

Contents

Part I Three-Dimensional Free-Radical Polymerization. Cross-Linked Polymers

1	Microheterogeneous Mechanism of Three-Dimensional Free-Radical Polymerization	3
1.1	Microheterogeneous Model of Polymerization Process	4
1.2	Polymerization Process: Stages of Formation of the Microheterogeneous Structure for Cross-Linked Polymers	5
1.2.1	Formation of Polymer Grains at the Initial Stage of Polymerization	5
1.2.2	Growth of Polymer Grains During Polymerization	7
1.2.3	Accretion of Polymer Grains at the Final Stages of Polymerization	12
1.3	Structural and Physical Processes Taking Place During Three-Dimensional Free-Radical Polymerization	17
1.3.1	Microsyneresis of Liquid Components in Reaction Medium	17
1.3.2	Microredistribution of Substances Dissolved in Liquid Components	20
1.3.3	Local Glass Transition of Highly Cross-Linked Micro-Volumes of Polymer	23
1.4	Microheterogeneous Structure of Cross-Linked Polymers	25
1.4.1	Interlayers Between Polymer Grains	27
1.4.2	Polymer Grains	30
	References	31
2	Kinetic Features of Three-Dimensional Free-Radical Polymerization .	33
2.1	Kinetic Features of Individual Stages of Polymerization	34
2.1.1	Initial Stage of Polymerization	34
2.1.2	Stages of Auto-Acceleration and Auto-Deceleration	41
2.2	Inhibited Polymerization	46
2.3	Polymerization in Solutions	51
2.4	Polymerization in Films Under the Conditions of Oxygen Diffusion	54

2.4.1	Vinyl Compounds	55
2.4.2	Allyl Compounds	66
2.5	Three-Dimensional Free-Radical Polymerization as a Tool for Macromolecular Design of Cross-Linked Polymers	75
	References	78
3	Living Chain Three-Dimensional Radical Polymerization	81
3.1	Living Chains in Free-Radical Polymerization	82
3.2	Implementation of Living Chains Conditions in Three- Dimensional Free-Radical Polymerization	86
3.2.1	Copolymerization of Styrene with Dimethacrylates in the Presence of Alkoxyamines	87
3.2.2	Polymerization of Tri(Ethylene Glycol) Dimethacrylate (tEGdMA) in the Presence of Complex CuBr_2 with Tetramethyl-Tiuramdisulfide	93
3.2.3	Polymerization of Dimethacrylates of Poly(Ethylene Glycol)s in the Presence of Complex CuBr with Organic Ligands	97
3.3	Living Chain Three-Dimensional Free-Radical Polymerization as a Tool for Macromolecular Design of Cross-Linked Polymers	99
	References	109
4	Kinetic Features of Three-Dimensional Free-Radical Copolymerization	111
4.1	Kinetic Features of Three-Dimensional Copolymerization of Oligomer and Vinyl Monomers	111
4.2	Variation of Copolymer Composition During Three-Dimensional Free-Radical Copolymerization of Oligomers and Vinyl Monomer	118
	References	127
5	Critical Conversion (Gel Point) in Three-Dimensional Free-Radical Polymerization	129
5.1	Inapplicability of Known Critical Conversion Calculation Methods to Three-Dimensional Free-Radical Polymerization	131
5.2	Novel Approach to Calculating Critical Conversion in Three- Dimensional Free-Radical Polymerization	133
5.3	Results of Critical Conversion Calculation for Different Cases of Three-Dimensional Free-Radical Polymerization	136
5.3.1	Living Chains Three-Dimensional Polymerization and Copolymerization (Without Chain Termination)	136
5.3.2	Three-Dimensional Polymerization and Copolymerization with Quadratic or Linear Chain Termination	143
5.3.3	Three-Dimensional Polymerization with "Pendent" Double Bonds Taken into Account (Chain Termination by Disproportionation)	145

