POLYMER SYNTHESES

Volume I

Second Edition

Stanley R. Sandler

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KING OF PRUSSIA, PENNSYLVANIA

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POLYSCIENCES, INC.
WARRINGTON, PENNSYLVANIA

ACADEMIC PRESS, INC.
Harcourt Brace Jovanovich, Publishers
Boston San Diego New York
London Sydney Tokyo Toronto

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ACADEMIC PRESS, INC.
1250 Sixth Avenue,
San Diego, California 92101

United Kingdom Edition published by
ACADEMIC PRESS LIMITED
24–28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Sandler, Stanley R., date.
Polymer synthesis / Stanley R. Sandler, Wolf Karo. —2nd ed.
p. cm. —— (Organic chemistry; v. 29)
Includes bibliographical references and index.
ISBN 0-12-618511-5 (v. 1: alk. paper)
1. Polymerization. I. Karo, Wolf, 1924– . II. Title.
III. Series: Organic chemistry (New York, N.Y.); v. 26.
QD281.P6S27 1992
547.8′4–dc20

91-29659
CIP

PRINTED IN THE UNITED STATES OF AMERICA
91 92 93 94 9 8 7 6 5 4 3 2 1

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This is Volume 29-I of
ORGANIC CHEMISTRY
A series of monographs
Editor: HARRY H. WASSERMAN

A complete list of titles in this series is available from the Publisher upon request.

PREFACE TO THE SECOND EDITION

The purpose of this Second Edition remains to give the student and industrial polymer chemist an in-depth source of procedures for the preparation of various classes of polymers by functional group types. Each of the chapters contains not only journal references but many up-to-date references to the patent literature (U.S.A. and World). This feature of having extensive references to the patent literature should make this book particularly valuable to the research scientist.

Several sections of each chapter have been either revised or updated. For example, Chapter 4 (Polyamides) contains a new section on aromatic polyamides. In addition, Chapter 9 (Thermally Stable Polymers) and Chapter 13 (Organophosphorus Polymers) contain many new developments in these areas. Chapters 14 and 15 have been rewritten into a new, single chapter that, instead of giving initiator syntheses, describes their use in appropriate polymer syntheses both in this volume and in the other two volumes of this set. The Appendix has also been updated in several areas.

This book should only be considered a guide and the questions of patentability are left up to the individual to research. In addition, the toxicity of all reagents, products, and by-products should be carefully examined by each researcher before proceeding. Material Safety Data Sheets (MSDS) should be read and the recommendations by the manufacturer or supplier followed. Good ventilation and protective equipment should be used at all times.

We extend again our special thanks to Ms. Emma Moesta for the typing of the manuscript of this Second Edition. Her continued untiring devotion in the preparation of both the First and Second Edition manuscripts has been an inspiration to the authors.

Finally, we thank our families and the Academic Press, Inc., staff for helping to make this project a success.

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Wolf Karo

PREFACE TO THE FIRST EDITION

The aspects of organic polymer theory and mechanisms, polymer processes, and practical chemistry have already appeared in other books. However, the synthesis of the various classes of polymers by functional group types remained unavailable. This book aims to fill this gap and to present detailed laboratory instructions for the preparation of polymers by various functional group classes. Each chapter contains a critical review of the best available synthetic methods. The classes of polymers covered include olefin and diolefin, hydrocarbon polymers, polyesters, polycarbonates, polymerization products of epoxides, cyclic ethers, aldehydes, polyureas, polyurethanes, thermally stable polymers, acrylic–methacrylic esters, polyacrylonitriles, polyacrylamides, and organophosphorus polymers. Some of the heterocyclic polymers included in the chapter on thermally stable polymers are polyimides, polybenzimidazoles, polyquinoxalines, poly-1,3,4-oxidazoles, poly-1,2,4-triazoles, polybenzothiazoles, and polybenzoxazoles.

This book is enhanced by the chapter on phosphorus-containing polymers. It appears to be the first review that presents detailed laboratory procedures for the preparation of polymers containing phosphorus in various oxidation states. The synthesis of phosphonitrilic polymers is also included in this chapter. This chapter should be especially valuable to those chemists involved in the designing of phosphorus polymers to meet present and future fire retardant requirements of their various products.

Added details on the synthesis of peroxide and hydroperoxide free radical initiators are of special interest. This information is included to aid those polymer chemists who may have to design special initiators for unusual applications.

In all chapters the latest journal articles and patents have been reviewed. Each chapter contains tables of data to show the scope of the various methods of synthesis with references given for each entry. Some preparations are taken from the older literature because they are of a classic nature and suitably describe the polymer preparation. Most are taken from present-day literature and are included only if they appear to be the best available.

In presenting preparative details of the various techniques of polymerization, an effort was made to select, if possible, methods which would have wide application not only for the formation of polymers of the specific system cited but also for many related situations. Thus, for example, the principles involved in the preparation of emulsion polymers are applicable to the preparation of polymers of a wide variety of vinyl monomers as well as to many copolymerizations.

This book is designed only to give helpful polymer synthesis information and not to override the question of legal patentability or to suggest allowable industrial use.

