Carbocationic Polymerization

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1807 175 YEARS OF PUBLISHING 1982

Library of Congress Cataloging in Publication Data:

Kennedy, Joseph Paul, 1928–
Carbocationic polymerization.

"A Wiley-Interscience publication."
Includes bibliographical references and index.
1. Polymers and polymerization. I. Maréchal, Ernest, 1931– joint author. II. Title.
QD381. K38 547'.28 80-26366
ISBN 0-471-01787-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Preface

This is an interdisciplinary book written for the organic chemist who wants to relate knowledge of cationic reactions of small molecules to the science of large molecules, for the physical chemist who wishes to apply basic chemical–physical principles to polymerization mechanisms, for the polymer scientist who wants comprehensive up-to-date critical information about a large segment of vigorously growing polymer science and technology, for the research entrepreneur who is on the lookout for well-defined but unexploited leads, for the industrial researcher who wants to survey the technology of cationic polymerization processes leading to useful products, and for the student who is searching for working relations between abstract ideas, contemporary research in polymer science, and, ultimately, some of today's important technologies.

If a change is slow, not sudden or abrupt, it is difficult to perceive that it is in progress; once the change is recognized it becomes a "quiet revolution." The area of cationic polymerization is undergoing such a quiet revolution right now. It will be some time before it is generally perceived as such because outlooks, like habits, change slowly. Indeed, our resolve to write this book, a most painful exercise, stemmed in part from our conviction that this quiet revolution should be exposed to the polymer community.

During the past decade the elucidation of cationic polymerization has undergone such a rapid increase and the exploitation of new mechanistic information in terms of new products and processes in the research laboratory was so rapid that serious students of this field had to reassess completely their views with regard to the capabilities, particularly preparative capabilities, of this discipline.

Polymer scientists and technologists at large know carbocationic polymerization as a well-established but colorless segment of polymer science offering some commercially attractive possibilities (witness butyl rubber) and allowing the preparation of some quaint structures (such as $-CH_2CH_2C(CH_3)_2-$ by isomerization polymerization), but one that is better avoided because it is a bewildering, unmappable maze beset by some insurmountable experimental difficulties such as the necessity of working at very low (cryogenic) temperatures. It is one of the objectives of this book to dispel this completely false and distorted notion and to rejuvenate the field by showing by many examples the tremendous promise and unexploited possibilities offered by carbocationic polymerizations. In view of the very large number and variety of cationically responsive monomers, low cost and high efficiency of cationic initiating systems, usually rapid reactions, and modest investment required for cationic manipulations, the lack of entrepreneurship in exploiting cationic polymerization is rather surprising. One possible reason for lagging interest in cationic polyreactions may be two decades of colorless research mired in difficultly reproducible kinetic minutiae and fruitless basic investigations. Another factor is that quantum jumps such as Szwarc's discovery of "living" polymerizations or Ziegler and Natta's discovery of stereoregulating catalysts, discoveries that created unexpected new vistas in other areas of ionic polymerizations, eluded the field of carbocations.

Another objective of this book is to present a unified, interlocking, in many respects new view of carbocationic polymerization. Although select parts of this discipline have been reviewed in the past by several authors, the whole field as such has not yet been comprehensively and critically examined in a book written by one or two authors.

We start by asking, in Chapter 1, why carbocationic polymerizations? What is so special about this science? We find some unique answers in the fields of chemistry, structure–property relationships and technology. In the next chapter we define terms, describe basic concepts, and lay down foundations to be built on when we turn to the discussion of mechanisms. In Chapter 3 we proceed to phenomenology to acquaint the reader with what carbocationic polymerizations *are* by examining monomers, initiators, coinitiators, and solvents. The next, long chapter (4) concerns the chemistry and mechanisms of the important elementary events: initiation, propagation, chain transfer, and termination. In Chapter 5 on kinetics, an attempt is made to combine these mechanistic steps and kinetic expressions are examined. The following chapter on copolymerization and reactivity starts with a comprehensive compilation and evaluation of all monomer pairs copolymerized by carbocationic initiation and proceeds to a discussion of experimental and theoretical determinations of reactivity. A review of relative reactivity relations is given and the influence of experimental parameters on reactivity is examined.

