

TKK Dissertations 242
Espoo 2010

**SYNTHESIS OF AMPHIPHILIC POLYMERS AND
THEIR APPLICATION AS NANOSCALE SURFACE
WETTABILITY MODIFIERS**

Doctoral Dissertation

Leena Nurmi



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Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Chemistry and Materials Sciences for public examination and debate in Auditorium KE2 (Komppa Auditorium) at the Aalto University School of Science and Technology (Espoo, Finland) on the 5th of November 2010 at 12 noon.

**Aalto University
School of Science and Technology
Faculty of Chemistry and Materials Sciences
Department of Biotechnology and Chemical Technology**

**Aalto-yliopisto
Teknillinen korkeakoulu
Kemian ja materiaalitieteiden tiedekunta
Biotekniikan ja kemian tekniikan laitos**

Distribution:

Aalto University
School of Science and Technology
Faculty of Chemistry and Materials Sciences
Department of Biotechnology and Chemical Technology
P.O. Box 16100 (Kemistintie 1)
FI - 00076 Aalto
FINLAND
URL: <http://chemtech.tkk.fi/>
Tel. +358-9-470 22616
E-mail: leena.nurmi@tkk.fi

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ISBN 978-952-60-3397-6
ISBN 978-952-60-3398-3 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)
URL: <http://lib.tkk.fi/Diss/2010/isbn9789526033983/>

TKK-DISS-2811

Aalto-Print
Helsinki 2010

ABSTRACT OF DOCTORAL DISSERTATION		AALTO UNIVERSITY SCHOOL OF SCIENCE AND TECHNOLOGY P.O. BOX 11000, FI-00076 AALTO http://www.aalto.fi	
Author Leena Nurmi			
Name of the dissertation Synthesis of amphiphilic polymers and their application as nanoscale surface wettability modifiers			
Manuscript submitted 7.6.2010		Manuscript revised	
Date of the defence 5.11.2010			
<input type="checkbox"/> Monograph		<input checked="" type="checkbox"/> Article dissertation (summary + original articles)	
Faculty	Chemistry and Materials Sciences		
Department	Biotechnology and Chemical Technology		
Field of research	Polymer Technology		
Opponent(s)	Professor Søren Hvilsted		
Supervisor	Professor Jukka Seppälä		
Instructor	Professor Jukka Seppälä		
<p>Abstract</p> <p>Amphiphilic polyelectrolytes with statistical or block copolymer structure were synthesized by atom transfer radical polymerization (ATRP). The copolymers contained 2-(dimethylamino) ethyl methacrylate (DMAEMA) or [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) as a hydrophilic monomer unit and methyl methacrylate (MMA), butyl methacrylate (BMA) or 2,2,2-trifluoroethyl methacrylate (TFEMA) as a hydrophobic monomer unit.</p> <p>Solution properties of the synthesized copolymers were studied in aqueous medium. The obtained solution conformations and structures were studied at varying conditions with e.g. dynamic light scattering, ¹H NMR and ¹⁹F NMR spectroscopy and surface tension measurements. The obtained conformations ranged from extended to collapsed and the obtained solution structures ranged from unimers to kinetically trapped nanoparticles.</p> <p>The copolymers were adsorbed or spin-coated on hydrophilic substrates from aqueous medium as ultra-thin layers. The effect of the thin polymer layer on surface wettability was studied by contact angle measurements. The surface structures were studied with atomic force microscopy and were found to correlate with the wetting properties. The effect of e.g. surface preparation process and annealing at elevated temperatures was studied. A range of wettability levels were obtained, with advancing contact angles up to 100° on inherently flat surfaces (mica) and up to 160° on inherently rough surfaces (cellulose fiber substrate). The level of contact angle hysteresis varied.</p> <p>In addition, carbohydrate based polymers were studied for their potential in a similar wettability modification. The studied polymers were starch graft copolymers prepared by ATRP and glycopolymers with e.g. cellobiose side chains, prepared by a combination of catalytic chain transfer polymerization and Cu(I)-catalyzed azide-alkyne cycloaddition.</p>			
Keywords amphiphilic polymer, polyelectrolyte, ATRP, ultra-thin film, wetting			
ISBN (printed) 978-952-60-3397-6		ISSN (printed) 1795-2239	
ISBN (pdf) 978-952-60-3398-3		ISSN (pdf) 1795-4584	
Language English		Number of pages 61 + 77 (app.)	
Publisher Aalto University, Department of Biotechnology and Chemical Technology			
Print distribution Aalto University, Department of Biotechnology and Chemical Technology			
<input checked="" type="checkbox"/> The dissertation can be read at http://lib.tkk.fi/Diss/2010/isbn9789526033983/			

VÄITÖSKIRJAN TIIVISTELMÄ		AALTO-YLIOPISTO TEKNILLINEN KORKEAKOULU PL 11000, 00076 AALTO http://www.aalto.fi	
Tekijä Leena Nurmi			
Väitöskirjan nimi Amfiifiilisten kopolymerien synteesi ja käyttö nanomittakaavassa pinnan kastuvuuden muokkaajina			
Käsikirjoituksen päivämäärä 7.6.2010		Korjatun käsikirjoituksen päivämäärä	
Väitöstilaisuuden ajankohta 5.11.2010			
<input type="checkbox"/> Monografia		<input checked="" type="checkbox"/> Yhdistelmäväitöskirja (yhteenveto + erillisartikkelit)	
Tiedekunta	Kemian ja materiaalitieteiden tiedekunta		
Laitos	Biotekniikan ja kemian tekniikan laitos		
Tutkimusala	Polymeeriteknologia		
Vastaväittäjä(t)	Professori Søren Hvilsted		
Työn valvoja	Professori Jukka Seppälä		
Työn ohjaaja	Professori Jukka Seppälä		
<p>Tiivistelmä</p> <p>Työssä syntetisoitiin amfiifiilisiä polyelektrolyyttejä käyttäen ”atom transfer radical polymerization” (ATRP) -menetelmää. Polyelektrolyytit olivat rakenteeltaan lohko- ja statistisia kopolymeerejä. Kopolymerien hydrofiilisiä monomeeriyksiköinä käytettiin joko 2-(dimetyyliamino)etyylimetakrylaattia (DMAEMA) tai [2-(metakryloksi)etyyli] trimetyyliammoniumjodidia (METAI), ja hydrofobisina monomeeriyksiköinä joko metyylimetakrylaattia (MMA), butyylimetakrylaattia (BMA) tai 2,2,2-trifluoroetyylimetakrylaattia (TFEMA).</p> <p>Syntetisoitujen kopolymerien konformaatiota ja rakenteita vesiliuoksissa tutkittiin vaihtelevissa olosuhteissa mm. dynaamisella valonsironnalla, ¹H NMR ja ¹⁹F NMR spektroskopialla ja pintajännitysmittauksilla. Polymeerikonformaatiot liuoksissa vaihtelivat ojentuneesta luhistuneeseen ja liuosrakenteet unimeerisistä polymeeriketjuista nanopartikkeleihin.</p> <p>Kopolymeereistä muodostettiin ohuita, nanomittakaavan kerroksia hydrofiilisille pinoille. Kerrokset valmistettiin polymeerien vesiliuoksista käyttäen joko adsorptiota tai ”spin-coating” -menetelmää. Polymeerikerrosten rakennetta tutkittiin atomivoimamikroskopialla ja niiden vaikutusta pinnan kastuvuuteen tutkittiin kontaktikulmamittauksilla. Kerrosten rakenteiden ja niiden kastuvuuden huomattiin olevan yhteydessä toisiinsa. Pintatutkimuksessa tarkasteltiin esimerkiksi polymeerikerrosten valmistusprosessin ja lämpökäsittelyn vaikutuksia. Pintojen kastuvuus vaihteli laajasti. Polymeerikerrosten etenevät kontaktikulmat olivat maksimissaan 100° sileillä alustoilla (mica) ja maksimissaan 160° karheilla alustoilla (selluloosakuitupinta). Kontaktikulman hystereesin suuruus vaihteli.</p> <p>Lisäksi tutkittiin hiilihydraattipohjaisten polymeerien potentiaalia samankaltaisessa pinnan kastuvuuden muokkauksessa. Tutkitut polymeerit olivat ATRP-menetelmällä syntetisoituja tärkkelyksen oksaskopolymeerejä ja sellobioosiyksiköitä sivuryhminä sisältäviä polymeerejä, jotka oli syntetisoitu katalyyttistä ketjunsiiirtopolymeroitua ja Cu(I) katalysoitua atsidi-alkyyni sykloadditiota käyttäen.</p>			
Asiasanat amfiifiilinen kopolymeri, polyelektrolyytti, ATRP, ohutkalvo, kastuvuus			
ISBN (painettu)	978-952-60-3397-6	ISSN (painettu)	1795-2239
ISBN (pdf)	978-952-60-3398-3	ISSN (pdf)	1795-4584
Kieli	englanti	Sivumäärä	61 + 77 (liitteet)
Julkaisija Aalto-yliopisto, Biotekniikan ja Kemian tekniikan laitos			
Painetun väitöskirjan jakelu Aalto-yliopisto, Biotekniikan ja Kemian tekniikan laitos			
<input checked="" type="checkbox"/> Luettavissa verkossa osoitteessa http://lib.tkk.fi/Diss/2010/isbn9789526033983/			

PREFACE

This work was carried out in the Department of Biotechnology and Chemical Technology at Aalto University between October 2004 and June 2010. Parts of the work were conducted at the University of Warwick, UK, and at the University of Queensland, Australia. Financial support from TEKES (the Finnish Funding Agency for Technology and Innovation), the Graduate School in Chemical Engineering, and Helsinki University of Technology is gratefully acknowledged.

