

□ 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	
	<i>The Nature of Polymerization-Active Carbocations, 16</i>	
	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	
	<i>Types of Electrophilic Reactions in Carbocationic Polymerizations, 29</i>	

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

($Z = \text{Organic Group}$) □ *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
 $n\text{-BuOTiCl}_3$, 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	
	<i>Differential Methods, 308</i>	
	<i>Integral Method, 309</i>	
	<i>Discussion of Reactivity Ratio Determination Methods, 309</i>	
	<i>The Kelen-Tüdös Method, 310</i>	
	<i>A Comprehensive Compilation of Reactivity Ratios, 312</i>	
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	
	<i>Use of Rate Constants, 338</i>	
	<i>Use of Reactivity Ratios, 338</i>	
	<i>Reactivity by ^{13}C-NMR, 339</i>	
6.8	Theoretical Study of Reactivity, 341	
	<i>Methods and Their Evolution, 341</i>	
	Huckel's Method. A Criticism, 341	
	Pople's Method, 342	
	<i>Use of Calculations, 342</i>	
	<i>Reactivities of Vinyl Ethers and β-Substituted Vinyl Ethers. Comparison with Unsaturated Hydrocarbons, 345</i>	
	<i>Q, e Scheme in Cationic Polymerization, 347</i>	

6.9	Effect of Experimental Conditions of Reactivity, 349	
	<i>The Effect of Temperature, 349</i>	
	<i>The Effect of the Nature of Solvent, 357</i>	
	<i>The Effect of the Nature of Coinitiator and Counteranion, 362</i>	
	<i>The Effect of Additives, 366</i>	
	<i>Quantum Study of the Effects of Solvent and Coinitiator on Reactivity, 368</i>	
	<i>The Effect of Electric Field on Reactivity, 374</i>	
6.10	Influence of Structural Factors on Reactivity, 374	
	<i>Influence of Electronic Factors, 374</i>	
	<i>Hammett's Postulate and Reactivity, 375</i>	
	<i>Influence of Steric Factors, 377</i>	
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	
	<i>Substrate and Positional Selectivity, 399</i>	
	<i>Steric and Substituent Effects, 399</i>	
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	
	<i>Synthesis of Block Copolymers, 412</i>	
	<i>A Summary of Block Copolymers, 419</i>	
8.4	Graft Copolymers, 422	
	<i>Generalities, 422</i>	
	<i>Synthesis Principles and Graft Characteristics, 423</i>	
	<i>Bigraft Copolymers, 432</i>	
	<i>Surface Grafting, 434</i>	
	<i>An Efficient Grafting Onto: The Synthesis of Poly(Butadiene-g-Styrene), 434</i>	
	<i>Graft Blocks, 436</i>	
	<i>Graft by Macromers, 437</i>	
	<i>Conclusions, 438</i>	
	<i>References, 440</i>	
9	MACROMOLECULAR ENGINEERING BY CARBOCATIONIC POLYMERIZATION	443
9.1	A Glance at the Past, 444	
9.2	Elements of Cationic Macromolecular Engineering, 446	
	<i>Controlled Initiation, 446</i>	
	<i>Propagation, 448</i>	
	<i>Control of Chain Transfer, 449</i>	
	The Inifer Method, 449	
	Proton Traps, 452	
	Quasi-Living Polymerization, 453	
	<i>Controlled Termination, 456</i>	
9.3	Combination of Elements and Summary, 458	
	<i>References, 462</i>	
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