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# Experiments in Polymer Science

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## Preface

*Experiments in Polymer Science* was written with two groups of readers in mind. Although they are different and will use the book in different ways, their needs are basically similar; thus we feel that this book can do double duty easily and efficiently.

The first and obvious user is the student, graduate or advanced undergraduate, who will use this book as a laboratory manual in a course in polymer science or engineering. His interest will center on the experiments in Part III, which he must perform in the laboratory. But he is hereby warned (if he chances to read this far in such an unlikely place as a Preface) that he will have a much better chance of understanding the experiment, completing it successfully in the allotted time, and preparing a satisfactory report, if he studies both the experimental procedure and the background material in Part I or Part II in advance of coming to the laboratory. The instructor should see that assignments to this end are made and adhered to.

The second reader to whom *Experiments in Polymer Science* is addressed is the industrial polymer scientist or engineer, which indeed the student may become in a few years. His approach to the book should, we feel, reflect our philosophy that the industrial career of the technically trained scientist or engineer--whether in research, production, sales, or another branch of the organization--is a continuing educational experience in which he is sometimes the student and sometimes the instructor. In either role, he will find (if we have been successful) much that will make his job easier and more meaningful, and much that will contribute to more effective communication with his co-workers and a clearer understanding of the problems they face. He will no doubt be interested first in Parts I and II, but he will find study of the experiments in Part III rewarding as well.

*Experiments in Polymer Science* is intended as a companion book to F. W. Billmeyer's *Textbook of Polymer Science*, 2nd edition, 1971, and frequent reference is made to topics discussed more fully in the *Textbook*, as well as to books dealing more specifically with polymer laboratory practice, and to the general literature.

The present book takes an integrated approach to the polymer science laboratory, by providing experiments leading to the synthesis of several polymers which are then used in the molecular, physical, and thermal characterization experiments that follow. Major emphasis, however, is on characterization and property measurement, for two reasons: First, the organic polymer chemist will find ample supplementary material allowing him to modify experiments and to broaden this phase of the course as desired; examples of such supplementary

material are Sorensen and Campbell's *Preparative Methods of Polymer Chemistry*, Braun, Cherdon, and Kern's *Techniques of Polymer Syntheses and Characterization*, and the series *Macromolecular Syntheses*. Second, the experiments on synthesis can be omitted--for example, for students with more interest in the polymer engineering disciplines--with readily available commercial polymer samples substituted for those prepared in the laboratory where required in the experiments on characterization and property measurement.

All experiments presented in this book have been tested in the laboratory. They are based on a schedule of one 3-hour laboratory period per week. Enough material is presented to provide a two-semester sequence, although the instructor may wish to select experiments for completion in one semester or an even shorter time period, based on interest and the availability of equipment. Selected experiments can also be included in other undergraduate and graduate laboratory courses, including those in organic and physical chemistry, instrumental analysis, and materials science and engineering.

The preparation of *Experiments in Polymer Science* has been in many respects a team effort. It grew from notes for a Polymer Science Laboratory course offered in Rensselaer's Department of Chemistry. Concepts and much background material were supplied by E. A. Collins, who taught the course with the assistance of J. Bareš and A. Mehta as laboratory assistant. F. W. Billmeyer coordinated and drafted the final manuscript. Several generations of students, at Rensselaer and elsewhere, contributed invaluable experience. Special thanks must go to Shirley Papp and Diane Rym at B. F. Goodrich Chemical Co. and Edis Hite for typing many drafts, and Helen Hayes at Rensselaer who typed the manuscript you are reading. Acknowledgement is also due to L. A. Chandler, C. A. Daniels, J. A. Davidson, H. V. Flint, R. A. Jones, R. Marsh, A. P. Metzger, R. G. Raikes, and C. Wilkes at B. F. Goodrich Chemical Co., to P. H. Geil and C. E. Rogers at Case Western Reserve University, and to B. Wunderlich at Rensselaer Polytechnic Institute. The encouragement and assistance of Walter H. Bauer, Dean Emeritus of Rensselaer's School of Science, is gratefully acknowledged. One of us (E.A.C.) thanks B. F. Goodrich Chemical Co. for permission to co-author this book.

