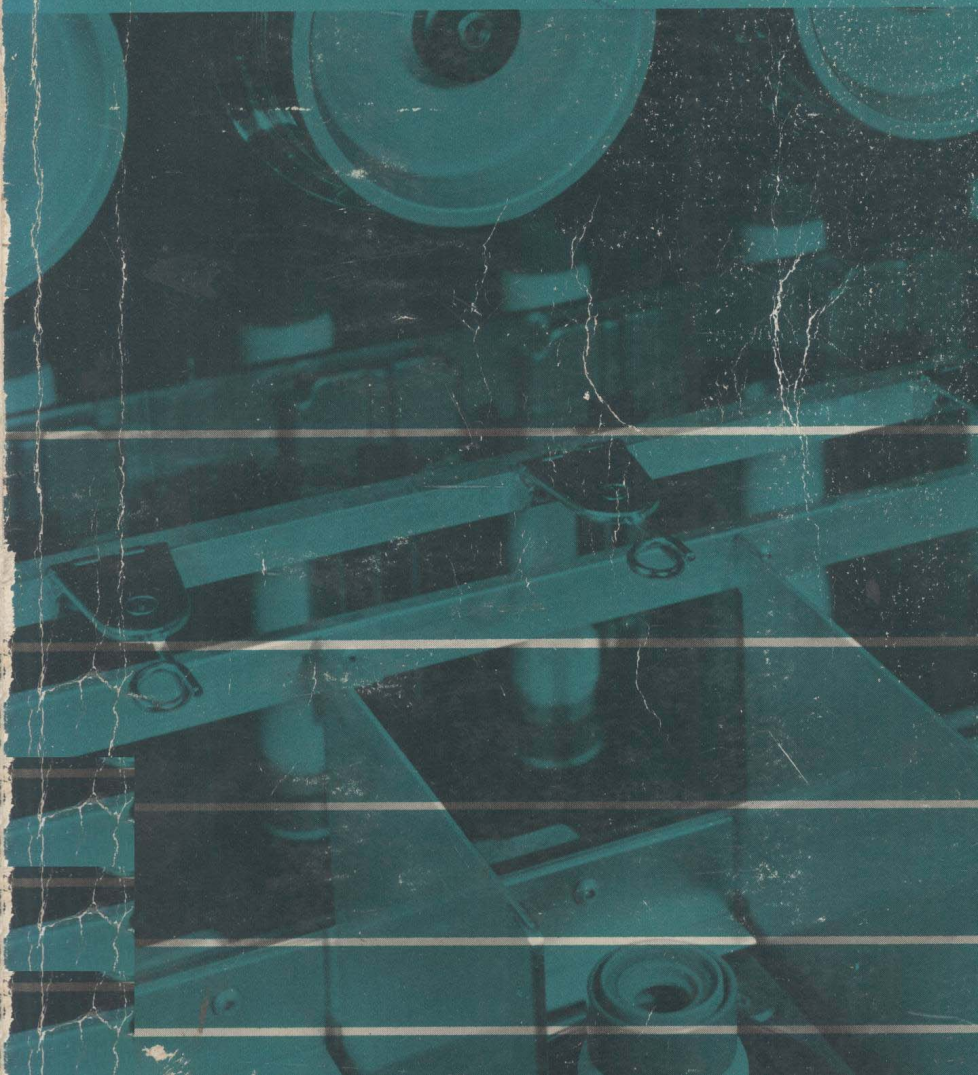


**Chemistry in
Industry**

High Polymers

Peter Tooley



Chemistry in Industry

High Polymers

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John Murray Albemarle Street London

Titles in this series

High Polymers

Fats, Oils and Waxes

Fuels, Explosives and Dyestuffs

Food and Drugs

Techniques

Handbook of Experiments

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High Polymers

to
Sheila, Anne and Wendy
for their patience and encouragement

Production of the nylon yarn 'Celon'

0733308 3

‘The whole fabric of modern civilization becomes every day more interwoven with the endless ramifications of applied chemistry.’