5.3.4	Summary of Results of Theoretical Calculations for Critical Conversion	150
5.4	Comparison of Results of Theoretical Calculations for Critical Conversion with Experimental Data	152
5.4.1	Inhibited Polymerization of Dimethacrylates	152
5.4.2	Copolymerization of Divinyl Benzene (<i>m</i> -DVB) with Styrene	154
	References	155
6	Properties of Cross-Linked Polymers and Copolymers	157
6.1	Cross-Linked Poly(acrylates). Physical and Mechanical Properties	157
6.1.1	Influence of Chemical Structure of Oligomers upon Physical and Mechanical Properties of Cross-Linked Poly(acrylates)	158
6.1.2	Influence of Physical Network Density upon Physical and Mechanical Properties of Cross-Linked Poly(acrylates)	166
6.2	Cross-Linked Copolymers. Physical and Mechanical Properties	172
6.2.1	Mechanism of Copolymers Transition into Forced-Elastic State	172
6.2.2	Influence of Cyclization on Physical and Mechanical Properties of Copolymers	181
6.3	Cross-Linked Copolymers. Thermo-Mechanical Properties	185
6.3.1	Mechanism of Copolymers Transition into High-Elastic State	185
6.3.2	Comparison of Transitions into High-Elastic State with those into Forced-Elastic State	193
6.4	Diffusion-Sorption Properties of Copolymers	195
	References	199

Part II Three-Dimensional Free-Radical Polymerization. Hyper-Branched Polymers

7	Synthesis of Hyper-Branched Polymers	203
7.1	Classification of Reactions for Hyper-Branched Polymer Synthesis	203
7.2	Synthesis of Hyper-Branched Polymers Via Three-Dimensional Free-Radical (Co)polymerization with Regulation of Polymer Chain Length	205
7.2.1	Regulation of Chain Length Through Initiation Rate Variation	206
7.2.2	Regulation of Chain Length by Chain Transfer Agents and Chain Transfer Catalysts	211
7.2.3	Regulation of Chain Length Through the Use of Intrachain Reactions of Chain Carrier Radicals	226
7.2.4	Regulation of Chain Length Through the Use of Molecular Oxygen as an Inhibitor	230

7.3	Synthesis of Hyper-Branched Polymers Via Living Chains	
	Free-Radical Three-Dimensional Polymerization	231
7.3.1	Living Chains Free-Radical Three-Dimensional Polymerization as Reaction for Hyper-Branched Polymers Synthesis	231
7.3.2	Living Chains Polymerization of Vinyl Monomers with Diethyldithiocarbamate Groups	233
	References	239
8	Properties and Application of Hyper-Branched Polymers	243
8.1	“Structure–Property” Relationship and Purposeful Generation of Hyper-Branched Polymer Properties That Are in Demand in Practice	244
8.2	Hyper-Branched Polymers as Modifiers of Polymeric Materials	248
8.3	Major Fields for Hyper-Branched Polymers Application	250
8.4	HBP: Main Achievements and Problems to Be Solved Without Delay	253
	References	254
9	Methods for Studying Three-Dimensional Free-Radical Polymerization and Cross-Linked Polymers	257
9.1	Calorimetry	257
9.2	IR Spectroscopy	258
9.3	Other Methods of Kinetic Measurements	259
9.4	Light Scattering	260
9.5	EPR	260
9.5.1	Studying the Kinetics of Free-Radical Accumulation in Nonstationary Mode	260
9.5.2	Studying the Kinetics of Decay of Accumulated Free Radicals	261
9.5.3	Method of Synchronous Comparison of Continuously Recorded Kinetic Curves $[R^\bullet] = f_1(t)$ and $W = f_2(t)$	262
9.5.4	Structural and Physical Studies Using EPR	262
9.6	NMR	263
9.7	Physicomechanical and Thermo-Mechanical Methods	263
9.8	Volumetric Method	264
9.9	Complex Methods	264
	References	265
	Index	267