Edward A. Collins  
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## Contents

### *Part I Introduction to Polymer Synthesis Techniques*

#### *Chapter 1 Polymerization Mechanisms 3*

- A Classification of Polymers 4
- B Step-Reaction (Condensation) Polymerization 5
- C Radical Chain (Addition) Polymerization 8
- D Ionic Chain Polymerization 14
- E Coordination and Ring-Opening Polymerization 18
- F Copolymerization 20
- G Chain Branching and Crosslinking 22

#### *Chapter 2 Polymerization Conditions 27*

- A Homogeneous Polymerization 29
- B Heterogeneous Polymerization 33
- C Interfacial Polymerization 35

#### *Chapter 3 Materials and Their Purification 38*

- A Monomers, Diluents, and Solvents 38
- B Initiators and Catalysts 42
- C Other Ingredients 46
- D Influence of Impurities 47

#### *Chapter 4 Experimental Methods and Apparatus 51*

- A Polymerization 51
- B Isolation and Purification of Polymer 62
- C Auxiliary Apparatus 70
- D Laboratory Safety 74

#### *Chapter 5 Following the Course of Polymerization 82*

- A Direct Weighing 82
- B Chemical Methods 83
- C Dilatometry 84
- D Refractometry 87
- E Other Methods 89

*Part II Introduction to Polymer Characterization Techniques*

*Chapter 6 Preliminary Evaluation of Polymer Properties 99*

- A Thermal Characteristics 100
- B Solubility and the Preparation of Solutions 105
- C Chemical, Environmental, and Thermal Stability 109
- D Mechanical Properties 111
- E Ultraviolet and Infrared Spectroscopy 113
- F Summary 115

*Chapter 7 Molecular Weight and its Distribution 121*

- A Number-Average Molecular Weight 124
- B Weight-Average Molecular Weight 135
- C Molecular Size 146
- D Molecular-Weight Distribution 153
- E Summary 172

*Chapter 8 Polymer Morphology 179*

- A Morphology of Crystalline Polymers 180
- B X-Ray Diffraction 188
- C Electron Microscopy 198
- D Optical Microscopy 204

*Chapter 9 Thermal Properties 216*

- A The Glass Transition 216
- B The Crystalline Melting Point 227
- C Thermal Analysis and Calorimetry 229
- D Thermal Conductivity 249
- E Thermogravimetric Analysis 252

*Chapter 10 Structure-Property Relationships 263*

- A Bulk Viscosity 266
- B Dynamic Mechanical Behavior 284
- C Dynamic Electrical Behavior 291
- D Stress-Strain Properties 300
- E Swelling of Network Polymers 305
- F Permeability of Polymers to Gases and Liquids 306
- G Summary 311

*Part III Experiments*

*A Synthesis Experiments 327*

- Experiment 1 Bulk Polycondensation of  $\omega$ -Aminoundecanoic Acid 327
- Experiment 2 Interfacial Polycondensation of Hexamethylene Diamine and Sebacyl Chloride 330
- Experiment 3 Bulk Polymerization of Methyl Methacrylate 333
- Experiment 4 Emulsion Polymerization of Styrene 337

- Experiment 5 Radical Copolymerization of Styrene and Methyl Methacrylate 342
- Experiment 6 Solid State Polymerization of Trioxane 345
- Experiment 7 Solution and Bulk Preparation of a Polyether-Based Polyurethane 347
- Experiment 8 Preparation of Crosslinked Polymers 353
- Experiment 9 Anionic Polymerization of Styrene 357