We would like to take this opportunity to thank Dr. Jack Dickstein, Research Manager of the Central Research Laboratories of Borden Chemical, Division of Borden, Inc., for encouragement and support in the preparation of this manuscript. Special thanks are due to Miss Emma Moesta for her untiring devotion in the preparation of the typed manuscript. Finally, we thank our wives and children for their patience, understanding, and encouragement during all stages involved in the preparation of the manuscript.

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POLYMER SYNTHESES II

CONTENTS

POLYMER SYNTHESES III

CONTENTS

CONTENTS

Chapter 5. **Polymerization of Aldehydes**

Chapter 6. **Polymerization of Epoxides and Cyclic Ethers**

Chapter 7. **Polyureas**

Chapter 8. **Polyurethanes**

Chapter 9. **Thermally Stable Polymers**

Chapter 10. Polymerization of Acrylate and Methacrylate Esters

Chapter 11. Polymerization of Nitrile Monomers

Chapter 12. Polyacrylamide and Related Amides

Chapter 13. Organophosphorus Polymers

Chapter 14. Free Radical Initiation of Vinyl and Related Monomers

Appendix

Chapter 1

POLYMERIZATION OF OLEFINIC AND DIOLEFINIC HYDROCARBONS (Styrene, Butadiene, Isobutylene, Ethylene and Related Monomers)

1. INTRODUCTION

Olefinic and diolefinic monomers can be polymerized using either free-radical, anionic, cationic, or coordination type initiators. These will be discussed individually in each of the four sections of this chapter. It is interesting to note that not all monomers respond equally well to each of the types of initiators.

The substituents placed on ethylene greatly affect stereochemistry, resonance, and polarity of the monomer, and have a decided effect on which initiator system works best with it. For example, propene and 1-butene can only be homopolymerized well with coordination catalysts (see Section 5), whereas isobutene responds mainly to cationic initiators. Styrene can be polymerized using any of the four types of initiators. Isoprene and 1,3-butadiene can be homopolymerized with all the initiators except the cationic type, whereas ethylene polymerization can be initiated by all except the anionic type. In the case of vinyl acetate, which has an intermediate electron density around the double bond, it can be polymerized mainly by use of a free radical process. Substituents around the double bond such as chlorine (as in vinyl chloride) will interfere when using cationic or anionic initiators, and it is preferable to polymerize them by a free radical process.

The free-radical initiating system has the practical advantage that the polymerizations can be carried out in the gas, solid, and liquid phases (bulk, solution, emulsion, suspension, and precipitation techniques). Free-radical reactions can be carried out in water, whereas the other initiators usually require anhydrous conditions.

Many of the anionic and cationic polymerizations can be considered to have no inherent termination step and may be called "living polymers."

The stereochemistry of the repeating units depends on the structure of the starting monomer, the initiating system, and the conditions of the polymerization reaction. Optical isomerism, geometric isomerism, repeat unit configuration (isotactic, syndiotactic, atactic) and repeat unit orientation (head-to-tail or head-to-head) are some important aspects of the stereochemistry problem.

The mechanisms of polymerization will not be discussed here but several worthwhile references should be consulted [1]. This chapter will give mainly examples of some selected preparative methods for carrying out the major methods of polymerization as encountered in the laboratory. All intrinsic viscosities listed in this chapter have units of dl/gm.

This chapter will also present some recent developments in ring-opening methathesis in polymerization in Section 5 (Coordination Catalyst Polymerization).

2. FREE RADICAL POLYMERIZATIONS

In 1838 Regnault [2] reported that vinylidene chloride could be polymerized. In 1839 Simon [3] and then Blyth and Hofmann (1845) [4] reported the preparation of polystyrene. These were followed by the polymerization of vinyl chloride (1872) [5], isoprene (1879) [6], methacrylic acid (1880) [7], methyl acrylate (1880) [8], butadiene (1911) [9], vinyl acetate (1917) [10], vinyl chloroacetate [10], and ethylene (1933) [11]. Klatte and Rollett reported that benzoyl peroxide is a catalyst for the polymerization of vinyl acetate and vinyl chloroacetate [10].

In 1920 Staudinger [12] was the first to report on the nature of olefin polymerizations leading to high polymers. A great many of his studies were carried out on the polymerization of styrene. These studies led to recognition of the relationship between relative viscosity and molecular weight [13]. The radical nature of these reactions was later elucidated by Taylor [14], Paneth and Hofeditz [15], and Haber and Willstätter [16]. The understanding of the mechanism of polymerization was greatly aided by Kharasch [17], Hey and Waters [18], and Flory [19].

No effort will be made to discuss the mechanism of polymerization in this chapter, but let it suffice to say that the polymerization is governed by the three main steps shown in Eqs. (2), (3), and (4), (5), (6), and (8).

The most common initiators are either acyl peroxides, hydroperoxides, or azo compounds. Hydrogen peroxide, potassium persulfate, and sodium perborate are popular in aqueous systems. Ferrous ion in some cases enhances the catalytic effectiveness. The use of acyl peroxides, hydroperoxides and other initiators is described in Chapter 14.

Ethylene is conveniently polymerized in the laboratory at atmospheric pressure using a titanium-based coordination catalyst (see Section 5) [20]. It may also be polymerized less conveniently in the laboratory under high pressures using free-radical catalysts at high and low temperatures [21]. Other