In Chapter 7 carbocationic step-growth polymerizations are discussed. The following chapter examines in detail the chemistries leading to recently developed sequential (block and graft) copolymers. Chapter 9 is devoted to macromolecular engineering and a glance toward the future. We conclude that the time for tailoring physical–mechanical–chemical properties by carbocationic techniques (i.e., macromolecular engineering) has arrived and develop a framework for the synthesis of new sequential, functional, telechelic polymers. The book ends with a survey of industrial processes employing carbocationic polymerizations currently in use.

Our most sincere thanks to Dr. P. Borzel, Professor T. Higashimura, Dr. I. Puskas, and Dr. W. A. Vredenburgh, and co-workers for letting us have

material prior to publication, and to Professor P. Sigwalt and Dr. T. Kelen for useful criticisms. Special thanks is due to Mrs. M. Israel for heroism during her most competent typing of our battle-scarred manuscript.

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November 1981

□ Contents □

1 WHY CARBOCATIONIC POLYMERIZATION? 1

1.1 Advantages and Uses of Carbocationic Polymerization, 2

1.2 Problems, Challenges, and the Future, 5

References, 8

2 DEFINITIONS, TERMINOLOGY, AND NOMENCLATURE 9

2.1 Carbocations, Counteranions, and Carbocationic Polymerizations, 10

2.2 Initiators, Coinitiators, and Initiating Systems, 10

2.3 Abbreviation of Multicomponent Systems, 13

2.4 A Note on the Definition of Friedel-Crafts Halides, 13

References, 14

3 PHENOMENOLOGY OF CARBOCATIONIC POLYMERIZATION 15

3.1 The Active Species, 16

The Nature of Polymerization-Active Carbocations, 16

Formation of Carbocations, 16

Relative Stability of Carbocations, 17

Structure Effects Influencing Carbocation Stability, 19

Carbocation Stability in Solution, 21

The Active Species in Carbocationic Polymerizations, 23

Ions and Ion Pairs, 23

Carbocations and Active Species in Propagation, 24

Pseudocationic Polymerizations, 26

Types of Electrophilic Reactions in Carbocationic Polymerizations, 29

3.2 Monomers, 31

Electronic Characteristics of Cationic Monomers, 31

Steric Prohibition of Vinyl Cationic Polymerization, 33

Monomers Containing More than One Nucleophilic Site capable of Polymerization, 36

Cationic Monomers, 36

3.3 Initiators, Coinitiators, and Initiating Systems, 36

Protic or Brønsted Acids, 56

Stable Cation Salts, 58

Friedel-Crafts Acid-Based Initiating Systems, 59

The Problem of Defining Friedel-Crafts Acids, 59

Acidity of Friedel-Crafts Acids and Nucleophilicity of Counteranions, 64

Reactivity of Friedel-Crafts Acid-Based Initiating Systems, 71

3.4 Solvents, 72

References, 75

4 THE CHEMISTRY OF CARBOCATIONIC POLYMERIZATION 81

4.1 The Chemistry of Initiation, 82

Definitions and Scope, 82

Chemical Methods, 82

Two-Electron (Heteroclytic) Transpositions, 83

Brønsted (Protic) Acids, 84

Stable Carbenium Ion Salts, 90

Friedel-Crafts Acids, 95

Introduction □ Cationogen/Friedel-Crafts Acid Systems □ Cationogen = Brønsted Acids □ Stopping Experiments □ A General Scheme of Initiation with Brønsted □ Acid/Friedel-Crafts Acid Systems □ Scope and Limitation of Brønsted Acid □ Friedel-Crafts Acid Initiating Systems □ Cationogen = Carbenium Ion Source □ Initiation Details with RX/MeX_n Systems □ Preparative Significance of RX/MeX_n