#### *B Experiments Measuring Molecular Weight and Distribution 362*

- Experiment 10 End-Group Analysis 362
- Experiment 11 Membrane Osmometry 367
- Experiment 12 Vapor-Phase Osmometry 374
- Experiment 13 Light-Scattering Molecular Weight 380
- Experiment 14 Particle Size by Light Scattering 388
- Experiment 15 Dilute-Solution Viscosity 394
- Experiment 16 Gel Permeation Chromatography 399
- Experiment 17 Turbidimetric Titration 405

#### *C Morphology and Thermal-Property Experiments 410*

- Experiment 18 X-Ray Diffraction 410
- Experiment 19 Electron Microscopy 418
- Experiment 20 Light Microscopy 422
- Experiment 21 Differential Thermal Analysis 428
- Experiment 22 Differential Scanning Calorimetry 435
- Experiment 23 Thermal Conductivity 441
- Experiment 24 Thermogravimetric Analysis 446

#### *D Experiments on Structure-Property Relations 451*

- Experiment 25 Melt Viscosity 451
- Experiment 26 Concentrated-Solution Viscosity 457
- Experiment 27 Dynamic Mechanical Properties 465
- Experiment 28 Dielectric Constant and Loss 470
- Experiment 29 Stress-Strain Properties 478
- Experiment 30 Swelling of Network Polymers 481
- Experiment 31 Permeability of Polymers to Gases 484
- Experiment 32 Infrared Spectroscopy 488

#### *Appendixes*

- I Standard Polymer Samples 493
- II Properties of Selected Polymers 504
- III Properties of Monomers and Solvents Used in the Experiments 506
- IV Errors and the Statistical Treatment of Data 510

#### *Index 525*



## **Part I**

# **INTRODUCTION TO POLYMER SYNTHESIS TECHNIQUES**



## Polymerization Mechanisms

On close examination, the history of polymers goes back farther than that of any other group of substances known to man. From the fig leaf in the Garden of Eden, man has been dependent upon naturally-occurring polymers for food, clothing, shelter, and communication. Today, his dependence on synthetic polymers, the primary subject of this book, is even more fundamental.

The history of synthetic polymers is relatively short, however, because of the complexity of their structure. Even their basic long-chain structure was still questioned only 50 years ago; it was only through the pioneering work of Staudinger (1920) and the quantitative studies of Carothers (1929, 1931) that the macromolecular concept was finally accepted. Long before this time, synthetic polymers were being produced, and natural polymers were being altered chemically, without a clear understanding of the processes involved. Styrene was first polymerized in 1839, and in that same year Goodyear discovered the vulcanization of rubber. Cellulose nitrate was first made in 1838 and commercialized in 1840. The first synthetic polymers to be produced commercially were phenol-formaldehyde resins, in 1907.

Today, with polymer science and engineering well developed, we can undertake the study of these important materials in the laboratory with a background of knowledge which allows, in most cases, a full understanding of the experiments we perform and, what is more important, the ability to define the areas which are not yet fully understood as the basis for future research. The objective of this book is to provide information on the experimental techniques and their scientific background for polymer synthesis and characterization.

As general reference to these introductory paragraphs we list a few general books on polymer science. Chief among these is *Textbook of Polymer Science* (Billmeyer 1971), hereafter referred to as the *Textbook*, which is cited extensively as a companion book to this laboratory manual.

### GENERAL REFERENCES

*Textbook*, Chap. 1; Flory 1953, Chap. II; Mark 1966a; Margerison 1967; Rodriguez 1970; Seymour 1971; Billmeyer 1972.

A. *Classification of Polymers*

Before entering a discussion of the ways in which polymers are synthesized, it is convenient to classify them, for simplification, in one or another way. There are many schemes of classification possible. First is that already mentioned: synthetic versus natural polymers. In this book, which is based on synthesis and the characterization of the resulting polymers, such a classification is of little practical value. Synthetic polymers could be further classified by monomer type, preparative techniques, polymer structure, physical properties, processing techniques, or end use, among others. For example, a classification according to processing techniques might first divide polymers into thermoplastics and thermosets, and carry on from there. A classification by end use might attempt to associate polymer classes to specific industries. For example, diene polymers are associated with the rubber industry, the olefin polymers with the sheet, film, and fiber industry, and the acrylics with coatings and decorative materials. Similar identifications could be made for the vinyls, polyesters, polyamides, alkyds, cellulose, phenolics, urethanes, and siloxane polymers. These classifications are useful in a practical sense, but offer little or no insight into the scientific principles distinguishing one polymer type from another.