Leo Baekeland, 1938

Preface

The rapid and often revolutionary advances in applied chemistry since World War II have made it increasingly difficult for the hard-pressed teacher to keep abreast of events and bridge the gap between school and industry. In addition the pupil, in daily contact with novel materials forged by the chemists' skill, and keen to discuss the related problems of scientific advance such as pollution and the misuse of knowledge, is unlikely to be satisfied by a narrow academic approach to the subject. In tracing the origin, current development and socio-economic implications of a score or so branches of chemical technology, the present series aims at providing the teacher with relevant background material. Emphasis has been placed upon changing patterns of industry such as the transition from batch to continuous production and other problems of large-scale manufacture. An attempt has also been made to show how the properties of substances are related to their structure and how these properties can be modified by molecular tailoring.

Two complementary volumes, *Techniques* and *Handbook of Experiments*, contain suggestions for related practical work and a survey of modern preparative and analytical techniques.

Although the text has been written primarily as a source-book for science teachers, it should also prove useful to students at universities and colleges as well as senior pupils carrying out project work. Bearing in mind the wide spectrum of the chemical industry covered it is inevitable that certain errors and omissions will have occurred but every effort has been made to give a concise and accurate account of the chosen topics.

Acknowledgments

It is a pleasure to acknowledge the ready help of many colleagues and friends in industry and Government departments who provided valuable advice, statistics and other material. I have also had to draw upon the published works of many authors who are too numerous to mention individually, but to whom my thanks are also due.

I am grateful for the help afforded by the staff of John Murray who have successfully steered the book through the hazards of production. Mention must also be made of the loyal assistance of my senior technician, Miss Sandra Fairbairn, who has not only deciphered and typed the MS but given freely of her time and technical expertise.

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Contents

- 1 Introduction 1**
 - Addition polymerization 2
 - Condensation polymerization 8
 - Copolymerization 12

- 2 Plastics 21**
 - Natural-based plastics 25
 - Synthetic plastics (resins) 31

- 3 Man-made fibres 93**
 - Fibres based on natural polymers 99
 - Synthetic fibres 117

- 4 Elastomers 151**
 - Synthetic elastomers 162

- 5 Silicones 177**
 - Silicone fluids 194
 - Silicone rubbers 199
 - Silicone resins 203

Index 207

Chapter I

Introduction

“‘Can you do Addition?’” the White Queen asked, “‘What’s one and one and one and one and one and one and one and one and one and one?’”

Through the Looking Glass, Lewis Carroll, 1871

‘Organic chemistry’, remarked Ludwig Wöhler in 1835, ‘appears to me like a primeval forest of the tropics, full of the most interesting things.’ After almost a century and a half of exploration, many exciting discoveries have been made in the field of carbon chemistry. Some of these have been stumbled upon by accident, most have been the result of brilliant experimentation and inspired research. The forest still holds secrets, however, and there are still prizes to be won. This is the fascination of chemistry.

Today we are surrounded by many materials which have been designed and tailored by the chemists’ skill. Probably the most spectacular advances in applied chemistry are associated with the development of synthetic high polymers. Thus it is fitting, that a survey of applied organic chemistry begins with this interesting family.

High polymers are substances possessing giant molecules with molecular weights of many thousands. Molecules of this type are built up of very large numbers of simple repeating units termed monomers (Gk. *monomer*—single part, *polymer*—many parts). These monomer units, which can be similar or different, are linked together in long chain-like structures which often form complex networks.

Many polymers, such as starches and proteins, occur naturally and have been used by man for centuries for such purposes as clothing and food. Indeed the body of man is itself partly fashioned from polymeric substances, such as the keratin of his hair and nails, and the strange coiled beauty of the deoxyribonucleic acid (DNA) found in the very nuclei of the body cells.

