CONTENTS

Acknowledgements i
Preface iii

CHAPTER 1. ROLE OF PHOTOACTIVE MONOMERS AND POLYMERIC INITIATORS IN LIGHT INDUCED POLYMERIZATION REACTIONS: A BRIEF REVIEW.

1.1. Introduction 1
1.2. Photoinitiators for Free Radical Initiated Polymerization 2
1.3. Sulfur-Containing Photoinitiators 5
1.4. Polymeric Free Radical Photoinitiators 8
1.4.1. Polymers containing pendant photoinitiator groups. Photoinduced Graft copolymer Synthesis 8
1.4.1.1. Type I polymeric photoinitiators 9
1.4.1.2. Polymeric photoinitiators containing pendant iniferter groups 11
1.4.1.3. Polymers containing pendant type II initiators. Photografting by H-abstraction mechanism 14
1.4.1.4. Use of organometallic complexes in photoinduced graft copolymerization 16
1.4.2. Light Induced Synthesis of Block Copolymers 17
1.4.2.1. Block copolymerization using polymers carrying photolabile groups in the main chain 18
1.4.2.2. Polymeric photoinitiators having photolabile groups at chain ends 25
CHAPTER 2. SYNTHESIS, CHARACTERIZATION AND COPOLYMERIZATION BEHAVIOUR OF A FEW XANTHATE DERIVED PHOTOACTIVE MONOMERS

2.1. Introduction 36
2.2. Results and Discussion 38
2.2.1. Preparation of monomers 38
2.2.2. Copolymerization of MAX with MMA and styrene (St) 45
2.2.3. Copolymerization of MBX with MMA and St 52
2.2.4. Thermal copolymerization behaviour of VBX with MMA and St 57
2.2.5. Determination of reactivity ratios 64
2.2.6. Q-e values 65
2.2.7. Influence of the structure and reactivity of monomers on the molecular weights and polydispersities of copolymers 67
2.2.8. Thermogravimetric studies 72
2.3. Conclusions 75
2.4. Experimental section 75
2.4.1. Synthesis of S-methacryloyl O-ethyl xanthate (MAX) (7) 76
2.4.2. Synthesis of 4-maleimidobenzoic acid (11) 77
2.4.3. Synthesis of 4-maleimidobenzoyl chloride (12) 77
2.4.4. Synthesis of S-(4-maleimido)benzoyl O-ethyl xanthate (MBX) (13) 77
2.4.5. Synthesis of (4-bromomethyl)benzoic acid (15) 78
2.4.6. Synthesis of (4-carboxy)benzyl triphenylphosphonium bromide (16) 78
2.4.7. Synthesis of 4-vinylbenzoic acid (17) 78
2.4.8. Synthesis of 4-vinylbenzoyl chloride (18) 79
2.4.9. Synthesis of S-(p-vinyl)benzoyl O-ethyl xanthate (VBX) (19) 79
2.4.10. Thermal copolymerization. General procedure 80
2.5. References 81

CHAPTER 3. ROLE OF XANTHATE DERIVED MONOMERIC INITIATORS IN CONTROLLING THE PHOTOPOLYMERIZATION PROCESSES OF METHYL METHACRYLATE AND STYRENE

3.1. Introduction 83
3.2. Results and Discussion 89
3.2.1. Photopolymerization of MMA and styrene using MAX 89
3.2.2. Photopolymerization of MMA and styrene using MBX 100
3.2.3. Photopolymerization of MMA and styrene using VBX 107
3.3. Experimental Section 113
3.3.1. Photopolymerization: General procedure 114
3.3.1.1. Photopolymerization of MMA using MAX as photoinitiator 114
3.3.1.2. Photopolymerization of styrene (bulk) using MAX as photoinitiator 115
3.3.1.3. Photopolymerization of styrene (bulk) under higher MAX concentration 115
3.3.1.4. Photopolymerization of styrene using MAX in benzene 115
3.3.1.5. Photopolymerization of MMA using MBX 116
3.3.1.6. Photopolymerization of styrene (bulk) using MBX 116
3.3.1.7. Photopolymerization of styrene (bulk) under low MBX concentration 116
3.3.1.8. Photopolymerization of styrene using MBX in benzene 117
3.3.1.9. Photopolymerization of MMA using VBX 117
3.3.1.10. Photopolymerization of styrene (bulk) using VBX 117

3.4. References 119

CHAPTER 4. PHOTOINDUCED GRAFT AND BLOCK COPOLYMER SYNTHESIS USING MACROINITIATORS CONTAINING XANTHATE CHROMOPHORES

4.1. Introduction 122
4.2. Results and Discussion 125
4.2.1. Photoinitiated grafting of MMA and styrene using macroinitiators containing pendant xanthate chromophores 125
4.2.2. Photografting of MMA using a heterogeneous photoinitiator containing xanthate chromophore 142
4.2.3. Photoinduced block copolymerization using macrophotoinitiators end-capped with xanthate moieties 145
4.2.4. Conclusions 148
4.3. Experimental 150
4.3.1. Preparation of S-benzoyl O-PHEMA xanthate resin 13 150

4.3.2. Photografting of MMA using MAX-co-St 151

4.3.3. Photografting of St using MAX-co-MMA 151

4.3.4. Photografting of MMA using S-benzoyl O-PHEMA xanthate resin 13 152

4.3.5. Block copolymerization of MA using the macroinitiator 16 152

4.4. References 153