In accord with our present concern with polymerization mechanisms, we shall adopt the widely used classification of Carothers (1929; also Mark 1940), in which polymers are divided into *addition* and *condensation* types on the basis of a difference in elemental composition between the polymer and its monomer. In the original meaning, any polymer formed from a polyfunctional monomer by a condensation reaction with the elimination of a small molecule such as water was classified as a condensation polymer.

The discovery of many more polymer types and many more ways of synthesizing polymers has required that this classification be modified, and the grounds for it clarified. Perhaps the most useful scheme for our purposes is based on polymerization mechanisms, as formulated by Mark (1950) and discussed in the *Textbook*, Chap. 8A. This classification divides polymers into those formed by *step-reaction* and by *chain* mechanisms. Polymers made by step-reaction mechanisms are formed by a series of reactions, often of the condensation type, in which any two species (monomers, dimers, trimers, etc.) can react at any time, leading to a larger molecule. Elimination of a small molecule is a possible but not an essential feature. Usually, but not essentially, such polymers contain functional groups (ester, amide, urethane, etc.) as part of the main chain.

Chain-reaction polymers, which can often be identified with Carothers' addition polymers, are produced by reactions in which monomers are added, one after another, to a rapidly growing chain. Usually they do not contain functional groups in the chain, and no small molecule is lost at each step in the polymerization. The differences between chain and step polymerization mechanisms are shown in Table 1-1, taken from the *Textbook*.

It is clear that no single classification can be all-inclusive, and we do not attempt to use any one rigorously; more important is the development of an understanding of the need for different classifications and the interrelations among them. In the course of this

TABLE 1-1. *Distinguishing features of chain- and step-polymerization mechanisms*

Chain Polymerization	Step Polymerization
Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at $DP^a$ 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Long reaction times give high yields but affect molecular weights little.	Long reaction times are essential to obtain high molecular weights.
Reaction mixture contains only monomer, high polymer, and about $10^{-8}$ part of growing chains.	At any stage all molecular species are present in a calculable distribution.

<sup>a</sup>Degree of polymerization.

book we shall further subdivide and reclassify as the occasion demands. Step reactions will be classified by reaction type as condensation, addition, ring-opening, amidation, ester interchange, or interfacial; and chain reactions by initiation mechanism as free-radical, anionic, cationic, or coordination. In Chap. 2, we reclassify polymers by preparative methods as bulk, suspension, solution, emulsion, or interfacial. The polymers synthesized or characterized in the experiments in this book, plus a few others of commercial importance, are classified as step-reaction (condensation) and chain-reaction (addition) types in Table 1-2.

### B. Step-Reaction (Condensation) Polymerization

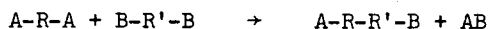
Step-reaction or condensation polymerizations take place by a variety of reactions, as described in the *Textbook*, Chap. 8B and the references cited therein. All of them proceed by the stepwise reaction between functional groups on the reacting molecules. In general, these reactions fall into two classes: *polycondensation*, in which a small molecule is eliminated at each step, and *polyaddition*, in which this does not occur. If A and B are functional groups which can react, attached to a nonreactive portion of the molecule R or R', these

TABLE 1-2. Classification of common polymers as resulting from step or chain reactions

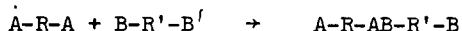
Step Reaction	Chain
Polyesters	Polystyrene
Polyamides <sup>a</sup>	Poly(methyl methacrylate)
Polyurethanes	Poly(vinyl chloride)
Phenol-formaldehyde resins	Polyethylene
Urea-formaldehyde resins	Poly(vinyl acetate)
Melamine-formaldehyde resins	Polyisoprene
Polyacetals	Polybutadiene
Polysulfides	Polypropylene

<sup>a</sup>Can also be formed by chain mechanisms, such as ionic ring-opening reactions.