For the last century or so the chemist has used his skill and ingenuity to imitate and improve upon nature. In this way the range of

polymers has been greatly extended to provide a host of valuable synthetic materials such as fibres, plastics and rubbers. This field of chemistry has achieved such importance that it is estimated that a third of the chemists and chemical engineers in the Western hemisphere are engaged today in the production of polymers.

Naturally such an important development in the chemical industry has only been made possible by intensive research into the structure and properties of high polymers. Much of our present knowledge of polymer chemistry is due to pioneer work carried out in Italy, the USA and Britain. Before considering each of the four great polymer families in detail therefore, the mechanism of polymerization and the properties of polymers will be discussed.

Certain polymers, such as the naturally occurring substances, rubber and cellulose, consist of single unbranched chain-like molecules. These are termed linear polymers, the length of the polymer chain depending upon the degree of polymerization or D.P. factor. Polymerization, however, often results in the formation of branched chains, as in the case of the silicone resins. Both branched and linear polymer chains may be joined at intervals by short connecting links known as bridging units. If this cross linking is extensive, three-dimensional networks are formed yielding polymers which are hard and rigid. In the case of the thermosetting polymers, this condition is produced by heat and pressure during the final stages of manufacture—a process called curing. Other types of polymer can be cured without heat and are termed cold-setting.

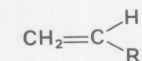
Many polymers do not cross link extensively and therefore possess a less rigid structure. These are described as thermoplastic since they soften on heating.

Polymerization of monomer units can take place by either of two chemical processes known respectively as addition and condensation. This provides a useful system of classification which was first suggested by the American chemist Carothers—the discoverer of nylon.

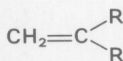
ADDITION POLYMERIZATION

This involves the simple linking together of monomer units by a chain reaction. Occasionally this takes place spontaneously, but

more usually a chemical initiator such as benzoyl peroxide is used to trigger off the polymerization reaction. Monomer molecules which behave in this way contain at least one double bond and are usually vinyl or vinylidene derivatives.

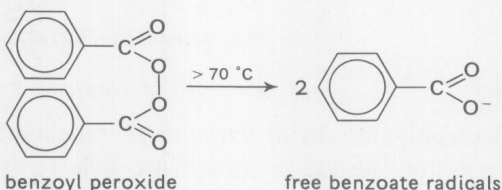


vinyl derivative



vinylidene derivative

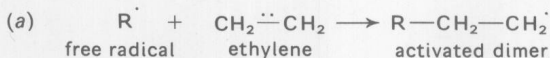
It is believed that a free radical mechanism is involved which activates the double bond and enables chain building to begin. Benzoyl peroxide for instance, decomposes on heating above 70 °C to give free benzoate radicals.



benzoyl peroxide

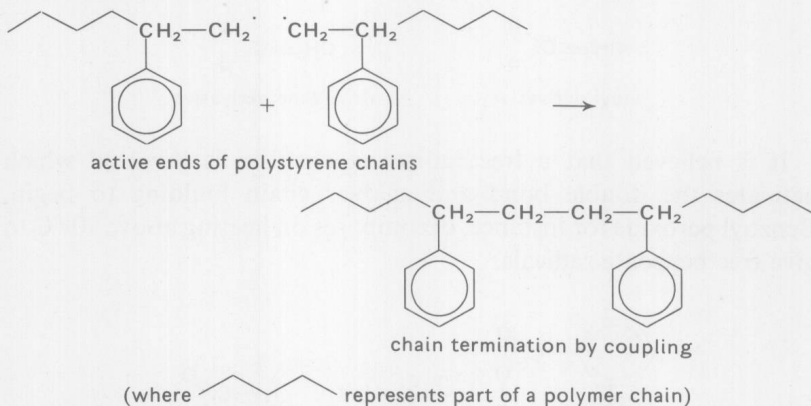
free benzoate radicals

The free radicals then pair with one of the double bond electrons of a monomer molecule, regenerating a further free radical. By this means repeated monomer linkages take place, propagating long polymer chains. Thus the growth of a polyethylene chain may be represented in the following way:

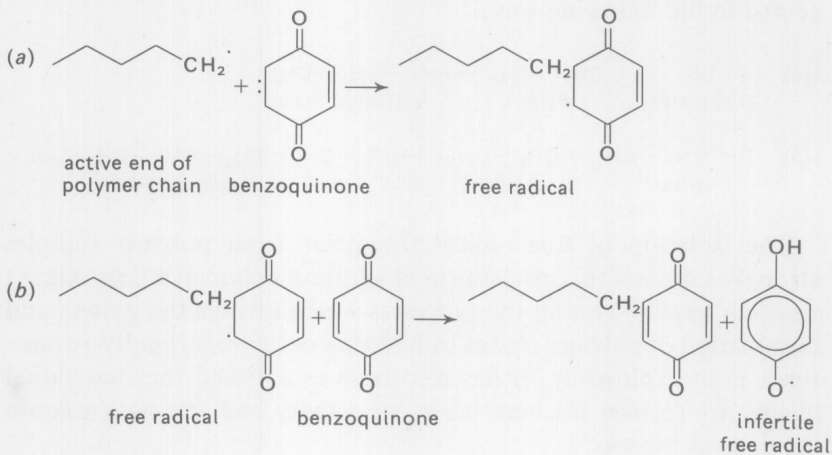


The isolation of free radical fragments from polymer samples strongly supports this mechanism of addition polymerization. Recent research has shown that the processes which involve the growth and termination of polymer chains by addition occur very rapidly—sometimes even explosively. It has also been established that individual chains are formed in short bursts of activity and not as a smooth continuous process.

The growth of polymer chains may be stopped in a number of ways. For instance, the active ends of two chains might link together to form an inactive polymer molecule. This occurs during the polymerization of styrene.



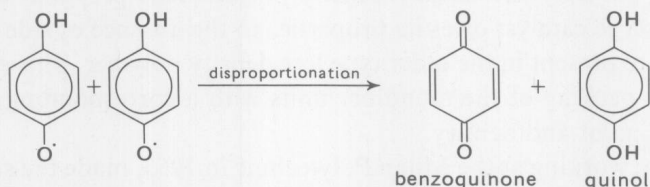
The growth of polymer chains can also be blocked by the use of 'stoppers'. These are substances which are able to 'soak up' free radicals and thus prevent further chain growth. A powerful inhibitor of this kind is benzoquinone and small amounts are often added to monomer solutions to guard against spontaneous polymerization. Removal of the inhibitor is carried out prior to polymerization by either shaking the monomer with a little sodium hydroxide solution,



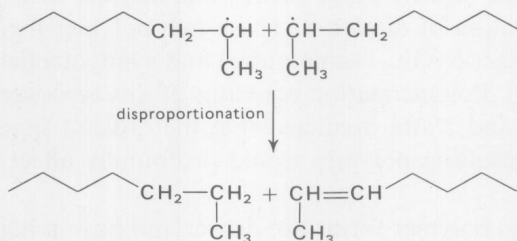
distilling it, or passing it through a column packed with a 'molecular sieve'.

The benzoquinone appears to produce a free radical which is unable to initiate polymer chains.

Hydrogen transfer occurs between pairs of these infertile free radicals to produce a mixture of quinol and benzoquinone. This type of reaction is an example of disproportionation.



Sometimes disproportionation occurs between growing chains, blocking further growth and producing a mixture of saturated and unsaturated terminal groups. Chain stopping of this kind occurs when the temperature of polymerizing methyl methacrylate ('Perspex') is allowed to rise above 60 °C.



Although addition polymerization is usually initiated by free radical mechanisms it has been shown that ionic mechanisms can also be effective in initiating polymer chains. Thus powerful electron acceptors such as the familiar Friedel-Crafts catalysts, aluminium trichloride and boron trifluoride, have proved excellent polymerizing agents for styrene. Styrene and methyl methacrylate have also been polymerized using anionic catalysts such as sodium in liquid ammonia. Unlike free radical reactions, polymerizations which are initiated by ionic means occur most readily at low temperatures.