I would like to express my gratitude to my supervisor, professor Jukka Seppälä, for providing me with an interesting topic, and for the trust and support throughout my post-graduate studies. I am also grateful to professors David Haddleton and Andrew Whittaker for giving me the opportunity to work at their groups, and for their guidance and insights during my time abroad.

I would like to thank Dr. Barbro Löfgren, Dr. Susanna Holappa, Katri Kontturi, and all the people involved in the TEKES project TailorPap for fruitful co-operation. I am also grateful to Dr. Giuseppe Mantovani, Dr. Josefina Lindqvist, and Dr. Hui Peng for the instructive discussions during my stays abroad. I would like to express my gratitude to all the co-authors for their valuable contributions. I would also like to thank Dr. Ulla Hippinen for proof-reading the manuscript of the thesis, and for all the pieces of advice.

A special thanks goes to the Polymer Technology research group for providing a pleasant working atmosphere, and for all the memorable moments spent together within the lab and elsewhere. I would also like to thank the members of the research groups I visited in UK and Australia for the warm welcome I received.

Finally, I would like to extend my warmest thanks to my parents Ulla and Timo[†], family and friends for their company and encouragement throughout the years.

Espoo, September 2010

Leena Nurmi

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REFERENCES

LIST OF PUBLICATIONS

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.

- I Nurmi L., Holappa S., Mikkonen H., Seppälä J., Controlled grafting of acetylated starch by atom transfer radical polymerization of MMA, *European Polymer Journal*, 43 (2007) 1372-1382.
- II Nurmi L., Lindqvist J., Randev R., Syrett J., Haddleton D.M., Glycopolymers via catalytic chain transfer polymerisation (CCTP), Huisgens cycloaddition and thiol-ene double click reactions, *Chemical Communications*, 2009 2727-2729.
- III Nurmi L., Holappa S., Nykänen A., Laine J., Ruokolainen J., Seppälä J., Ultra-thin films of cationic amphiphilic poly(2-(dimethylamino)ethyl methacrylate) based block copolymers as surface wettability modifiers, *Polymer*, 50 (2009) 5250-5261.
- IV Nurmi L., Peng H., Seppälä J., Haddleton D.M., Blakey I., Whittaker A.K., Synthesis and evaluation of partly-fluorinated polyelectrolytes as components in ¹⁹F MRI-detectable nanoparticles, *Polymer Chemistry*, 1 (2010) 1039-1047.
- V Nurmi L., Kontturi K., Houbenov N., Laine J., Ruokolainen J., Seppälä J., Modification of surface wettability through adsorption of partly fluorinated statistical and block polyelectrolytes from aqueous medium, *Langmuir*, accepted.

The author's contribution to the appended publications

- I Leena Nurmi planned and carried out the experiments, excluding the dispersion and surface experiments, and wrote the manuscript with the assistance of the co-authors.
- II Leena Nurmi planned and carried out the cycloaddition and thiol-ene reactions, including the synthesis of the required reagents, and wrote the corresponding part of the manuscript.
- III Leena Nurmi planned and carried out the experiments, excluding the cryo-TEM experiments and a major part of the contact angle and AFM experiments, and wrote the manuscript with the assistance of the co-authors.
- IV, V Leena Nurmi, with the assistance of the co-authors, planned and carried out the experiments, and wrote the manuscript.

ABBREVIATIONS AND SYMBOLS

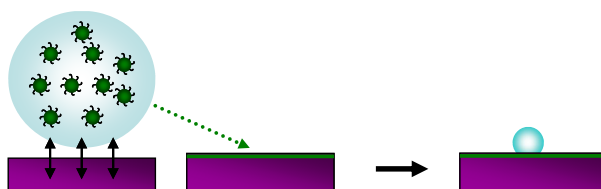
AFM	atomic force microscopy
AS	acetylated starch oligomer
ATRP	atom transfer radical polymerization
BMA	butyl methacrylate
CCTP	catalytic chain transfer polymerization
Cryo-TEM	cryogenic transmission electron microscopy
CuAAC	Cu(I)-catalyzed azide–alkyne cycloaddition
DLS	dynamic light scattering
D_H	hydrodynamic diameter
DMAEMA	2-(dimethylamino) ethyl methacrylate
DMSO	dimethyl sulfoxide
DRI	differential refractive index
DS	degree of substitution
DSC	differential scanning calorimetry
METAI	[2-(methacryloyloxy)ethyl] trimethyl ammonium iodide
MMA	methyl methacrylate
M_n	number average molecular weight
MRI	magnetic resonance imaging
NMR	nuclear magnetic resonance spectroscopy
PBMA	poly(butyl methacrylate)
PDI	polydispersity index
PDMAEMA	poly[2-(dimethylamino) ethyl methacrylate]
PMETAI	poly{[2-(methacryloyloxy)ethyl] trimethyl ammonium iodide}
PMMA	poly(methyl methacrylate)
PTFEMA	poly(2,2,2-trifluoroethyl methacrylate)
RSA	random sequential adsorption
SEC	size exclusion chromatography
SNR	signal-to-noise ratio
TFEMA	2,2,2-trifluoroethyl methacrylate
THF	tetrahydrofuran
T_1	spin-lattice relaxation time
T_2	spin-spin relaxation time
UV	ultraviolet

1 INTRODUCTION

1.1 Overview

Amphiphilic polymers are an interesting class of materials because of their ability to form self-assembled structures, e.g. in aqueous solutions and on various interfaces.¹⁻³ Copolymerization is a flexible way for their synthesis, as it allows a multitude of functionalities (both hydrophilic and hydrophobic) and architectures (e.g. statistical, block and graft copolymer) to be applied. Easily applicable methodologies for the synthesis of tailored polymer architectures by controlled radical polymerization have been developed during the past 15 years.⁴

Amphiphilic copolymers could potentially be utilized to modify the wetting properties of hydrophilic substrates, when applied as ultra-thin films from aqueous medium, as shown in Scheme 1. Only a very small amount of polymer is expected to be needed for the modification due to the nanoscale thickness of the layer. The hydrophilic moieties in the copolymer would ensure that the polymer can be dissolved or dispersed in water. In addition, it is advantageous if the hydrophilic groups form strong interactions with the substrate through electrostatic attraction or hydrogen bonding, so that the polymer can be easily attached on the substrate by adsorption.⁵ The hydrophobic moieties in the copolymer could subsequently be utilized to significantly modify the surface wetting properties, provided that during the modification process they finally end on the uppermost layer of the surface. All in all, the wetting properties of the modified surfaces can be expected to correlate with the surface chemistry, homogeneity, roughness and mobility of the obtained layers, as predicted by the current understanding on wetting phenomena.^{6, 7}



Scheme 1. Amphiphilic polymers are applied from aqueous medium to a hydrophilic substrate (left), forming an ultra-thin layer of nanoscale thickness (middle). The surface wettability has been modified by the polymer layer, as depicted by the water droplet placed on the surface (right).^V

The aqueous medium allows the modification procedure to be used in applications where such environment is necessary, e.g. in industrial processes utilizing native materials, such as papermaking.⁸ Only relatively hydrophilic polyelectrolytes are directly soluble in water, and therefore only a limited range of wettability levels are attainable with them. However, even quite hydrophobic polyelectrolytes can often be assembled to aqueous nanoparticles, for example through a solvent exchange process, allowing also their adsorption from aqueous medium.^{2, 9}

1.2 Scope of the thesis

The main targets of this thesis work were 1) to synthesize amphiphilic copolymers in a controlled manner 2) to study the properties of the synthesized copolymers in aqueous medium and 3) to apply the polymers on hydrophilic substrates as ultra-thin layers from aqueous medium, and to study the properties, especially wettability, of the obtained layers.

The polymer synthesis was studied in publications **I**, **II**, **III** and **IV**. The synthesized amphiphilic copolymers were designed to allow strong interactions with hydrophilic substrates through the hydrophilic moieties, either through electrostatic attraction (cationic groups in the polymer, aimed for anionic substrates) or hydrogen bonding (carbohydrate groups in the polymer, aimed for carbohydrate substrates). In publication **I**, graft copolymers with acetylated starch backbone and poly(methyl methacrylate) (PMMA) grafts were synthesized by atom transfer radical polymerization (ATRP). In

publication **II**, glycopolymers were synthesized. In publications **III** and **IV**, poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) based amphiphilic polyelectrolytes with statistical and block copolymer structure were synthesized. The polymers had either 2-(dimethylamino)ethyl methacrylate (DMAEMA) or its quaternized form [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) as a hydrophilic monomer and either methyl methacrylate (MMA), butyl methacrylate (BMA) or 2,2,2-trifluoroethyl methacrylate (TFEMA) as a hydrophobic monomer.