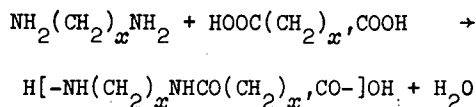
can be represented as follows: polycondensation



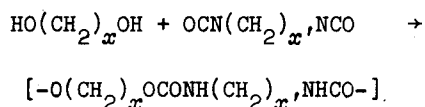
and polyaddition



An example of polycondensation is the formation of a polyamide from a diamine and a dibasic acid with the elimination of water, the first step of which is



The formation of a polyurethane by the reaction of a glycol and a diisocyanate is an example of polyaddition. Again, the first step is



Other examples are given in Table 8-2 of the *Textbook*. These reactions

are well known in small molecules; their application to polymerization requires only that the reactants be difunctional so that the product of each reaction step can participate in further reactions.

The *degree of polymerization*  $\bar{x}_n$ , that is, the number-average\* number of monomers or repeat units in the chain, can easily be predicted from kinetic or statistical considerations (*Textbook*, Chap. 8) in terms of the *extent of reaction*  $p$ . The latter is easily measured in most cases as the fraction of the functional groups used up. The two quantities are related by the Carothers equation,

$$\bar{x}_n = 1/(1-p) \quad (1-1)$$

from which it follows that the *number-average molecular weight* is given by

$$\bar{M}_n = M_0/(1-p) \quad (1-2)$$

where  $M_0$  is the molecular weight of the repeat unit, usually that of the monomer less the weight of any small molecule lost at each reaction step.

Examination of this equation will show that the preparation of high-molecular-weight polymers by step-reaction polymerization places unusually demanding and rigorous requirements on the purity of the reactants. Stoichiometry must be exactly balanced; that is, the number of each type of functional group must be the same. Conversion must be high, and there must be no monofunctional reactants present and little or no tendency to form cyclic compounds. Practically, high reaction rates are desirable. Some of the characteristics of step-reaction polymerization made understandable by the Carothers equation are listed in Table 1-1.

It is obvious that an excess of one type of functional group limits the maximum chain length obtainable, and this technique is occasionally used industrially to provide molecular-weight control. The resulting value of  $\bar{x}_n$  can be predicted if the initial ratio of functional-group concentrations is known, as is amplified in the *Textbook*. If the stoichiometry were exact, infinite chain length would theoretically be possible. Practically, the highest molecular weight attainable is limited by two factors: First, the reaction is one of equilibrium, and to shift it in the direction of high polymer requires essentially complete removal of the water or other small molecule formed. In practice, step-reaction polymerizations in bulk systems are often finished with a long high-temperature high-vacuum step to accomplish this. Second, the reaction slows down at higher conversions as the concentrations of the reactants are reduced; thus, the final equilibrium is approached more and more slowly.

Kinetic analysis shows that the time dependence of the extent of reaction is given by

$$p = kc_0t/(1 + kc_0t) \quad (1-3)$$

\*The concepts of the number- and weight-averages are defined and discussed with respect to molecular weight in Chap. 7.

where  $k$  is the rate constant, which can be demonstrated to be independent of  $p$  over most of the range of interest, and  $c_0$  is the initial functional-group concentration. It follows that

$$\bar{x}_n = kc_0 t + 1 \quad (1-4)$$

Since the constant term is small, the degree of polymerization increases linearly with time. These considerations apply to catalyzed polymerizations, as discussed in the *Textbook*, Chap. 8C.

