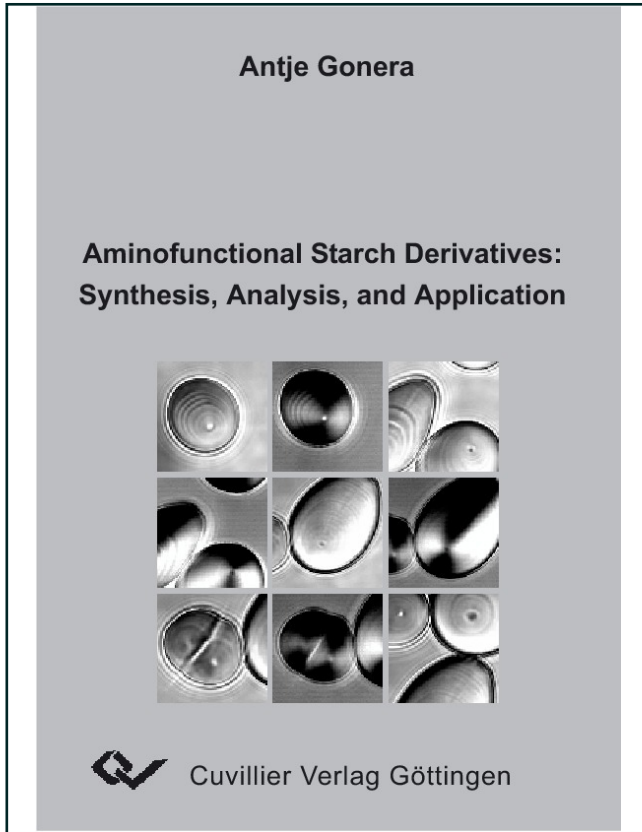




Antje Gonera (Autor)
**Aminofunctional Starch Derivatives: Synthesis,
Analysis, and Application**



<https://cuvillier.de/de/shop/publications/2817>

Copyright:
Cuvillier Verlag, Inhaberin Annette Jentsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen,
Germany
Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

TABLE OF CONTENTS

1	INTRODUCTION	1
1.1	Starch	1
1.1.1	The granular and molecular structure of starch	2
1.1.2	Application	5
1.1.3	Derivatives	5
1.2	Aminomodification of polysaccharides	9
1.3	Analytical Aspects ^[43]	10
2	SCOPE OF THE THESIS	12
3	SYNTHESIS OF O-AMINOPROPYL STARCH AND AMYLOSE	14
3.1	Approaches to synthesize amino modified glucans	14
3.1.1	Direct alkylation	14
3.1.2	Introduction of nitrogen via reactive intermediates	15
3.1.3	Introduction in a higher oxidation state with subsequent reduction	18
3.1.4	Introduction of a functional group and further modification	21
3.1.5	Using <i>N</i> -protected reagents with subsequent deprotection	23
3.2	Strategy	25
3.3	<i>Michael</i> addition of acrylonitrile and subsequent reduction	26
3.3.1	Model studies with methyl glucoside	27
3.3.2	Cyanoethylation of starch	32
3.3.3	Comparative studies with amylose	40
3.3.4	Reduction of the cyano group to the primary amine	42
3.4	<i>Williamson</i> etherification with <i>N</i>-(3-bromopropyl)phthalimide and subsequent deprotection	48
3.4.1	Preliminary studies with methyl glucoside and potato starch	50
3.4.2	Reaction of amylose in aqueous NaOH	53
3.4.3	Reaction of amylose in DMSO with NaOH as base	55
3.4.4	Reaction of amylose in DMSO with Li-dimsyl as base	56
3.4.5	Deprotection to the primary amine	66
3.4.6	Upscale to gram-scale	73

4	FURTHER STUDIES ON THE CE-, PP-, AND AP-DERIVATIVES	75
4.1	Investigation on the substituent distribution along the polymer chain after enzymatic degradation	75
4.2	Differential scanning calorimetry	83
5	APPLICATION	85
5.1	Paper additive	85
5.2	Immobilization on surfaces	86
5.3	Implant surface coating	89
5.3.1	Binding of APA to poly(vinylidene fluoride) surfaces	90
5.3.2	X-ray photoelectron spectroscopy	91
5.3.3	Contact angle determination	92
5.3.4	Investigation of protein adsorption on biomaterial surfaces using Surface-MALDI-TOF-MS	93
5.4	Stabilization of horseradish peroxidase	95
5.4.1	Addition of <i>O</i> -aminopropylamylose	96
5.4.2	Cross-linking with <i>O</i> -aminopropylamylose	98
6	SUMMARY	107
7	ZUSAMMENFASSUNG	111
8	PERSPECTIVES	115
9	MATERIALS AND METHODS	116
9.1	Substances	116
9.2	Thin layer chromatography	116
9.3	Silylation of glassware	116
9.4	Gas chromatography	117
9.5	Gas chromatography-Mass spectrometry (GC-MS)	119
9.6	ESI-MS	119
9.7	Nuclear magnetic resonance spectroscopy (NMR)	120
9.8	Elemental analysis	120
9.9	Differential scanning calorimetry	121
9.10	IR spectroscopy	121
9.11	Synthesis of <i>O</i> -cyanoethyl derivatives	121
9.11.1	Synthesis of methyl <i>O</i> -cyanoethyl glucosides	121
9.11.2	Synthesis of <i>O</i> -cyanoethyl starch	122

9.11.3	Synthesis of <i>O</i> -cyanoethyl amylose	122
9.12	Reduction of <i>O</i>-cyanoethyl starch to <i>O</i>-aminopropyl starch	122
9.13	Williamson etherification with <i>N</i>-(3-bromopropyl)phthalimide	123
9.13.1	Preparation with NaOH in water or DMSO	123
9.13.2	Preparation with Li-dimsyl in DMSO	123
9.14	Deprotection of <i>O</i>-(<i>N</i>-phthalimido)propyl amylose to <i>O</i>-aminopropyl amylose	124
9.15	Enzymatic degradation	124
9.16	Immobilization of APA on microtiterplate surfaces	125
9.17	Stabilization of POD with APA via addition and cross-linking	126
9.17.1	POD assay	126
9.17.2	APA-addition	127
9.17.3	POD oxidation and cross-linking (optimized conditions)	127
9.18	Paper additive (sheet forming trial)	127
9.19	Implant surface coating	128
10	APPENDIX	129
10.1	General	129
10.1.1	ECR-factors and molar masses of compounds	129
10.1.2	Diagnostic <i>m/z</i> values of fragments obtained from EI-MS analysis ^[99-103]	131
10.1.3	EI-MS spectra	133
10.1.4	Characteristic <i>m/z</i> values of pseudomolecular ions formed by ESI-MS	145
10.1.5	ESI mass spectra after enzymatic and after partial acid hydrolysis	148
10.1.6	¹ H NMR characteristic shifts	150
10.1.7	IR spectra	151
10.2	<i>O</i>-Cyanoethyl-substituted derivatives	154
10.2.1	<i>O</i> -Cyanoethyl methyl glucoside	154
10.2.2	<i>O</i> -Cyanoethyl starch	158
10.2.3	<i>O</i> -Cyanoethyl amylose	158
10.3	<i>O</i>-(<i>N</i>-Phthalimido)propyl-substituted derivatives	160
10.4	<i>O</i>-Aminopropyl-substituted derivatives	164
10.5	Calibration curves	165
11	ABBREVIATIONS	167
12	REFERENCES	170