The aqueous solution properties of the synthesized PDMAEMA based amphiphilic polyelectrolytes were studied in publications **III**, **IV** and **V**. The solution structures in varying conditions were studied with dynamic light scattering, ^1H NMR spectroscopy, cryogenic transmission electron microscopy and surface tension measurements. In publication **IV**, the aqueous conformations of PDMAEMA-PTFEMA copolymers were studied by ^{19}F NMR measurements.

The ultra-thin layers of PDMAEMA based amphiphilic polyelectrolytes were studied in publications **III** and **V** on silica, mica and cellulose fiber substrates. The surface structures were studied with atomic force microscopy and the wetting properties were studied with contact angle measurements.

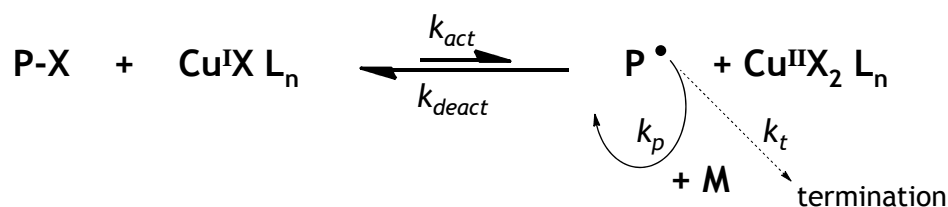
The aqueous and surface layer properties of starch graft copolymers are briefly discussed in publication **I**. The aqueous and surface layer properties of glycopolymers synthesized in publication **II** were not published, but they are briefly discussed in this thesis.

1.3 Review of the concepts

1.3.1 Synthesis of the polymers

Controlled radical polymerizations. Over the past 15 years, there has been a great deal of interest in the field of controlled ‘living’ radical polymerizations. These polymerizations allow the synthesis of polymers with low polydispersities, predictable molecular weights and tailored architectures. At the moment several techniques enabling controlled radical polymerizations exist, of which atom transfer radical polymerization (ATRP) is one of the most commonly applied.^{4, 10, 11}

The mechanism of ATRP is commonly presented as shown in Scheme 2, even though the subject remains controversial to some extent.^{12, 13} In ATRP, a catalyst system is utilized, that typically consists of a transition metal (e.g. Cu), a counter-ion X (e.g. Cl or Br) and one or several ligands (L). In the mechanism, as seen in Scheme 2, the growing polymer chains are present in dormant P-X state during majority of the polymerization, with –X groups at the chain ends. The catalyst/ligand complex can reversibly capture the –X group, leaving the polymer chain with a radical end group that can react with monomers by a traditional radical polymerization mechanism. In this capture step, the oxidation number of the transition metal catalyst is increased. However, as the reaction equilibrium in Scheme 2 is strongly shifted towards the dormant species, the active polymer chain end is soon returned to the dormant state. In the system, the undesired termination through combination of two active polymer chain ends is suppressed, as the active radicals mainly couple with the X groups from the catalyst.



Scheme 2. The ATRP mechanism, presented with copper catalyst.

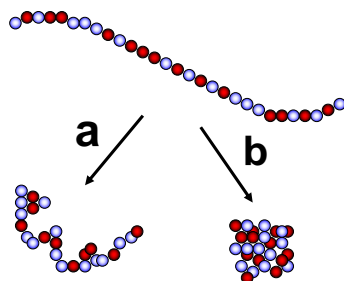
Many types of unsaturated monomers can be polymerized by ATRP, as the method is relatively tolerant towards different functionalities. However, the propagating radical group needs to be stabilized to some extent with suitable substituents. Methacrylates and acrylates are typical examples of monomers that can be polymerized successfully by ATRP. A range of methacrylates with various functionalities have been previously polymerized by ATRP, including the monomers that were applied in this thesis: methyl methacrylate (MMA),¹⁴⁻¹⁶ butyl methacrylate (BMA),¹⁷⁻¹⁹ 2-(dimethylamino)ethyl methacrylate (DMAEMA),^{17, 18, 20-24} and 2,2,2-trifluoroethyl methacrylate (TFEMA).²⁵⁻²⁷

Polysaccharide based graft copolymers were also synthesized in this thesis by ATRP. A ‘grafting-from’ method was applied, that involves the polymerization of grafts starting from initiator sites generated on the polysaccharide backbone. Polysaccharide grafting by ATRP has been studied by several groups.²⁸⁻³² The advantages of ATRP in graft copolymerizations, when compared to traditional ‘grafting-from’ radical polymerizations, include the ability to polymerize grafts with controlled density and length, and narrow molecular weight distribution. In addition, homopolymer impurities are not formed in the polymerization.³³ However, as the copolymer molecules contain a multitude of growing grafts during the polymerization, they are prone to intermolecular termination and therefore also to gelation.³³⁻³⁷

‘Click chemistry’. ‘Click chemistry’ is a concept with an objective to simplify synthesis work by highlighting reactions that are easy to carry out in varying chemical environments. The requirements for ‘click’ reactions include that the reaction is robust, selective (i.e. side reactions do not occur with common functional groups) and that it works at mild conditions. Therefore, ‘click’ reactions can be utilized to easily produce complex macromolecular structures, functional polymers and polymer conjugates.³⁸ The Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) has been the most widely studied and employed of the available ‘click’ reactions.³⁹⁻⁴¹ However, there are several reactions potentially fulfilling the ‘click’ requirements, including the thiol-ene chemistry.⁴²⁻⁴⁴

1.3.2 Aqueous solutions

Conformation of amphiphilic polymers in aqueous solutions. The conformation of dissolved amphiphilic polymer chains in aqueous medium can vary from collapsed globules to extended chains, depending on the interactions of the polymer with itself and the solvent. In the case of amphiphilic polyelectrolytes, the aqueous conformation is controlled on one hand by the long-range repulsive electrostatic interactions between charged groups and on the other hand by the short-range attractive hydrophobic interactions between hydrophobic groups (Scheme 3).^{1, 5, 45}



Scheme 3. The conformation of amphiphilic polyelectrolytes in aqueous solutions can vary from extended chains (a) to collapsed globules (b).

The balance between the repulsive and attractive interactions in amphiphilic polyelectrolytes in aqueous solutions is determined by various parameters, including the relative contents of charged and hydrophobic groups, polymer concentration, solution ionic strength and solution pH. The effects of these parameters on the solution conformation of amphiphilic polyelectrolytes have been widely studied theoretically^{46, 47} and experimentally.⁴⁸⁻⁵¹

Structures of amphiphilic block copolymers in aqueous solutions. In optically transparent aqueous solutions, amphiphilic block copolymers can be present as unimers, as equilibrium micelles, or as kinetically trapped nanoparticles.¹ Equilibrium micelles are characterized by dynamic equilibrium between aggregated polymer chains and unimers. Micellar solutions have a characteristic critical micelle concentration, below which the solution consists of only dissolved unimers.

If the interfacial tension between water and the hydrophobic block is high, the unimer-micelle equilibrium is not attainable. However, kinetically trapped nanoparticles can be assembled of such block copolymers with suitable dissolving methods, e.g. by solvent exchange from non-selective solvent. The sizes and shapes of trapped particles are dependent on the dissolving process.^{2, 9, 52} It has been shown that surface tensions observed in trapped systems are high due to the inability of the hydrophobic blocks to reach the surface of the solution, and that such systems behave like colloidal suspensions of charged solid particles.⁵³

1.3.3 *Ultra-thin layers*

Ultra-thin film is a layer of defined material with thickness in the nanometer scale. Polymeric ultra-thin layers can be prepared e.g. by adsorption,^{5, 54} spin-coating,^{55, 56} or casting⁵⁷ from polymeric solutions on various substrates.

In order to prepare polymeric ultra-thin films by adsorption, attractive interactions between the substrate and the polymer are needed. There have been several studies on the adsorption of polyelectrolyte films on surfaces of opposite charge from aqueous solutions through electrostatic attraction,⁵⁸⁻⁶² including the adsorption of amphiphilic polyelectrolytes.^{46, 63-67} The properties of the films have been studied both in contact with the polymer solution and after rinsing and drying. The effect of various adsorption parameters to the surface morphology and adsorbed amount have been studied, including solution pH, ionic strength, polyelectrolyte charge density and polymer concentration. A few studies have also briefly examined the wetting properties of the amphiphilic polyelectrolyte films.^{65, 67}

Also hydrogen bonding⁶⁸⁻⁷¹ and van der Waals^{72, 73} interactions have been utilized in the adsorption of ultra-thin polymer films from aqueous solutions. For example, cellobiose functionalized polymethacrylates⁷¹ and various hemicelluloses⁶⁹ have been shown to adsorb on cellulose substrates, probably due to the similarities in the molecular structures that can promote the formation of hydrogen bonds.