If, as is usual, all molecules have equal reactivity, step-reaction polymerization is a completely random process in that any species present can react with any other. Statistical considerations (*Textbook*, Chap. 8C, or for a simple treatment, Billmeyer 1972) show that the distribution of chain lengths or molecular weights achieved at equilibrium is a function of  $p$  given by

$$w_x = x(1-p)^2 p^{x-1} \quad (1-5)$$

where  $w_x$  is the weight fraction of the polymer consisting of chains with degree of polymerization  $x$ . From this distribution function one can calculate the weight-average degree of polymerization  $\bar{x}_w$ :

$$\bar{x}_w = (1 + p)/(1 - p) \quad (1-6)$$

and of course  $\bar{M}_w = M_0 \bar{x}_w$ . The ratio of weight-average to number-average molecular weight (or degree of polymerization) is a convenient measure of the breadth of the molecular-weight distribution,

$$\bar{x}_w/\bar{x}_n = \bar{M}_w/\bar{M}_n = 1 + p \quad (1-7)$$

and can be seen to approach 2 at high conversion as  $p$  approaches unity.

#### GENERAL REFERENCES

*Textbook*, Chap. 8C; Flory 1953; Sokolov 1968; Carmichael 1970; Odian 1970; Rodríguez 1970, Chap. 4; Braun 1971, Chap. 4; Williams 1971, Chap. 3.

#### C. Radical Chain (Addition) Polymerization

In this section we discuss chain polymerization in which the growing polymer molecule is a free radical, that is, a substance containing one unpaired electron, but no net electric charge. Other types of growing chains are possible, including both cations and anions; these are discussed in Sec. D. Regardless of the nature of the chain itself, there are three fundamental steps in any chain reaction, and chain polymerization is no exception. They are *initiation*, in which the chain is formed; *propagation*, in which (in polymerization) monomer is added to the growing chain; and *termination*, in which the

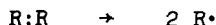


growth activity of the chain is destroyed, leaving the polymer molecule. Other reactions may be involved, and some are discussed below, but they are not essential. The steps of initiation, propagation, and termination refer to molecular reactions of a single chain and not to the system as a whole; all occur concurrently in the polymerizing mass. The time between initiation and termination of a given chain is typically from a few tenths second to a few seconds; during this time, thousands or tens of thousands of monomers add to the growing chain.

### Initiation

Initiation in radical-chain polymerization is the process by which a monomer molecule acquires an active site for the propagation of the chain reaction, that is, becomes a free radical. This can take place as the result of a number of processes, including oxidation-reduction reactions, reaction of another free radical with the monomer, interaction of high-energy radiation with the monomer, or in some cases thermal decomposition of the monomer without the need for any other agent. Some of these agents and mechanisms are discussed further in Chap. 3B; here we take as an example the most common form of initiation: the production of a free radical by the thermal decomposition of a relatively unstable *initiator* molecule, and the subsequent addition of a monomer to this primary radical to form the first chain radical. This is a two-step process, but we shall assume, as is usually the case, that the second step is rapid compared to the first.

Among the common thermal initiators for free-radical polymerization are peroxides, such as benzoyl peroxide, and azo compounds, such as azobisisobutyronitrile, whose structures are given in Chap. 3B. If we designate such a molecule  $R:R$ , where the two dots represent the electrons of the unstable bond, e.g., the O-O bond in benzoyl peroxide (and note that the two fragments  $R$  do not have to be identical), the primary initiation step is the thermal rupture of this bond, one electron remaining with each radical fragment:



where the single dot represents the unpaired electron characteristic of a free radical. The second step of initiation, in which  $R\cdot$  adds to a monomer  $M$ , may be represented schematically as



In terms of molecular structure, in the typical case of a *vinyl* monomer of the general structure  $CH_2=CHX$ , where  $X$  is hydrogen in ethylene,  $CH_3$  in propylene,  $Cl$  in vinyl chloride, phenyl in styrene, etc., the radical  $R\cdot$  adds to the double bond, regenerating the unpaired electron at the substituted end (usually) of the monomer:



As a result of this step, the initiator fragment  $R$  is chemically bonded to the growing chain and thus incorporated into the final