

BestMasters

Inga Lilge

Polymer Brush Films with Varied Grafting and Cross-Linking Density via SI-ATRP

Analysis of the Mechanical
Properties by AFM



Springer Spektrum

BestMasters

Springer awards „BestMasters“ to the best master’s theses which have been completed at renowned Universities in Germany, Austria, and Switzerland.

The studies received highest marks and were recommended for publication by supervisors. They address current issues from various fields of research in natural sciences, psychology, technology, and economics.

The series addresses practitioners as well as scientists and, in particular, offers guidance for early stage researchers.

More information about this series at <http://www.springer.com/series/13198>

Inga Lilge

Polymer Brush Films with Varied Grafting and Cross-Linking Density via SI-ATRP

Analysis of the Mechanical
Properties by AFM



Springer Spektrum

Inga Lilge
Siegen, Germany



BestMasters

ISBN 978-3-658-19594-6

ISBN 978-3-658-19595-3 (eBook)

<https://doi.org/10.1007/978-3-658-19595-3>

Library of Congress Control Number: 2017952937

Springer Spektrum

© Springer Fachmedien Wiesbaden GmbH 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer Spektrum imprint is published by Springer Nature

The registered company is Springer Fachmedien Wiesbaden GmbH

The registered company address is: Abraham-Lincoln-Str. 46, 65189 Wiesbaden, Germany

Acknowledgements

I would like to express my gratitude to all those who helped me out to finish this thesis.

First, I would like to thank Prof. Dr. Holger Schönherr for his constant support, guidance and help. I am especially thankful for the help of Dr. Davide Tranchida and his useful comments on the AFM experiments.

Moreover, I like to express my sincere thanks to all members of the Physical Chemistry I, for their valuable suggestions and kindness during all days of my thesis. Especially, I would like to thank my colleagues for their valuable help for the experiments, endless discussions during coffee breaks and the presence on long days in the syntheses laboratory. At the same time, I express my sincere appreciation to Dipl. Ing. Gregor Schulte for the helpful discussions, the construction of the UV-LED setup and the fabrication of numerous gold substrates. And also to Dr. Lars Birlenbach for encouraging conversations to retry the fabrication of PAAm polymer brushes via PMP.

I give my warmest thanks to my parents for their constant support, motivation and encouragement especially during the last 8 months.

List of Content

List of Figures.....	9
List of Tables.....	15
Abstract	19
1 Motivation	21
2 Introduction to Polymer Brushes.....	27
2.1 Surface Initiated Polymerization (SIP)	28
2.1.1 Photoiniferter-mediated Polymerization (PMP)	28
2.1.2 Atom Transfer Radical Polymerization (ATRP).....	29
2.2 Self-Assembled Monolayer (SAM)	31
2.3 SAMs by Micro-Contact Printing (μ -CP)	32
2.4 Variation of Polymer Brushes.....	35
2.4.1 Grafting Density	35
2.4.2 Cross-linking Density.....	36
3 Characterization Methods	37
3.1 Contact Angle (CA) Measurements.....	37
3.2 Fourier Transform Infrared (FTIR) Spectroscopy	39
3.3 Atomic Force Microscopy (AFM)	39
4 Experimental Part	43
4.1 Materials.....	43
4.1.1 Initiator.....	43
4.1.2 Polymers.....	44
4.2 Preparation.....	45
4.2.1 Preparation of Gold Substrates.....	45
4.2.2 SAMs.....	47
4.2.3 Micro-Contact Printing (μ -CP)	47
4.2.4 Preparation of Polymer Brushes.....	48

4.3	Characterization	49
4.3.1	Contact Angle (CA) Measurements	49
4.3.2	Ellipsometry.....	50
4.3.3	Fourier Transform Infrared (FTIR) Spectroscopy	50
4.3.4	Atomic Force Microscope (AFM)	51
5	Results and Discussion	53
5.1	Polymer Brushes	53
5.1.1	Polymerization Kinetics	53
5.1.2	Grafting Density	60
5.1.3	Cross-linking Density.....	68
5.2	Polymer Brush Analysis by AFM.....	72
5.2.1	Surface Morphology.....	74
5.2.2	Thickness	81
5.2.3	Wettability	84
5.2.4	Mechanical Properties.....	87
6	Discussion, Conclusions and Outlook.....	99
7	References	103
8	Appendix	107
8.1	PAAm Brushes via PMP	107
8.1.1	Iniferter.....	107
8.1.2	Modification of Silicon Substrates with Iniferter.....	110
8.1.3	Construction of the UV-LED setup	112
8.1.4	Preparation of Polymer Brushes	113
8.2	PAAm Brushes via ATRP.....	115

