

Table of Contents

1 Abstract	1
2 Introduction	2
2.1 PEGs Application in Biomedicine.....	3
2.1.1 Surface Modification	3
2.1.2 Drug Delivery	4
2.1.3 Tissue Engineering.....	5
2.2 Towards Multifunctional PEGs	8
2.2.1 Bifunctional PEGs	8
2.2.2 Branched PEGs	14
2.2.3 Multifunctional PEGs	17
4.1 Anionic Ring-Opening Polymerization of EO and Its Derivatives.....	25
4.1.1 Overview.....	25
4.1.2 EO Polymerization.....	27
4.1.3 Synthesis of α,ω -Heterottelechelic PEGs.....	30
4.1.4 Synthesis of Homomultifunctional PEGs	35
4.1.4.1 Synthesis of Functional Epoxides	35
4.1.4.2 Polymerization of Functional Epoxides	38
4.1.5 Synthesis of Block Copolymers	56
4.1.6 Post-Polymerization Cleavage of Protecting Groups in Multifunctional PEGs	59
4.2 Biomedical applications of Functional Epoxides and Multifunctional PEGs... 	61
4.2.1 Surface Modification with Functional Epoxides	61
4.2.1.1 Overview	61
4.2.1.2 Surface Modification with Reactive Epoxide for Copper-Free Click Chemistry.....	62

4.2.2	Reactive Hydrogels Based on Multifunctional Photosensitive Protected Aldehyde PEG	67
4.2.2.1	Overview	67
4.2.2.2	Synthesis of an Epoxide with PPA Group	69
4.2.2.3	Synthesis of Multifunctional PPAPEG	70
4.2.2.4	Photoinduced Cleavage of Aldehyde Protecting Group	72
4.2.2.5	Synthesis of Water Soluble PPAPEG- <i>b</i> -PEG- <i>b</i> -PPAPEG.....	75
4.2.2.6	Synthesis of Multifunctional Hydrazide PEG	80
4.2.2.7	Hydrogels Fabrication	82
4.2.3	Multifunctional Hydrazide PEG and Sugar Reactive Particles	83
4.2.3.1	Overview	83
4.2.3.2	Synthesis of Water Insoluble Multifunctional P(HZ- <i>co</i> -BnGE).....	86
4.2.3.3	Fabrication and Modification of P(HZ- <i>co</i> -BnGE) Microparticles.....	90
4.2.4	Multifunctional <i>o</i> -Nitrobenzyl PEG and Photodegradable Particles	93
4.2.4.1	Overview	93
4.2.4.2	Synthesis of Multifunctional NBPEG	96
4.2.4.3	Oxidation of Thioether into Sulfoxide Groups in NBPEG	99
4.2.4.4	Photocleavage of NB Protection	100
4.2.4.5	Fabrication and Degradation of NBPEG/ONBPEG Microparticles	103
4.2.4.6	Cellular Uptake of ONBPEG Particles	108
5	Summary and Perspectives.....	111
5.1	Polymerization of EO and Functional Epoxides	111
5.2	Biomedical Applications of Multifunctional PEGs	112
5.3	Perspectives for the Future Development and Applications of Multifunctional PEGs.....	114
6	Experimental Section	116
6.1	Materials and Methods	116
6.1.1	Reagents and Solvents	116
6.1.2	Preparative Procedure	116
6.1.3	Product Purification	117

6.1.4	Characterization	117
6.2	Synthesis and Characterization of Small Molecular Weight Compounds.....	122
6.2.1	Initiating Functional Alcohols	122
6.2.2	Functional Epoxides.....	123
6.2.3	Other Small Molecular Weight Compounds.....	133
6.3	Synthesis and Characterization of Polymers	135
6.3.1	General Procedures	135
6.3.2	α,ω -Heterottelechelic PEGs	136
6.3.3	Homomultifunctional PEGs.....	137
6.3.4	Copolymers	143
6.4	Surface Modification.....	150
6.4.1	Immobilization of Epoxide	150
6.4.2	Immobilization of Alexa Fluor 555	150
6.4.3	Immobilization of Biotine-Azide.....	150
6.4.4	Conjugation of RB-Streptavidin	150
6.5	Photo Induced Reactions on a Surface.....	151
6.5.1	Cleavage of Acetal Protecting Groups in PPAPEG.....	151
6.5.2	Cleavage of NB Protecting Groups in ONBPEG.....	151
6.6	Photo Induced Reactions in Solution.....	152
6.6.1	Cleavage of Photosensitive Acetal Protection Combined with <i>in situ</i> Reaction with Hydrazide.....	152
6.6.2	Cleavage of NB Protecting Groups in ONBPEG.....	153
6.7	Fabrication and Modification of Microparticles	154
6.7.1	General Procedures	154
6.7.2	Fabrication and Modification of PLGA/P(HZ- <i>co</i> -BnGE) Microparticles.....	155
6.7.3	Fabrication and Modification of PLGA/NBPEG and PLGA/ONBPEG Microparticles	156

7	List of Abbreviations.....	158
8	References	163
9	Appendices	187
9.1	List of Publications.....	187
9.2	Curriculum Vitae	189
9.3	Acknowledgements.....	190