

# □ Contents □

1	WHY CARBOCATIONIC POLYMERIZATION?	
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 <i>Polymerization-Active</i> Carbocations, 16	
	<b>Formation of Carbocations, 16</b>	
	<b>Relative Stability of Carbocations, 17</b>	
	<b>Structure Effects Influencing Carbocation Stability, 19</b>	
	<b>Carbocation Stability in Solution, 21</b>	
	The Active Species in Carbocationic Polymerizations, 23	
	<b>Ions and Ion Pairs, 23</b>	
	<b>Carbocations and Active Species in Propagation, 24</b>	
	<b>Pseudocationic Polymerizations, 26</b>	
	Types of <i>Electrophilic</i> 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<sub>n</sub>** Systems □ Preparative Significance of **RX/MeX<sub>n</sub>**

*Systems* □ *Cationogen = Halogen* □ *Cationogen = Miscellaneous Compounds*  $\text{BF}_3\text{OR}_2$  *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 Ili-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**
- $\alpha$ -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  $\pi$  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, <b>218</b>	
Neutralization by Reversal of Ionization (Macroester Formation), 218	
Neutralization with the Formation of Two Species, <b>220</b>	
<b>Alkylations</b> and Arylations of Growing Cation ( $Z = \text{Organic Group}$ ) □ Hydrization of Growing Cation ( $Z = \text{H}$ ) □ Halogenation of Growing Cation ( $Z = \text{Cl, Br}$ )	
Termination Involving Stable Cation Formation, <b>227</b>	
Quenching, <b>232</b>	
Conclusions, <b>233</b>	
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, <b>262</b>	
Kinetic Studies of Representative Systems, <b>265</b>	
Polymerization of $\alpha$ -Methylstyrene Coinitiated by <i>n</i> -BuOTiCl <sub>3</sub> , <b>265</b>	
Polymerization of Isobutyl Vinyl Ether Initiated by Trityl Salts, <b>267</b>	
Determination of $k_{tr,M}$ : Polymerization of <i>p</i> -Methoxystyrene Initiated by Trityl Salt, <b>269</b>	
Polymerization of Isobutyl Vinyl Ether Initiated by X-Rays, <b>270</b>	
5.4 The Effect of Solvent and Temperature on Rates, Rate Constants, and Activation Parameters, 273	
Rates and Rate Constants, <b>273</b>	
Activation Parameters, <b>277</b>	
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, <b>308</b>	
	Integral Method, <b>309</b>	
	Discussion of Reactivity Ratio Determination Methods, <b>309</b>	
	The <i>Kelen-Tüdös</i> Method, <b>310</b>	
	A Comprehensive Compilation of Reactivity Ratios, <b>312</b>	
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, <b>338</b>	
	Use of Reactivity Ratios, <b>338</b>	
	Reactivity by <sup>13</sup> C-NMR, <b>339</b>	
6.8	Theoretical Study of Reactivity, 341	
	Methods and Their Evolution, <b>341</b>	
	<b>Huckel's Method. A Criticism, 341</b>	
	<b>Pople's Method, 342</b>	
	Use of Calculations, <b>342</b>	
	Reactivities of Vinyl Ethers and $\beta$ -Substituted Vinyl Ethers. Comparison with Unsaturated Hydrocarbons, <b>345</b>	
	Q, e Scheme in <i>Cationic</i> Polymerization, <b>347</b>	

6.9	Effect of Experimental Conditions of Reactivity, 349	
	The Effect of Temperature, <b>349</b>	
	The Effect of the Nature of Solvent, <b>357</b>	
	The Effect of the Nature of Coinitiator and Counteranion, <b>362</b>	
	The Effect of Additives, <b>366</b>	
	Quantum Study of the Effects of Solvent and Coinitiator on Reactivity, <b>368</b>	
	The Effect of Electric Field on Reactivity, <b>374</b>	
6.10	Influence of Structural Factors on Reactivity, 374	
	Influence of Electronic Factors, 374	
	Hammett's Postulate and Reactivity, <b>375</b>	
	Influence of Steric Factors. <b>377</b>	
6.11	An Application of Reactivity Analysis: Azeotropic Copolymerization, 380	
6.12	Molecular Weight Depression in Copolymerization, 381	
	References, 386	
<b>7</b>	<b>STEP-GROWTH POLYMERIZATION</b>	<b>395</b>
7.1	Introduction, 396	
7.2	Reaction Mechanism, 398	
	Substrate and Positional Selectivity, <b>399</b>	
	Steric and Substituent Effects, <b>399</b>	
7.3	Polybenzyls, 401	
	References, 406	
<b>8</b>	<b>SEQUENTIAL (BLOCK AND GRAFT) COPOLYMERS</b>	<b>409</b>
8.1	Introduction, 410	
8.2	A Note on Terminology, 410	

8.3	Block Copolymers, 412	
	Synthesis of Block Copolymers, <b>412</b>	
	A Summary of Block Copolymers, <b>419</b>	
8.4	Graft Copolymers, 422	
	Generalities, <b>422</b>	
	Synthesis Principles and Graft Characteristics, <b>423</b>	
	<b>Bigraft</b> Copolymers, <b>432</b>	
	Surface Grafting, <b>434</b>	
	An Efficient Grafting Onto: The Synthesis of Poly( <i>But</i> adiene- <i>g</i> -Styrene), <b>434</b>	
	Graft Blocks, <b>436</b>	
	Graft by Macromers, <b>437</b>	
	Conclusions, <b>438</b>	
	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, <b>446</b>	
	Propagation, <b>448</b>	
	Control of Chain Transfer, <b>449</b>	
	<b>The Inifer Method</b> , <b>449</b>	
	<b>Proton Traps</b> , <b>452</b>	
	<b>Quasi-Living Polymerization</b> , <b>453</b>	
	Controlled Termination, <b>456</b>	
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* **$\beta$ -Pinene** Resins, **492**Dipentene Resins, **494** **$\alpha$ -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**