An interesting and important breakthrough in the study of polymer initiation was the discovery by Ziegler in 1953 that polyethylene ('Polythene') could be polymerized at room temperature and pressure using a special catalyst. The Ziegler catalysts consist of a combination of metallic halide and an organo-metallic compound used in an inert solvent such as hexane. Titanium tetrachloride and a trialkyl aluminium compound are now extensively used in the industrial preparation of polyethylene. Heavy density polyethylene prepared using a Ziegler type catalyst owes its properties to the absence of side chains which are present in the older type low density polymer. This enables a closer packing of the monomer units with a corresponding rise in melting point and density.

Natta, working at the Milan Polytechnic in 1955, made the surprising discovery that polymers, such as polypropylene, produced using Ziegler catalysts differed from those produced by other methods. Thus instead of the random atactic (Gk.—without order) structure normally produced during polymerization, the groups attached to the carbon backbone were found to be orientated to form a regular pattern. In one type of Ziegler product all the groups were directed to the same side of the carbon chain while in other cases there was a regular alternation of direction. These two polymer forms were described as isotactic (Gk.—same order) and syndiotactic (Gk.—contrasting order). Polymerization reactions of this type were said to be stereospecific and Natta predicted that the ordered spatial arrangement of the resulting polymer would profoundly affect its physical properties.

In fact tactic polymer forms are denser and have a higher melting point than the corresponding atactic forms. Furthermore the syndiotactic polymers have a tough cohesive structure because of the interlocking of the side chains which project above and below the carbon backbone.

More recently, other catalysts having similar stereospecific properties to the Ziegler type have been discovered by the Phillips Petroleum and Standard Oil Companies (USA). Phillips catalysts consist of chromium oxide supported on a base of alumina-silica. The Standard Oil catalysts are either of molybdenum oxide based on alumina or nickel mounted on activated carbon.

The preparation of addition polymers on an industrial scale makes use of a number of ingenious techniques. One of the problems to be faced is the large amount of heat which is liberated during polymerization. This restricts the quantity of polymer which can be produced in any one operation by direct treatment of the pre-polymer with an initiator such as benzoyl peroxide. Mass polymerization of this kind is still used, however, for the manufacture of small batches of 'Perspex' and polyvinyl ethers.

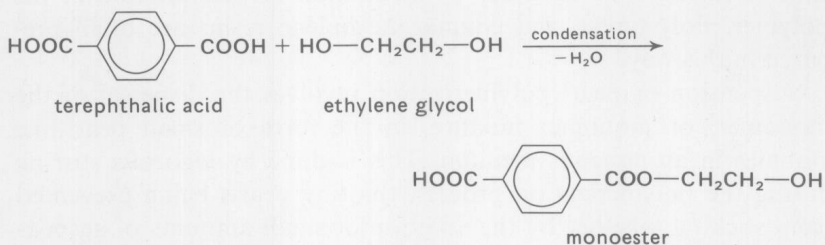
Another objection to mass polymerization is the difficulty of stirring and handling the highly viscous solutions produced. This can be partly overcome by dissolving both the initiator and the pre-polymer in a suitable solvent, a technique which also helps to dissipate the heat of polymerization. Large glass-lined iron vessels are used for this kind of solvent polymerization, and on completion of the reaction the solvent is removed either by distillation or precipitation of the polymer. Polystyrene and coumarone indene resins are often prepared in this way.

Suspension or pearl polymerization involves the dispersal of the monomer, or monomer mixture, in the form of small pearl-like globules in an aqueous medium. This is done by vigorous stirring during the polymerization process, the tiny pearls being prevented from sticking together by the addition of small amounts of suspension stabilizers such as talc or methyl cellulose. The initiator can be included in either of the liquid phases. An advantage of this method is that the heat of polymerization is mostly absorbed by the aqueous phase, thus allowing the reaction to be more easily controlled. In addition the end-product is in a convenient form for subsequent manufacturing processes.