1.3.4 *Wetting*

Wetting is the process of making contact between a solid and a liquid. The wetting properties of a surface with regard to a certain liquid are commonly described with contact angle values. Contact angle is defined as the angle that forms at the three-phase contact line between a solid, liquid and fluid phase. A common system of interest is a droplet of water placed on a surface and surrounded by air. High contact angle between a surface and a water droplet indicates that the surface is hydrophobic.⁶

Apparent macroscopic contact angles on surfaces with topographically and chemically heterogeneous features, i.e., on almost all real surfaces, result from averaging over the various local contact angles that appear along the length of the droplet contact line. On such surfaces, there exists a multitude of allowed, metastable macroscopic contact angles, each representing a local energy minimum. These energy minima are obtained from the interplay between the local contact angles and the geometrical shape of the droplet. Therefore, if the contact angle is measured simply by placing a droplet on a surface, as in static contact angle measurement, a multitude of values may be obtained, depending on the method of drop application.^{6, 7, 74}

The highest and lowest obtainable macroscopic contact angles on a given surface with a given liquid are the advancing and receding contact angles, respectively. Their magnitudes depend on the details of the movement of the three-phase contact line, as it either advances or recedes over heterogeneous surface features. The difference between these angles is referred to as contact angle hysteresis.^{6, 7, 75-77} Measurement of advancing and receding contact angles allows a more accurate view on the surface wetting properties than the static measurement. On polymeric surfaces, not only the surface heterogeneity, but also the ability of the surface to reorganize when in contact with the measurement droplet has been shown to have an effect on the hysteresis range.^{78, 79}

2 EXPERIMENTAL

2.1 Polymer syntheses

Starch graft copolymers.^I Oligomeric acetylated starch derivative (AS) was provided by the VTT Technical Research Center of Finland, where it had been synthesized with a method described in patent literature.⁸⁰ AS was functionalized to ATRP macroinitiator with different amounts of 2-bromo isobutyryl bromide, in tetrahydrofuran (THF) solutions containing pyridine. The AS macroinitiator was applied in the polymerization of methyl methacrylate with CuBr/bipyridine catalyst system either in bulk or in 50 v/v-% THF solution at 70°C, under oxygen-free atmosphere. In some polymerizations, CuBr₂ was added to the reaction mixture.

Glycopolymers.^{II} Poly(propargyl methacrylate) was synthesized by catalytic chain transfer polymerization (CCTP), after which sugar azides were attached to the side-chains through Cu(I)-catalyzed azide-alkyne cycloaddition. Generally, trimethylsilyl-protected propargyl methacrylate⁴⁰, α -azido-D-mannose⁸¹ and β -azido-D-galactose⁸¹ were synthesized with methods described in the literature. The β -azido-D-cellobiose was synthesized by reacting D-cellobiose octaacetate with trimethylsilyl azide to obtain β -azido-D-cellobiose heptaacetate, which was further deprotected with sodium methoxide. The trimethylsilyl-protected propargyl methacrylate was polymerized by CCTP in toluene under nitrogen atmosphere with bis(boron difluorodimethylglyoximate) cobalt(II) catalyst at 60°C. The polymer was deprotected in THF solution containing acetic acid and tetra-*n*-butylammonium fluoride. The purified polymer was reacted with sugar azides in dimethyl sulfoxide (DMSO) solution containing triethylamine and CuBr/bipyridine catalyst at 60°C overnight.

In some cases the double-bond end-groups of poly(propargyl methacrylate) were functionalized through thiol-ene chemistry with various thiols (e.g. benzyl mercaptan) in acetone solution at ambient temperature overnight, with dimethylphenyl phosphine as a catalyst.

PDMAEMA-PMMA and PDMAEMA-PBMA copolymers.^{III} The copolymers were synthesized by ATRP. In the block copolymer synthesis PDMAEMA homopolymer was prepared first, by applying a catalyst/solvent system described by Mao et al.²² The polymerizations were conducted with CuCl/ 1,1,4,7,10,10-hexamethyltriethylenetetramine catalyst system and *p*-toluene sulfonyl chloride initiator, at 25°C, with water and methanol added to the reaction mixture. The hydrophobic second blocks were subsequently polymerized by using the purified PDMAEMA as a macroinitiator. The polymerizations of the second blocks were conducted with CuCl/bipyridine catalyst, at 90°C, with either anisole (for PMMA) or toluene (for PBMA) as a solvent. The PDMAEMA-PBMA block copolymers were purified from traces of PDMAEMA homopolymer by exclusive precipitation of the PDMAEMA-PBMA block copolymer in water. The statistical copolymers of PDMAEMA and PMMA were polymerized with CuCl/bipyridine catalyst and ethyl 2-bromoisobutyrate initiator, in anisole at 90°C.

Quaternization of the amine groups of PDMAEMA was done by applying a post-polymerization reaction described by Baines et al.⁸² In the method, the DMAEMA units of the polymer were quaternized with methyl iodide in THF solution at ambient temperature.

PDMAEMA-PTFEMA copolymers.^{IV} The copolymers were synthesized by ATRP. CuBr/*N*-(*n*-pentyl)-2-pyridylmethanimine was used as catalyst and benzyl 2-bromoisobutyrate as initiator in 50 v/v-% toluene at 90°C. The block copolymers were prepared by one-pot sequential polymerization, where PTFEMA block was prepared first and DMAEMA monomer was added at around 80% TFEMA conversion. The block copolymers were purified from traces of PTFEMA homopolymer by acidification of a solution of the crude polymer in THF with diluted HCl (aq), which led to the exclusive precipitation of the PTFEMA-PDMAEMA block copolymer. The quaternization of the DMAEMA units was conducted in a similar manner to PDMAEMA-PMMA and PDMAEMA-PBMA copolymers (see previous section). The reactivity ratios of TFEMA and DMAEMA were measured by Jaacks method.⁸³

2.2 Preparation of aqueous polymer solutions and dispersions

Starch graft copolymers.^I The aqueous microparticle dispersions were prepared by a method described in patent literature.⁸⁴ Polymeric particles were formed spontaneously when polymer dissolved in aqueous THF was rapidly diluted with water, after which THF was evaporated by slight warming of the dispersion. The dispersion was concentrated through reversible flocculation by Na₂SO₄.

Glycopolymers.^{II} The synthesized glycopolymers were directly dissolved in water.

PDMAEMA-PMMA and PDMAEMA-PBMA copolymers.^{III} The synthesized copolymers were directly dissolved in water (containing 0 – 0.1 M NaCl).

PDMAEMA-PTFEMA copolymers.^{IV,V} The block copolymers containing non-quaternized DMAEMA were assembled to aqueous nanoparticles through solvent exchange process from acetone to water. Two slightly different solvent exchange methods were used. In the results part of this thesis (chapters 3-7), the solvent exchange method resulting in 1 w/v-% solutions^{IV} is referred to as solvent exchange method A and the solvent exchange method that resulted in 0.05 w/v-% or 0.005 w/v-% solutions^{IV,V} is referred to as solvent exchange method B. In the solvent exchange method A, water was slowly added into 1 w/v-% polymer solution in acetone, until 1:1 acetone:water solution was obtained, after which the solutions were dialyzed against water to remove the acetone. In the exchange method B, water was slowly added into 1 w/v-% polymer solution in acetone, until either 1:1 or 10:1 acetone:water solutions were obtained (depending on the polymer). Water was then added quickly to provide a 0.1 w/v-% solution of polymeric particles in 90:10 water:acetone mixture, after which they were dialyzed against water to remove the acetone. In both methods, the polymer concentration, solution ionic strength and pH were adjusted as the final step of the process.

The block copolymers containing META1 units were dissolved directly in water at 80 °C. The statistical copolymers containing non-quaternized DMAEMA units were either assembled to aqueous nanoparticles through solvent exchange method B from acetone to water, or dispersed in water followed by a pH adjustment to dissolve the polymer. The statistical copolymers containing quaternized META1 units were dissolved directly in water. In all the solutions, the ionic strength was adjusted with NaCl and pH was adjusted with HCl or NaOH.

2.3 Preparation of ultra thin polymer layers on surfaces

Starch graft copolymers.^I Starch graft copolymers were spin coated on purified hydrophilic silica surfaces at 1500 rpm from 5 w/v-% aqueous dispersions and 5 w/v-% THF solutions. The effect of annealing at elevated temperatures on surfaces spin-coated from aqueous dispersions was studied by heating the samples in an oven at 180°C for either 5 min or 15 min.

PDMAEMA-PMMA and PDMAEMA-PBMA copolymers.^{III} Polymers were deposited on purified hydrophilic silica substrates by adsorption and spin coating methods. In adsorption, the substrate was first immersed for 15 min in 1 w/v-% polymer solution. The sample was then rinsed extensively with water and dried at room temperature by allowing the solvent to evaporate. In spin coating, the polymers were spin coated at 2800 rpm from 1 w/v-% polymer solutions.

PDMAEMA-PTFEMA copolymers.^V Polymers were adsorbed on mica and cellulose fiber substrates. In the case of mica, the freshly cleaved substrate was immersed for 10 min in 0.005 w/v-% polymer solution, after which it was thoroughly rinsed with water and dried with N₂ flow. The effect of annealing at elevated temperatures was studied by heating the samples in a clean oven at 150°C in N₂ atmosphere at 2 bar for 24 h. In the case of cellulose fiber substrates, cellulosic filter paper was immersed for 10 min in 0.05 w/v-% polymer solutions, after which it was immersed in water for 10 min and thoroughly rinsed. The filter paper samples were either dried overnight at ambient

conditions (non-annealed samples) or for 3 h at 120°C in a clean oven (annealed samples).