Systems □ Cationogen = Halogen □ Cationogen = Miscellaneous Compounds BF_3OR_2 Complexes □ Direct Initiation by Friedel-Crafts Acids □ Halometalation: The Sigwalt-Olah Theory □ Autoionization: The Korshak-Plesch-Marek Theory □ Allylic Self-Initiation: The Kennedy Theory □ Conclusions Relative to Direct Initiation

Miscellaneous Methods, 116

Inorganic Complexes □ Iodine □ Miscellaneous Systems Including Acidic Solids

One-Electron (Homolytic) Transpositions, 120

Introduction, 120

Direct Radical Oxidation, 121

Charge Transfer Polymerizations, 122

Thermally Induced Charge Transfer Polymerization □ Photoinduced Charge Transfer Polymerization

Conclusions: Initiation by One-Electron Transpositions, 135

Physical Methods, 137

High-Energy or Ionizing Radiation, 138

X-ray Initiated Carbocationic Polymerization, 138

Pulse Radiolysis, 140

UV Radiation, 140

Direct Techniques Including Ion Injection, 140

Indirect Techniques, 141

High Electric Fields: Field Emission and Field Ionization, 142

Electroinitiation, 144

Significant Contributions, 144

Conclusions on Electroinitiated Carbocationic Polymerizations, 147

Conclusions: Initiation by Physical Methods, 148

Conclusions: Toward a Comprehensive View of Initiation in Carbocationic Polymerization, 152

Organization and Classes of Initiating Systems, 153

A Simplified View of Initiation, 156

4.2 The Chemistry of Propagation, 158

Overview, 158

Ionicity of the Propagating Species, 159

Effect of Electron Acceptors on Propagation, 163

Isomerization Polymerization, 165

Isomerizations by Bond (Electron) Rearrangement, 166

Intra-Intermolecular Polymerization, 166

Transannular Polymerization, 167

Polymerization by Strain Relief and Ring Opening, 168

Isomerization by Material Transport, 169

Controversial Ill-Supported Claims in the Field of Isomerization Polymerizations, 178

Stereochemistry of Propagation, 180

Vinyl Ethers, 180

Influence of Monomer Geometry on Stereochemistry, 180

Effect of the Nature and Concentration of Coinitiator and Solvent on Stereochemistry, 181

Effect of Temperature on Stereochemistry, 184

The Penultimate Effect, 185

Stereoselective Polymerization of Racemic Monomer Mixture, 186

α-Methylstyrene, 187

Stereochemical Mechanism of Propagation, 188

4.3 The Chemistry of Chain Transfer, 192

Introduction and Terminology, 192

Chain Transfer Reactions, 194

Chain Transfer by Counteranion, 194

Chain Transfer by Unshared Electron Pair, 202

Chain Transfer by π Electron Systems, 206

Chain Transfer by Olefin, 206

Chain Transfer by Aromatic Group, 209

Chain Transfer by Hydride Transfer, 211

Conclusions, 213

4.4 The Chemistry of Termination, 216

Introduction, 216

Termination Reactions, 218

Termination by Neutralization, 218
Neutralization by Reversal of Ionization (Macroester Formation), 218
Neutralization with the Formation of Two Species, 220
Alkylations and Arylations of Growing Cation (Z = Organic Group) □ Hydridation of Growing Cation (Z = H) □ Halogenation of Growing Cation (Z = Cl, Br)
Termination Involving Stable Cation Formation, 227
Quenching, 232
Conclusions, 233
References, 239

5 KINETICS OF CARBOCATIONIC POLYMERIZATION 255

5.1 Introduction, 256
5.2 Validity of the Steady State Assumption in Carbocationic Polymerizations, 257
5.3 Determination for Rates and Rate Constants, 262
Difficulties Relative to k_p Determination, 262
Kinetic Studies of Representative Systems, 265
Polymerization of α-Methylstyrene Coinitiated by n-BuOTiCl$_3$, 265
Polymerization of Isobutyl Vinyl Ether Initiated by Trityl Salts, 267
Determination of k_{trM}: Polymerization of p-Methoxystyrene Initiated by Trityl Salt, 269
Polymerization of Isobutyl Vinyl Ether Initiated by X-Rays, 270
5.4 The Effect of Solvent and Temperature on Rates, Rate Constants, and Activation Parameters, 273
Rates and Rate Constants, 273
Activation Parameters, 277
5.5 Rate Constant Ratios by Molecular Weight Determination, 282
5.6 The Effect of Temperature on Molecular Weight, 284