List of Figures

Figure 1.1: Wet thickness of PAAm brushes as a function of the grafting density	23
Figure 1.2: Growth kinetics of PAAm brushes and covalently cross-linked hydrogel brushes	24
Figure 2.1: Schematic representation of a) polymer brushes and b) the “grafting to” and “grafting from” approach	27
Figure 2.2: Mechanism of the photoiniferter-mediated polymerization	29
Figure 2.3: Mechanism of the atom transfer radical polymerization	30
Figure 2.4: Schematic illustration of the stamp preparation for μ -contact printing by photolithography	33
Figure 2.5: Schematic illustration of the actual μ -contact printing	33
Figure 2.6: Model of the varied grafting density of polymer brushes	35
Figure 3.1: Equilibrium contact angle with the assigned notations of the Young’s equation	37
Figure 3.2: Scheme of a) an atomic force microscope and b) Scheme of a typical cantilever deflection vs. piezo position curve.	40
Figure 4.1: Molecular structure of the thiol molecules a) MUBiB, b) ODT, c) MHDA	44
Figure 4.2: Molecular structure of the monomer a) AAm and b) bisAAm	44
Figure 4.3: Schematic illustration of the preparation of template-stripped gold	46
Figure 4.4: Schematic illustration of the stripping of a Si-Au-epoxy glue-glass “sandwich”	46
Figure 4.5: Scheme of the monolayer formation of the initiator on a gold substrate.....	47
Figure 4.6: Scheme of the ATRP with AAm	49
Figure 5.1: Schematic representation of the polymer brush growth.....	53
Figure 5.2: Dependence of the water contact angles on the polymerization time of PAAm	54
Figure 5.3: Thickness of PAAm as a function of polymerization time characterized by ellipsometry.....	54
Figure 5.4: Comparison of the polymerization kinetic determined by Liu et al. with my results.....	55
Figure 5.5: Comparison of polymer brushes in a wet and dry state with the results determined by Liu et al.....	55
Figure 5.6: Reflection mode FTIR spectra of PAAm brushes on gold.....	56
Figure 5.7: ATR-FTIR spectra of PAAm purchased from Aldrich compared to reflection mode FTIR spectra of PAAm brushes	57

Figure 5.8: Reflection mode FTIR spectra of PAAm brushes with different thicknesses due to the variation of the polymerization time.....	58
Figure 5.9: Linear relationship between the peak areas of the C=O vibrations and the polymer layer thickness	59
Figure 5.10: Schematic representation of the polymer brush growth on mixed SAMs	60
Figure 5.11: Contact angle of a) a pure MHDA SAM and b) a pure MUBiB SAM.....	60
Figure 5.12: Comparison of the contact angles with the fraction of MUBiB in the solution.....	61
Figure 5.13: Comparison of the fraction of MUBiB in solution with the fraction of MUBiB on the surface	62
Figure 5.14: Reflection mode FTIR spectra of mixed SAMs prepared with different fractions of initiator in solution	62
Figure 5.15: Thickness of PAAm as a function of the initiator content in solution during SAM formation; characterized by ellipsometry brushes with varied grafting density	63
Figure 5.16: Reflection mode FTIR spectra of PAAm brushes with different thicknesses due to the content of initiator (MUBiB) in solution during SAM formation.....	64
Figure 5.17: Linear relationship between the peak areas of the C=O vibrations and the polymer layer thickness	65
Figure 5.18: Comparison of the thicknesses [nm] of PAAm on mixed SAMs with MHDA with the fraction of MUBiB on the surface	65
Figure 5.19: Influence of initiator density on the water contact angle.....	67
Figure 5.20: Schematic representation of the polymerization with a cross-linking moiety	68
Figure 5.21: Thickness of PAAm as a function of cross-linking content in solution characterized by ellipsometry	68
Figure 5.22: Reflection mode FTIR spectra of PAAm brushes with different thicknesses due to the fraction of cross-linker in solution.....	69
Figure 5.23: Linear relationship between the peak areas of the C=O vibrations and the polymer layer thickness	70
Figure 5.24: Influence of cross-linking density on the water contact angle of the polymer brush layer	70
Figure 5.25: Schematic representation of the polymerization of patterned gold substrate.....	72
Figure 5.26: Reflection mode FTIR spectra of polymerized ODT monolayers pure & with overnight treatment in a MUBiB solution	73

Figure 5.27: Light microscope images of the PDMS stamp a) overview of the stamp and b) more detailed image recorded with polarized light	74
Figure 5.28: Schematic of the PDMS stamp with estimations of the dimensions out of SEM measurements	74
Figure 5.29: TM-AFM height image of PAAm brushes to demonstrate the roughness analysis	75
Figure 5.30: Roughness of PAAm brushes compared to the ODT monolayer as a function of the polymerization time; characterized by AFM	75
Figure 5.31: Roughness of PAAm brushes compared to the ODT monolayer as a function of the initiator content in solution during SAM formation; characterized by AFM	76
Figure 5.32: TM-AFM height images of representative surface morphologies recorded for PAAm brushes polymerized on sputtered gold with SAMs composed of a) 40%, b) 60% and c) 100% initiator in solution during self-assembly	76
Figure 5.33: Roughness of PAAm brushes compared with the contact angle as a function of the initiator content in solution during SAM formation	77
Figure 5.34: Roughness of PAAm brushes compared to the ODT monolayer as a function of the cross-linker content in solution during polymerization; characterized by AFM	77
Figure 5.35: Roughness of PAAm brushes compared with the contact angle as a function of the cross-linker content in solution	78
Figure 5.36: TM-AFM height images of representative surface morphologies recorded for a) sputtered gold, b) silicon and c) template-stripped gold	78
Figure 5.37: Micrographs to the corresponding TM-AFM height images of a) sputtered gold, b) silicon and c) template-stripped gold	79
Figure 5.38: Roughness of PAAm brushes grown from sputtered and template-stripped gold as a function of the cross-linker content in solution during polymerization	80
Figure 5.39: TM-AFM height images of representative surface morphologies recorded for a) 100% bisAAm, b) 5% bisAAm, c) 2.5% bisAAm and d) 0% bisAAm brushes	80
Figure 5.40: TM-AFM images of PAAm brushes a) 3D height image and b) corresponding phase image in a different color scale	81
Figure 5.41: Section analysis by NanoScope 5.3 of PAAm brushes	81
Figure 5.42: Step height analysis by NanoScope 5.3 of PAAm brushes	82