2.4 Characterization

¹H NMR and ¹³C NMR spectroscopy. The NMR spectra were recorded either on a Varian Gemini 2000 300-MHz spectrometer^{I,III} or on Bruker DPX-400 and Bruker AV-400 spectrometers.^{II,IV}

¹⁹F NMR spectroscopy and imaging experiments were performed on a Bruker AMX300 spectrometer interfaced to a 7 T vertical super-wide bore magnet. ¹⁹F spin-spin (T_2) relaxation times were measured using the CPMG pulse sequence, which had from 2 to 256 180° pulses in the echo train. Spin-lattice (T_1) relaxation times were measured using the standard inversion-recovery pulse sequence, with 16 values of inversion times used. ¹⁹F images were collected using the 3D spin-echo pulse sequence.^{IV}

Size exclusion chromatography (SEC). Apparent molecular weights and molecular weight distributions were determined by SEC. Following systems were used: 1) Four Waters Styragel columns (10², 10³, 10⁴ and 10⁵ Å) and a Waters 410 differential refractometer, with either chloroform or THF/triethylamine 98/2 v/v mixture as eluent, delivered at 1 ml/min.^{I,III} 2) Two PL gel 5 µm mixed D columns, one PL gel 5 µm guard column and a differential refractometer, with chloroform/triethylamine 95:5 v/v as eluent, delivered at 1 ml/min.^{II} 3) Two PL gel 5 µm mixed D columns, one PL gel 5 mm guard column and both differential refractometer and ultraviolet (UV) (at 250 nm) detectors, with THF/triethylamine 95:5 v/v as eluent, delivered at 1 ml/min.^{IV} The systems were calibrated with either polystyrene or poly(methyl methacrylate) standards.

Differential scanning calorimetry (DSC). Glass transition temperatures were measured with a Mettler Toledo DSC 821e differential scanning calorimeter.^{I,IV}

Surface tension was measured with a Kibron AquaPi tensiometer by the Du Nouy maximum pull force method.^{III}

Dynamic light scattering (DLS) measurements were conducted with Nanoseries (Malvern, UK) instruments. In the DLS samples, solvent was filtered with 0.25 μm filters before the addition of the polymer.^{III-V}

Cryogenic transmission electron microscopy (cryo-TEM) analysis was conducted with a Tecnai 12 Bio Twin transmission electron microscope in bright field mode. In the cryo-TEM samples, solvent was filtered with 0.25 μm filters before the addition of the polymer.^{III}

Atomic force microscopy (AFM) experiments were conducted with either Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc.)^{III} or Veeco Dimension 5000 scanning probe microscope with Nanoscope V controller (Digital Instruments, Inc.).^V Thicknesses were studied by scratching the samples with a needle and determining the z-directional difference between the bottom of the scratch and the intact areas of the film.^{III} Local surface concentration of adsorbed nanoparticles was determined from the AFM images by counting the number of surface aggregates whose centers were within a given area on the substrate.^V

Contact angle measurements. Contact angles of water on the polymer layers were measured using a KSV CAM 200 instrument (KSV Instruments Ltd., Finland) with a sessile drop method. The advancing and receding contact angles were obtained by slowly increasing (0.02 $\mu\text{l/s}$) and decreasing (0.1 $\mu\text{l/s}$) the volume of a small droplet (originally 5 μl) with a thin needle.^{I,III,V}

3 SYNTHESIS OF STARCH GRAFT COPOLYMERS AND THEIR POTENTIAL IN SURFACE WETTABILITY MODIFICATION¹

Starch graft copolymers were studied as potential surface wettability modifiers. It has been shown, that carbohydrate polymers can have strong affinity towards carbohydrate substrates through hydrogen bonding,⁶⁹ and can therefore be applied in the modification of e.g. cellulose based materials. In this study atom transfer radical polymerization (ATRP) was used to produce poly(methyl methacrylate) (PMMA) grafts onto acetylated starch oligomer (AS) in a controlled manner, with varying graft densities and lengths, in order to increase the hydrophobicity of AS. The graft copolymers were spin-coated onto silica surfaces from water dispersions as well as from THF solutions. The wetting properties of the produced graft copolymer layers were studied by contact angle measurements.

Starch consists of interconnected anhydroglucose units, each of which contains three hydroxyl groups. The properties of starch, such as its solubility in different solvents, can be routinely modified through converting the hydroxyl groups to other functionalities. Grafting of starch (and other polysaccharides) with synthetic polymers by various methods has gained a lot of interest.⁸⁵⁻⁸⁸

A series of ATRP macroinitiators was produced by functionalization of AS. Part of the hydroxyl groups of AS were converted to 2-bromo-isobutyryl groups, which are able to initiate polymerization by the ATRP mechanism. Three different macroinitiators were prepared with different degrees of substitution for the initiator group. The degree of substitution (DS) was defined as the number of hydroxyl groups per anhydroglucose unit, which have been substituted by other groups. Since anhydroglucose units contain originally three hydroxyl groups, the maximum possible DS is three. However, since AS used in this study already contained acetyl groups with DS of 2.2, the maximum DS for the initiator groups (DS_{ini}) was 0.8.

The three prepared macroinitiators enabled grafting with low (DS_{ini} 0.02), intermediate (DS_{ini} 0.09) and high (DS_{ini} 0.76) grafting density. The achieved degrees of substitution corresponded to 51.4, 10.5 and 1.3 anhydroglucose units per initiating site, respectively.

A series of graft copolymers was polymerized by using the three macroinitiators that had been synthesized. All the prepared macroinitiators were grafted both in bulk and in 1:1 v/v THF solution. The reason for the THF addition was to dilute the polymerization mixtures, some of which were already highly viscous in the beginning. THF has also been reported to increase MMA polymerization control with CuCl/bipyridine catalyst system due to the better solubility of the catalyst.⁸⁹ All the polymerization mixtures in the graft copolymerizations were partly heterogeneous with respect to the catalyst.

The polymerizations were followed by 1H NMR and SEC. At low conversions, the polymerization kinetics were first order and the molecular weights of the graft copolymers increased linearly with conversion. However, the reaction mixtures were observed to form a highly viscous mass at relatively low conversions (below 35 %). The reason for the observed viscosity increase was most probably the intermolecular termination leading to gelation. This type of behavior is typical for controlled radical polymerizations initiated from multifunctional initiators.³³⁻³⁷

It has been reported, that addition of $CuBr_2$ deactivator to ATRP reactions can decrease the tendency for termination by decreasing the concentration of active radicals.³⁴ Therefore an additional polymerization was conducted, where $CuBr_2$ was added to the reaction mixture. This polymerization (AS-PMMA11)^I was slightly less prone towards gelation, but effects of intermolecular termination were also in this case clearly visible already at low conversions. The SEC chromatograms of AS-PMMA11 at different conversions are shown in Figure 1.

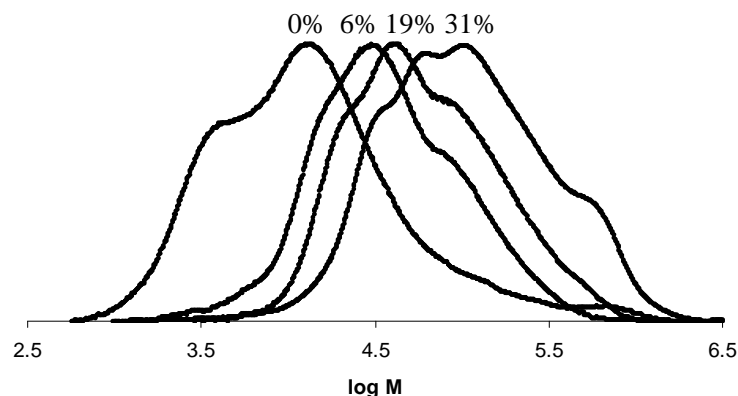


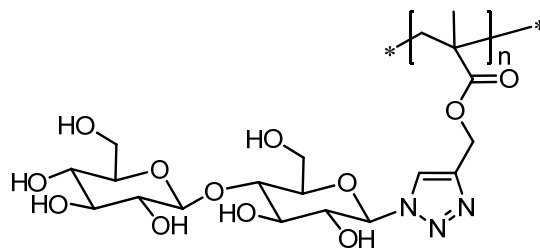
Figure 1. SEC chromatograms obtained from the AS-PMMA11 polymerization at different conversions. The deformation in the shapes of the curves as the polymerization proceeded indicates intermolecular termination.

In order to study the actual grafts produced and get more information about the level of control in the polymerizations, a sample of AS-PMMA11 graft copolymer was treated with sulphuric acid to decompose the AS backbone of the copolymer. The SEC trace of the disintegrated grafts showed relatively low polydispersity of 1.33, which indicates the polymerization was controlled.