5.7 Molecular Weight Distributions, 289

5.8 Conclusions: Compilation and Analysis of Reliable Kinetic Data, 292

References, 301

6 COPOLYMERIZATION AND REACTIVITY 305

6.1 Introduction, 306

6.2 Definitions and Fundamentals, 306

6.3 Determination of Reactivity Ratios, 307

Differential Methods, 308

Integral Method, 309

Discussion of Reactivity Ratio Determination Methods, 309

The Kelen-Tüdős Method, 310

A Comprehensive Compilation of Reactivity Ratios, 312

6.4 Penultimate Effect, 332

6.5 Prediction of Ionic Copolymerization Reactivity Ratios, 334

6.6 Sequence Distribution Analysis, 336

6.7 Experimental Study of Reactivity, 338

Use of Rate Constants, 338

Use of Reactivity Ratios, 338

Reactivity by ^{13}C-NMR, 339

6.8 Theoretical Study of Reactivity, 341

Methods and Their Evolution, 341

Huckel's Method. A Criticism, 341

Pople's Method, 342

Use of Calculations, 342

Reactivities of Vinyl Ethers and β-Substituted Vinyl Ethers. Comparison with Unsaturated Hydrocarbons, 345

Q, e Scheme in Cationic Polymerization, 347

6.9 Effect of Experimental Conditions cf Reactivity, 349

The Effect of Temperature, 349

The Effect of the Nature of Solvent, 357

The Effect of the Nature of Coinitiator and Counteranion, 362

The Effect of Additives, 366

Quantum Study of the Effects of Solvent and Coinitiator on Reactivity, 368

The Effect of Electric Field on Reactivity, 374

6.10 Influence of Structural Factors on Reactivity, 374

Influence of Electronic Factors, 374

Hammett's Postulate and Reactivity, 375

Influence of Steric Factors, 377

6.11 An Application of Reactivity Analysis: Azeotropic Copolymerization, 380

6.12 Molecular Weight Depression in Copolymerization, 381

References, 386

7 STEP-GROWTH POLYMERIZATION 395

7.1 Introduction, 396

7.2 Reaction Mechanism, 398

Substrate and Positional Selectivity, 399

Steric and Substituent Effects, 399

7.3 Polybenzyls, 401

References, 406

8 SEQUENTIAL (BLOCK AND GRAFT) COPOLYMERS 409

8.1 Introduction, 410

8.2 A Note on Terminology, 410

8.3 Block Copolymers, 412

Synthesis of Block Copolymers, 412

A Summary of Block Copolymers, 419

8.4 Graft Copolymers, 422

Generalities, 422

Synthesis Principles and Graft Characteristics, 423

Bigraft Copolymers, 432

Surface Grafting, 434

An Efficient Grafting Onto: The Synthesis of Poly(Butadiene-g-Styrene), 434

Graft Blocks, 436

Graft by Macromers, 437

Conclusions, 438

References, 440

9 MACROMOLECULAR ENGINEERING BY CARBOCATIONIC POLYMERIZATION 443

9.1 A Glance at the Past, 444

9.2 Elements of Cationic Macromolecular Engineering, 446

Controlled Initiation, 446

Propagation, 448

Control of Chain Transfer, 449

The Inifer Method, 449

Proton Traps, 452

Quasi-Living Polymerization, 453

Controlled Termination, 456

9.3 Combination of Elements and Summary, 458

References, 462

10 INDUSTRIAL PROCESSES, TECHNOLOGICAL ASPECTS 465

10.1 Introduction, 466

10.2 Isobutylene-Based Carbocationic Polymerizations, 467

Low Molecular Weight Polyisobutylenes, 468

Polybutenes, 469

Manufacture, 469
Molecular Weight Control of Polybutenes, 473
Structure, Properties, and Uses, 474

