, unit of a polymer ("—A—"), superpolymer, Carothers showed how polyesters, polyethers, polyamides, and polyanhydrides, as examples, could be made, theoretically with infinite chain lengths, but was careful to limit and discuss the polymerization reaction (6). He says:

. . . It may be observed that each of these starting compounds contains two (and only two) functional groups capable of participating in the condensation. I call such compounds bifunctional compounds, and their reactions bifunctional reactions. My invention is concerned not with polyfunctional condensations generally, but only with bifunctional condensations. This restriction is necessary since the presence of more than two functional groups in any of the reacting compounds introduces the possibility of developing a three-dimensional polymeric structure; and this involves a complication with which my invention is not concerned.

It is a characteristic feature of bifunctional condensations . . . that they present the formal possibility of producing molecules of infinite length. Thus the self-esterification of ten molecules of hydroxy acid,



would lead to the formation of the polyester,



and this, since its molecule still bears the terminal groups which were responsible for the initial reaction, is potentially capable of reacting with itself to produce a new molecule twice as long. A continuation of this progressive coupling would finally yield a molecule of infinite length.

In practice there are several factors that may be expected to interrupt this progressive coupling before the molecules have grown to any very great length. The following may be mentioned:

(1) Reaction may be intramolecular at some stage (i.e., it may lead to the formation of a ring).

(2) The terminal functional groups responsible for the progressive coupling may be lost or mutilated through side reactions.

(3) Mechanical factors such as solubility and kinetic effects may come into play.

I have devoted considerable study to reactions of the type defined above as bifunctional condensations and have discovered the following facts: Such reactions are usually exclusively intermolecular at every stage, and the terminal groups responsible for the initial reaction are still present at the ends of the product molecule. Interruption of the progressive coupling through intramolecular reaction (ring formation) occurs generally only through the formation of 5-atom rings, less frequently through the formation of rings of 6 atoms, and rarely through the formation of rings of 7 or 3 atoms. The loss or mutilation of terminal groups through side reaction occurs only when patently inappropriate experimental conditions are adopted. Thus in most cases there is nothing theoretically to preclude the possibility of producing exceedingly long molecules in bifunctional condensations.

It is well known that reactions such as esterification, ester interchange, amide formation, etherification, anhydride formation or acetal formation are reversible reactions, and that such reactions can be forced to completion by the separation of the reaction products as they are formed. But from the facts outlined above it follows that if the reversible reaction is a bifunctional condensation, the degree of completeness of the reaction will regulate the size of the molecule in the polymeric product; the more nearly complete the reaction, the longer the molecule; and the reaction can be absolutely complete only when the product molecule is infinitely long. According to the present invention reactions of this type are brought to a degree of completeness heretofore unknown.

This invention has as an object the preparation of linear condensation superpolymers, and by this I mean linear condensation polymers capable of being formed into useful fibres. A second object is the manufacture of synthetic fibres. A third object resides in a method of propagating reversible chemical reactions involving the simultaneous formation of volatile and non-volatile products.

The first of these objects, briefly expressed, is accomplished by subjecting the linear polymers resulting from reversible bifunctional condensations to the action of heat under conditions which particularly facilitate the removal of any possible volatile reaction products. The second of these objects is accomplished by spinning or drawing filaments from a synthetic linear condensation superpolymer. The third object is accomplished by utilizing a molecular still for removing the volatile product or products of a reaction where their effective vapor pressure is too low to be removed by the usual distillation technique and where the non-volatile product is substantially completely non-volatile.

It may be observed that the results described herein furnish a very satisfactory verification of my theory. It is to be understood, however, that I do not desire the claims to be limited thereby inasmuch as the theory has been presented in detail merely to make clear the nature of the invention and especially to explain the terminology used in describing it.

Carothers did much more than prepare and describe a few "superpolymers." He showed in summary that a polymer capable of