A set of graft copolymers varying in graft density and graft length were applied on silica model surfaces by spin-coating either from THF solutions or from aqueous dispersions. The static contact angles of the obtained surface layers were measured. On surfaces prepared from THF solutions, the contact angles of all the samples were between the contact angles of AS and PMMA homopolymers. On surfaces prepared from aqueous dispersions the contact angles were much lower, but the values could be increased by annealing at 180°C so that similar contact angle values as in the surfaces prepared from THF solutions were obtained.

4 SYNTHESIS OF GLYCOPOLYMERS AND THEIR POTENTIAL IN SURFACE WETTABILITY MODIFICATION ^{II}

It has been observed that many polysaccharides and polymers with pendant sugar units show affinity towards cellulose surfaces.^{69, 71} Therefore, amphiphilic copolymers containing both sugar units and hydrophobic units could potentially be applied in wettability modification of cellulosic substrates. The amphiphilic glycopolymers could be adsorbed on cellulose through the sugar units, and surface wettability could subsequently be modified through the hydrophobic units. The adsorption properties would be independent on electrostatic parameters. In this study, glycopolymers with mannose, galactose and cellobiose containing side groups were successfully synthesized (Scheme 4).

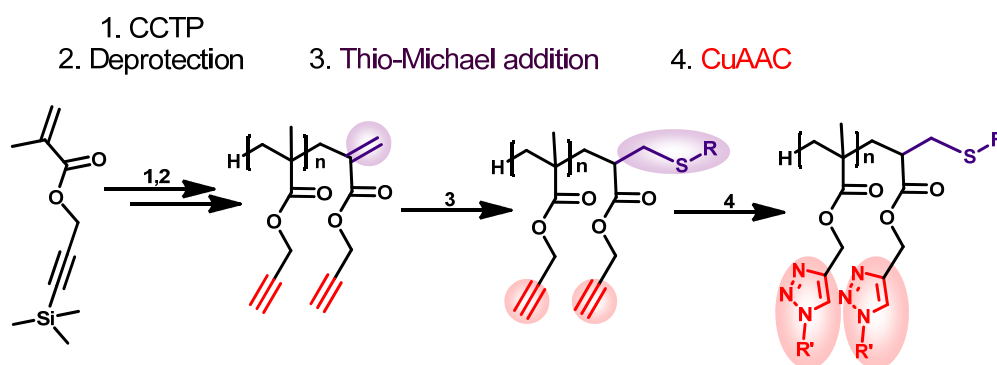


Scheme 4. The chemical structure of the synthesized cellobiose pendant polymers. Also polymers with pendant mannose and galactose units were synthesized.

Catalytic chain transfer polymerization (CCTP) is an efficient way to prepare vinyl terminated methacrylic oligomers.^{90, 91} In this study, CCTP was applied in the polymerization of protected propargyl methacrylate to obtain polymers with alkyne functionality in the side-groups and double bond functionality in the end group. The side-groups were subsequently reacted with sugar azides through copper catalyzed azide-alkyne cycloaddition reaction (CuAAC) to yield the glycopolymers. Only homopolymers were synthesized, but the synthesis procedure allows also the preparation of amphiphilic statistical copolymers.

The double bonds at the polymer chain ends allowed functionalization of the polymers through thiol-ene Michael addition with various thiols. Both CuAAC and thiol-ene

Michael addition are considered to be reactions fulfilling the requirements of ‘click chemistry’.^{38, 41, 43} Therefore, the utilized synthetic approach is potentially useful and versatile route not only to glycopolymers but also to many different types of functional copolymers and polymer conjugates, as shown in Scheme 5.



Scheme 5. A wide range of structures can be obtained by utilizing ‘click chemistry’ with the applied synthetic approach. A polymer with alkyne and double bond functionalities is obtained by CCTP. The end groups can be functionalized or conjugated through thiol-ene chemistry and the side groups can be functionalized through CuAAC.

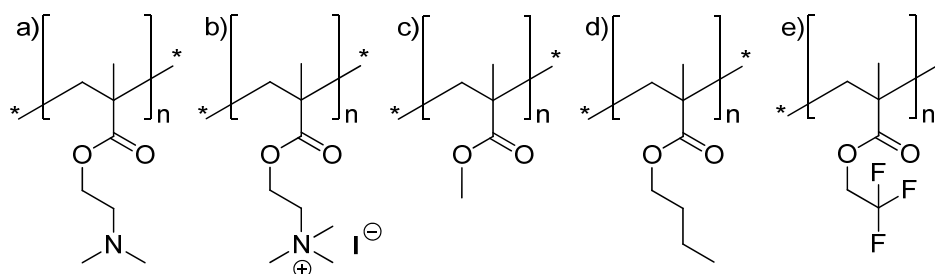
The adsorption of cellobiose pendant polymers was tested on cellulose model substrates by quartz crystal microbalance measurements from aqueous solutions.* Unfortunately, adsorption did not occur. The degree of polymerization of the polymer applied in the experiments was ca. 50. It is likely, that higher molecular weight polymers and/or longer polysaccharide units in the side groups are necessary to obtain high enough affinity towards the substrate for significant adsorption to occur.

In biomedical systems glycopolymers are often shown to interact with carbohydrate-binding proteins, lectins, in a similar manner to natural glycoproteins. In this study it was observed, that the synthesized mannose and galactose pendant polymers could be recognized by immobilized lectins.

* Unpublished results. Measurements conducted by Niko Aarne, Department of Forest Products Technology, Aalto University.

5 SYNTHESIS OF AMPHIPHILIC POLYELECTROLYTES BY ATRP^{III, IV}

A major objective of this thesis was to modify the wetting properties of hydrophilic surfaces with an ultra-thin layer of amphiphilic polymer. A large part of the study was conducted with amphiphilic polyelectrolytes, which can be easily attached on surfaces of opposite charge through electrostatic interactions.⁵ The applied amphiphilic polyelectrolytes were copolymers that contained either 2-(dimethylamino)ethyl methacrylate (DMAEMA) or its quaternized form [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) as a hydrophilic monomer and either methyl methacrylate (MMA), butyl methacrylate (BMA) or 2,2,2-trifluoroethyl methacrylate (TFEMA) as a hydrophobic monomer. Both DMAEMA and METAI have potential to obtain cationic charge in aqueous solutions. The structures of the applied repeating units are presented in Scheme 6. The copolymers were polymerized by ATRP and both statistical and block copolymers were synthesized.



Scheme 6. The repeating unit structures used in the amphiphilic polyelectrolytes. a) 2-(dimethylamino)ethyl methacrylate (DMAEMA) b) [2-(methacryloyloxy)ethyl] trimethyl ammonium iodide (METAI) c) methyl methacrylate (MMA) d) butyl methacrylate (BMA) e) 2,2,2-trifluoroethyl methacrylate (TFEMA).

5.1 Synthesis of PDMAEMA-PMMA and PDMAEMA-PBMA copolymers^{III}

A series of copolymers with either DMAEMA or METAI as the hydrophilic monomer and either MMA or BMA as the hydrophobic monomer was synthesized. These copolymers are referred to as PDMAEMA-PMMA and PDMAEMA-PBMA copolymers throughout this thesis. Their properties are presented in Table 1.

Table 1. The PDMAEMA-PMMA and PDMAEMA-PBMA copolymers.^{III}

Sample	Composition (NMR)	DMAEMA content (mol-%)	M_n^a (g/mol) (NMR)	PDI (SEC)
<i>Block copolymers</i>				
B1(D ₇₆ M ₁₇) ^b	P(DMAEMA ₇₆ - <i>b</i> -MMA ₁₇)	82	13600	1.08
B2(D ₈₁ M ₂₁) ^b	P(DMAEMA ₈₁ - <i>b</i> -MMA ₂₁)	79	14900	1.09
B3(QD ₇₆ M ₁₇)	P(META ₇₆ - <i>b</i> -MMA ₁₇)	82	24400	1.08 ^c
B4(QD ₆₁ M ₇₉)	P(META ₆₁ - <i>b</i> -MMA ₇₉)	44	26100	1.10 ^c
B5(QD ₆₆ B ₇₆)	P(META ₆₆ - <i>b</i> -BMA ₇₆)	47	30500	1.17 ^c
<i>Statistical copolymer</i>				
C1(QD ₆₀ M ₆₂)	P(META ₆₀ - <i>co</i> -MMA ₆₂) ^d	49	15600 ^d	1.19 ^c

^acalculated from ¹H NMR spectra by comparing end-group peaks to appropriate side-chain peaks.

^bB1(D₇₆M₁₇) and B2(D₈₁M₂₁) samples were approximated to behave identically. B1(D₇₆M₁₇) was used in the surface studies and B2(D₈₁M₂₁) was used in the solution studies. ^cbefore quaternization ^dmolecular weight estimated from the SEC result.

The block copolymers were synthesized by first polymerizing the PDMAEMA block by ATRP and then using the purified block as a macroinitiator in the polymerization of the PMMA or PBMA block. In META_I containing polymers, the DMAEMA units were quaternized as the final step of the synthesis.

In the homopolymerization of DMAEMA, a solvent/catalyst system described by Mao et al. was used.²² The DMAEMA blocks prepared by this method had low polydispersities (approximately 1.1) in all the polymerizations. However, the obtained molecular weights were approximately two times higher than what was theoretically expected. The polymerization mixtures turned deep blue immediately when the reaction was initiated, indicating that large amount of copper(II) chloride was formed at the beginning of the reaction due to termination by radical-radical coupling.