Polyisobutylenes, 475
Manufacture, 476
Structure, 478
Properties and Uses, 478

Medium and High Molecular Weight Polyisobutylenes, 479

Manufacture, 479

Structure, Properties, and Uses, 480

Isobutylene Copolymers, Terpolymers, and Derivatives, 481
Butyl Rubber, 481
Manufacture, 481
Structure, Properties, and Uses, 482
Liquid Butyl: Manufacture, Properties, and Uses, 484
Isobutylene-Isoprene-Divinylbenzene Terpolymers, 484
Halogenated Butyl Rubbers, 485

Miscellaneous Polyisobutylene Derivatives, 486
Carboxy-Terminated Polyisobutylene, 486
Hydroxy-Terminated Polyisobutylene, 486
Conjugated Diene Butyl, 487
S-Polymer, 487
Isobutylene-Cyclopentadiene Copolymers, 487
Butyl Latex, 488

10.3 Hydrocarbon Resins, 488

Petroleum Resins: Feeds, Manufacture, Varieties, 488

Properties and Uses, 490

Polyterpene Resins, 491

β-Pinene Resins, 492

Dipentene Resins, 494

α-Pinene Resins, 496

Resin Characteristics, 496

Production, 497

Applications, 498

β-Piene Resins, 498
Dipentene Resins, 498
α-Piene Resins, 498
Terpene-phenolic Resins, 498

10.4 Polybutadiene Oils, 499

10.5 Vinyl Ether-Based Industrial Polymerization Processes and Products, 499

References, 501

INDEX 505

1
Why Carbocationic Polymerization?

1.1 Advantages and Uses of Carbocationic Polymerization 2
1.2 Problems, Challenges, and the Future 5
References 8

Why should one be interested in carbocationic polymerizations? Justification for the writing of this book lies in answering this question satisfactorily.

1.1 □ ADVANTAGES AND USES OF CARBOCATIONIC POLYMERIZATION

Cationic polymerization comprises an important body of techniques for the synthesis of a great variety of *useful* polymers; it provides a unique route to many high, medium, and low molecular weight materials with unique structures exhibiting a unique combination of properties; and last but not least it is a vigorously growing segment of polymer science which occupies many researchers, whose steady flow of discoveries bespeaks an intellectually challenging, indeed underexplored field and assures the long-range health of the discipline. A closer look at some of these points is rewarding.

Cationic polymerization is a useful branch of science that contributes greatly to the wealth, safety, and comfort of mankind. Many hundreds of people all over the world are gainfully employed by industries practicing cationic polymerizations, and if those who are involved in occupations only indirectly related to these industries, such as tire makers, who work with halobutyl rubber inner liners and compounders, who use pinene resins in pressure-sensitive tapes, are included, this number would probably be closer to many thousands.

Cationic polymerizations have two main roots in industry: technologies based on carbocationic polymerizations and those based on cationic heterocyclic ring-opening polymerizations. The latter fall outside the scope of this book, which focuses only on carbocationic or carbenium ion polymerization processes.

No doubt the largest carbocation-based polymerization industry by volume and monetary value to date is butyl rubber and halogenated (chlorinated and brominated) butyl rubber manufacture. Butyl rubber is a general-purpose elastomer obtained by copolymerizing isobutylene and a conjugated diene (isoprene); the halobutyls are specialty rubbers obtained by halogenating butyl rubber. These materials are used in a variety of applications in the tire, automotive, building, and construction industries.

Carbocation polymer industries of more modest scope include petroleum and indene–coumarone resin manufacture, polymerization of β-pinene, α-pinene, and mixed terpenes, and limited quantities of styrene and α-methylstyrene polymerization by acid initiators. In this class belong also "polybutenes" and "polyisobutenes" used, for example, as oils, viscosity index improvers, and additives, and low molecular weight (liquid) polybutadienes used in specialty coatings. Similarly, certain vinyl ethers are cationically polymerized and employed in adhesive formulations, pressure-sensitive tapes, blending agents, and additives.