Another commercial polymerization process relies upon the emulsification of the monomer with water using an anionic soap as an emulsifying agent. The initiator is dissolved in the aqueous phase from which it diffuses into the soap micelles coating the monomer. A high degree of polymerization is achieved by this method. The rate of polymerization is greatly increased by the use of a redox system as the initiator, such as glucose and cumene hydroperoxide. The resulting polymer emulsion may be coagulated using aluminium sulphate, or used directly as an aqueous emulsion, as, for example, in the preparation of emulsion paints.

CONDENSATION POLYMERIZATION

Condensation polymerization proceeds in steps, each step involving either a monomer unit and a growing chain or the ends of two growing chains. As each condensation occurs, a small molecule such as water is usually eliminated. Unlike addition polymerization, steady chain growth takes place continuously, the monomer quickly giving rise to dimers, which in turn react to form low polymers. The production of long chains is, therefore, protracted and reaction times are usually long. Most condensation polymers are copolymers involving two types of monomer units. Thus 'Terylene' is a copolyester of terephthalic acid and ethylene glycol.



As in the case of addition polymerization, chain building can only take place if the reacting molecules possess at least two active sites, so that they can attach themselves to a growing chain without acting as stoppers. Molecules of this type are said to have a functionality greater than unity. Growth of a polymer chain can be likened to the building of a model railway. Each rail must have two 'joining' ends in order that the line can be extended. If a line with a buffer is fixed to the end of a rail then this will act as a 'stopper' and the line will be terminated. If 'points' are used, which have more than two 'joining' ends, then branching lines can be built.

In the same way, by using mixtures of monomer units with different functionalities, i.e. numbers of 'joining' points, plastics with different chain lengths and varying degrees of branching and cross linking can be produced. This explains why terephthalic acid and ethylene glycol

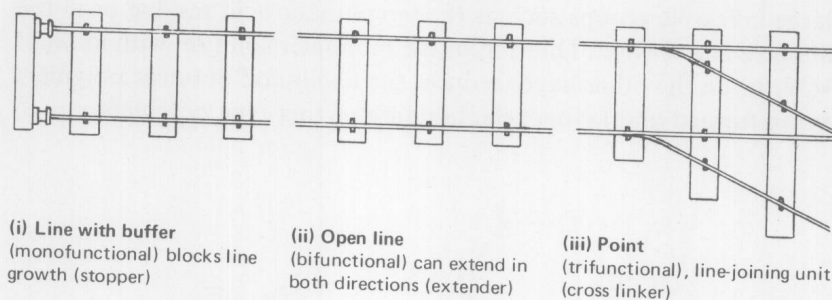
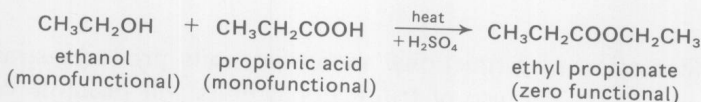
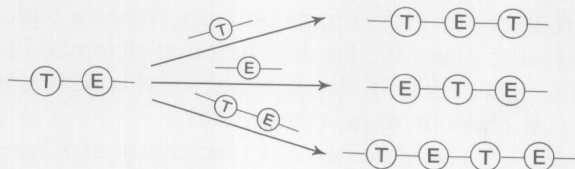


Fig. 1.1

can react to form a polyester, while a monobasic acid and a monohydric alcohol, being both monofunctional, react to form a monoester.



A bifunctional ester can react with additional molecules of an ester, acid or alcohol to produce further bifunctional products containing mixtures of the two monomer species. Thus if we represent the terephthalic acid monomer unit as —T— and the ethylene glycol monomer unit as —E— then the monoester can polymerize further as follows:



There is also the possibility that ring structures might be formed by head-to-tail type reactions between the ends of individual polymer chains, or those of different chains.