The polydispersities of the copolymers were also low (below 1.2, Table 1). In the block copolymerizations the molecular weight clearly shifted to a higher value when compared to the homopolymer macroinitiator. Significant macroinitiator traces were not visible in the SEC curves of the purified block copolymers. The SEC curves of the B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) block copolymers are shown as examples in Figure 2.

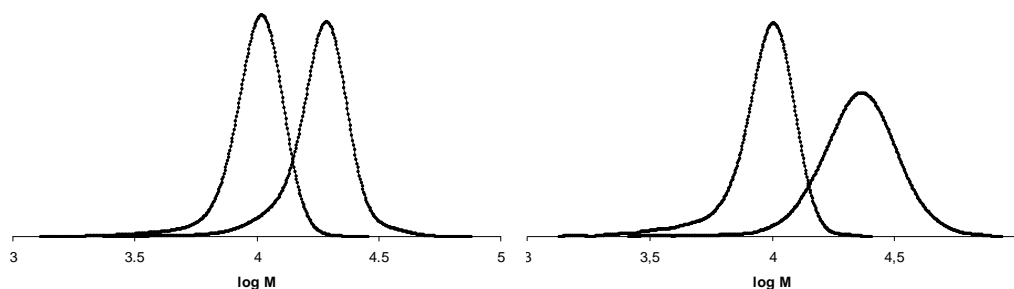


Figure 2. SEC curves of B4(QD₆₁M₇₉) (left) and B5(QD₆₆B₇₆) (right). The macroinitiator curves are presented alongside the block copolymer curves.^{III}

5.2 Synthesis of PDMAEMA-TFEMA copolymers^{IV,V}

Another series of copolymers was synthesized, with either DMAEMA or METAI as the hydrophilic monomer unit and with TFEMA as the hydrophobic monomer unit. These copolymers are referred to as PDMAEMA-PTFEMA copolymers throughout this thesis. Their properties are presented in Table 2.

Table 2. The PDMAEMA-PTFEMA copolymers. The samples are named according to their molar TFEMA content.^{IV,V}

Sample	Composition (NMR)	TFEMA content (mol-%)	M_n^a (g/mol) (NMR)	PDI ^b (SEC)
<i>Statistical copolymers</i>				
C-12	P(TFEMA ₁₇ -co-DMAEMA ₁₂₂)	12	22000	1.39
C-24	P(TFEMA ₃₄ -co-DMAEMA ₁₀₉)	24	22900	1.39
C-51	P(TFEMA ₇₅ -co-DMAEMA ₇₃)	51	24100	1.24
QC-51	P(TFEMA ₇₅ -co-METAI ₇₃)	51	34400	1.24 ^c
<i>Block copolymers</i>				
B-20	PTFEMA ₃₉ -b-P(DMAEMA ₁₉₇ -co-TFEMA ₁₂)	20	39500	1.55
B-47	PTFEMA ₉₁ -b-P(DMAEMA ₁₂₂ -co-TFEMA ₁₉)	47	37700	1.43
QB-47	PTFEMA ₉₁ -b-P(METAI ₁₂₂ -co-TFEMA ₁₉)	47	55000	1.43 ^c
B-77	PTFEMA ₁₀₇ -b-P(DMAEMA ₃₆ -co-TFEMA ₂₂)	77	27300	1.40

^acalculated from ¹H NMR spectra by comparing end-group peaks to appropriate side-chain peaks. ^bwith DRI detection, after purification. ^cbefore quaternization.

DMAEMA was used as a hydrophilic monomer in statistical copolymers C-12, C-24 and C-51 and in block copolymers B-20, B-47 and B-77. METAI was used in statistical

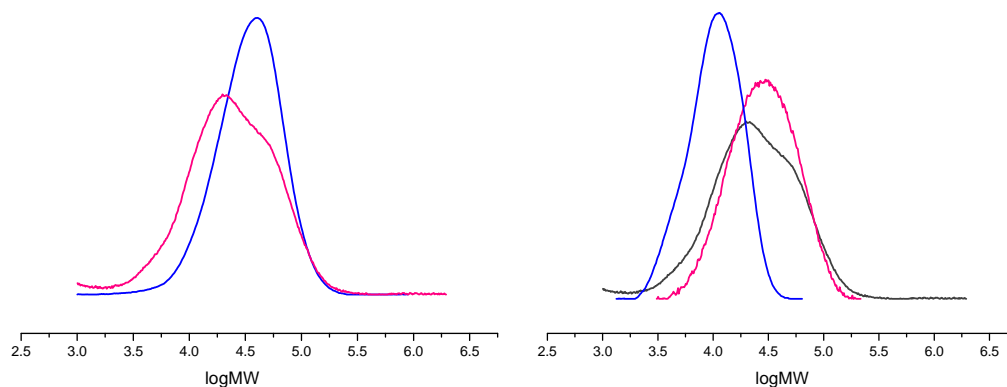
copolymer QC-51, which was a completely quaternized version of C-51 and in block copolymer QB-47, which was a completely quaternized version of B-47.

The copolymers were polymerized by ATRP in toluene with CuBr/*N*-(*n*-pentyl)-2-pyridylmethanimine as catalyst.^{26, 27} The method provided copolymers with reasonably low polydispersities (Table 2). The kinetic curves of the polymerizations were linear up to high conversions.^{IV}

The block copolymers were polymerized in a sequential manner; the TFEMA block was polymerized first and DMAEMA was added when 70-80% TFEMA conversion was reached. Due to the preparation method, the second block was a statistical copolymer, and 20-30% of TFEMA present in the polymer was in the hydrophilic block.

The SEC curves of block copolymer B-20 are shown as an example in Figure 3. It was noticed, that chromatograms obtained using differential refractive index (DRI) detection did not give correct shape for molecular weight distribution, which could be ascribed to the fact that PDMAEMA and PTFMA blocks have very different intrinsic refractive indices. Ultraviolet (UV) detection revealed unreacted PTFMA homopolymer in the crude product which could be removed by precipitation of pure PDMAEMA-containing block copolymer under acidic conditions.

The molecular weights of the copolymers were determined from the ¹H NMR spectra of the purified copolymers, by comparing the end-group peaks deriving from the initiator to the appropriate side-chain peaks. The molecular weights calculated from the ¹H NMR spectra were higher than what was theoretically expected, especially in the case of purified block copolymers.^{IV} As the crude block copolymers contained a rather large amount of PTFEMA homopolymer traces, the average molecular weights of the block copolymers increased when the homopolymer impurity was removed from the samples.



*Figure 3. SEC curves of block copolymer B-20. Left: Non-purified block copolymer with DRI (blue) and UV (pink) detection. Right: Non-purified block copolymer (black), purified block copolymer (pink) and the trace removed in the purification step (blue), with UV detection.**

The reactivity ratios of the TFEMA/DMAEMA monomer pair were measured by Jaacks method.^{83, 92, 93} They were found to be $r_{\text{TFEMA}} = 0.76$ and $r_{\text{DMAEMA}} = 0.81$. This indicates that there was no tendency towards formation of blocks within the statistical copolymers or the statistical hydrophilic blocks of the block copolymers.

* Unpublished results.

6 AMPHIPHILIC POLYELECTROLYTES IN AQUEOUS MEDIUM^{III, IV, V}

The amphiphilic polyelectrolytes described in Table 1 and Table 2 were dissolved or dispersed in water, as the aim in the thesis was to apply the polymers on surfaces from aqueous medium. DMAEMA is a basic monomer unit, and therefore the degree of cationic charge in the DMAEMA-containing polymers in aqueous solutions is dependent on pH, and increases with decreasing pH. The pK_a value of 8.4 has been reported for the DMAEMA monomer.⁹⁴ The average pK_a of PDMAEMA, defined as the pH at which 50 % of the DMAEMA units are protonated, is dependent on e.g. polymer molecular weight, polymer architecture and the ionic strength of the solution. For multibranched PDMAEMA star polymers in salt-free solutions, average pK_a values as low as 5.9 have been measured.⁹⁵

In contrast, the quaternized form of DMAEMA, METAI unit is cationically charged relatively independent of pH. Therefore, at neutral pH conditions in water, polymers containing METAI units have a significantly higher charge density than polymers containing DMAEMA units and therefore have higher solubility in water. The hydrophobicity of the applied hydrophobic monomer units increases in the order: MMA (least hydrophobic), BMA, TFEMA (most hydrophobic).

6.1 PDMAEMA-PMMA and PDMAEMA-PBMA copolymers in aqueous medium^{III}

The PDMAEMA-PMMA and PDMAEMA-PBMA copolymers (Table 1) formed optically clear solutions when dissolved in water without pH adjustment. The relatively hydrophilic nature of the copolymers is explained by the rather hydrophilic METAI units that were applied in the majority of the samples, i.e., most of the samples in Table 1 were strong polyelectrolytes. Only two block copolymer samples in the series, B1(D₇₆M₁₇) and B₂(D₈₁M₂₁), contained non-quaternized DMAEMA units.

In optically clear aqueous solutions, amphiphilic block polyelectrolytes can be present either as unimers, as equilibrium micelles or as kinetically trapped nanoparticles. Roughly similar alternatives apply also for amphiphilic statistical polyelectrolytes.¹ The structure of the PDMAEMA-PMMA and PDMAEMA-PBMA samples in aqueous solutions was studied by surface tension measurements, ¹H NMR spectroscopy, dynamic light scattering (DLS) and cryogenic transmission electron microscopy (cryo-TEM). Typically, 1 w/v-% polymer was dissolved in low ionic strength aqueous solution (0 M or 0.0001 M NaCl) with no pH adjustment. The scattering intensities and the determined solution structures of the samples are presented in Table 3. The determination of the solution structure was based on results of all the conducted measurements. The key characteristics that were used in the determination of each individual structure are also listed in Table 3.

Table 3. Solution properties of PDMAEMA-PMMA and PDMAEMA-PBMA copolymers at low ionic strength (0.0001 M NaCl), at 1 w/v-% polymer concentration.^{III}

Sample	Scattering intensity (kcps) ^a	Structure in solution	Key characteristics
D2 ^b (PDMAEMA reference)	13	unimers	low scattering intensity
B2(D ₈₁ M ₂₁)	190	equilibrium micelles	higher scattering intensity, $D_H = 12$ nm in DLS, high surface activity
B3(QD ₇₆ M ₁₇)	28	unimers	low scattering intensity
B4(QD ₆₁ M ₇₉)	4160	trapped nanoparticles	high scattering intensity, low surface activity
B5(QD ₆₆ B ₇₆)	7690	trapped nanoparticles	high scattering intensity, low surface activity, particles visible in cryo-TEM
C1(QD ₆₀ M ₆₂)	79	unimers	low scattering intensity, narrow PMMA peak in ¹ H NMR

^afrom the DLS measurement. ^b $M_n = 11400$ g/mol (by NMR), PDI = 1.10 (by SEC). For more details, see publication III.

The distinction between unimeric and aggregated species could be observed in the scattering intensity results, since the scattering intensity increases significantly when aggregates are present. On the other hand, the distinction between equilibrium micelles and kinetically trapped nanoparticles could be observed in the surface tension measurements. The samples with longest hydrophobic blocks, B4(QD₆₁M₇₉) and

B5(QD₆₆B₇₆), showed low surface activity even when compared to PMETAI homopolymer, which indicates presence of trapped non-equilibrium particles.⁵³ The ¹H NMR results provided support for the determined conformations. For example, the statistical copolymer C1(QD₆₀M₆₂) had a narrow PMMA peak in the aqueous ¹H NMR spectrum, which indicates the sample was non-aggregated.

The hydrodynamic diameters (D_H) of the aggregates containing METAI units could not be measured by DLS at these low ionic strength solutions, since the dynamics of unscreened strong polyelectrolyte solutions are determined by the electrostatic interactions, preventing the size measurement.⁹⁶ However, the hydrodynamic diameters of the aggregates were measured at solutions containing 0.1 M NaCl.^{III}

The conformations of the kinetically trapped nanoparticles of B4(QD₆₁M₇₉) and B5(QD₆₆B₇₆) were further studied with cryo-TEM. There was a clear difference in the aggregates of the two samples. The B4(QD₆₁M₇₉) image contained a wide distribution of varying particles, whereas B5(QD₆₆B₇₆) image contained clearly defined particles with diameters between 20-70 nm.

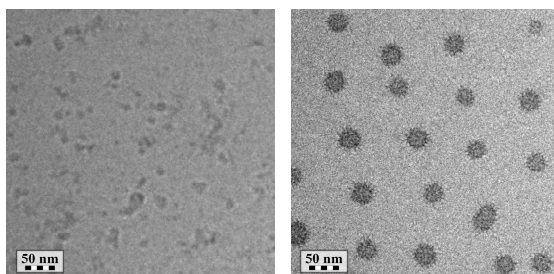


Figure 4. Cryo-TEM images of B4(QD₆₁M₇₉) (left) and B5(QD₆₆B₇₆) (right). 1 w/v-% solutions in 0.0001 M NaCl.^{III}

6.2 PDMAEMA-PTFEMA copolymers in aqueous medium^{IV,V}

The PDMAEMA-PTFEMA copolymers (Table 2) were more hydrophobic than the PDMAEMA-PMMA and PDMAEMA-PBMA copolymers discussed in previous section, because majority of the PDMAEMA-PTFEMA copolymers contained non-

quaternized DMAEMA units instead of METAI units, and also because the TFEMA units were more hydrophobic than MMA or BMA units. Only the copolymers QB-47 and QC-51, which contained quaternized METAI units, could be dissolved directly in water with unadjusted pH.

The aqueous conformations of PDMAEMA-PTFEMA polymers, i.e. whether the polymer chains were extended or collapsed in water, were studied with 1 w/v-% polymer solutions by ^{19}F NMR measurements. TFEMA units have three equivalent fluorine nuclei, resulting in a single peak of potentially high signal-to-noise ratio (SNR) in the ^{19}F NMR spectrum. The spin-lattice (T_1) and spin-spin (T_2) relaxation times of the ^{19}F nuclei were measured of the prepared polymer solutions. Both T_1 and T_2 of the fluorine nuclei are affected by the mobility of the nuclei, which further depends on the conformation of the polymer.⁹⁷⁻¹⁰²

The polymer solutions for the ^{19}F NMR measurements were prepared either by dispersing the polymer in water and adjusting the pH until the polymer dissolved (statistical copolymers containing non-quaternized DMAEMA units, C-12, C-24 and C-51 in Table 2), by assembling the polymer to aqueous nanoparticles through solvent exchange from acetone to water (block copolymers containing non-quaternized DMAEMA units, B-20 and B-47 in Table 2, solvent exchange method A* was applied) or by direct dissolution, possibly at elevated temperature (copolymers containing METAI units, QB-47 and QC-51 in Table 2). The statistical copolymers containing non-quaternized DMAEMA units were studied at varying pH and ionic strength conditions in order to study the effect of polymer charge density on its aqueous conformation.

In addition to the ^{19}F NMR measurements, DLS measurements were conducted of the 1 w/v-% block copolymer solutions. The expected solution structure for the block copolymers was a nanoparticle, where the hydrophobic PTFEMA block formed the core and the statistical P(TFEMA-*co*-DMAEMA) copolymer block formed the corona. Because the block copolymers were not directly soluble in water, and since the

* See chapter 2, experimental

PTFEMA blocks were under their glass transition temperature ($T_{g,TFEMA} = 74\text{ }^{\circ}\text{C}$ as measured by DSC), the nanoparticles were expected to be kinetically trapped non-equilibrium structures. The T_1 , T_2 and DLS results of the polymers, alongside with the determined aqueous conformations, are presented in Table 4.

Table 4. ^{19}F NMR and DLS results of the PDMAEMA-PTFEMA copolymer solutions and the expected aqueous conformations. The polymer concentration was 1 w/v-%.^{IV}

Sample	Solution conditions ^a		D_H (nm) ^b (DLS)	^{19}F T_1 (ms)	^{19}F T_2 (ms)	Expected conformation of the copolymer in solution
	pH	[NaCl] (M)				
C-12	8	0		320	13	collapsed globule
	6.5	0		520	140	extended coil
	2	0		550	140	extended coil
C-24	6.5	0		430	81	extended (intermediate) coil
	2	0		540	150	extended coil
C-51	2	0		360	11	collapsed globule
QC-51		0.25		330	11	collapsed globule
B-20		0	45	340	0.12 (69%) 11 (31%)	collapsed nanoparticle
B-47		0	29	400	0.22 (86%) 11 (14%)	collapsed nanoparticle
QB-47		0.25	20 – 1000 ^c	480	0.73 (89%) 81 (11%)	extended nanoparticle

^a the statistical copolymers C-12, C-24 and C-51 were studied also at 0.25 M NaCl solutions, but the results are not presented here, as they were in most cases similar to the results in salt-free solutions ^b relative standard deviation was <2% ^c broad distribution, extreme values are presented.

Significant differences were observed especially in the T_2 values of the samples, where variation greater than two orders of magnitude was measured (from values less than 1 ms to 160 ms). The longer the T_1 and T_2 values were, the more extended the aqueous conformation of the polymer was expected to be. However, it must be noted that the conformation estimations in Table 4 represent only relative qualities between the samples, and do not indicate the absolute extent of the collapse or extension of the chains. In statistical copolymers (C-12, C-24, C-51 and QC-51), increasing fluorine content increased the association between the more abundant fluorine groups, and lower pH values were necessary to maintain the extended conformation or even solubility of the polymers.

Two different T_2 values could be separated from the T_2 relaxation curves of all the block copolymer nanoparticle solutions. The presence of two separate T_2 values indicates the

presence of separate ^{19}F populations, at least on the time scale of the relaxation time measurements. It can be assumed that the shorter T_2 derives from the TFEMA units within the kinetically trapped core blocks of the particles, while the longer T_2 is due to the TFEMA units within the statistical copolymer blocks forming the coronas of the particles. The relative populations of short and long ^{19}F T_2 values could be estimated from the relaxation decays and correspond to the relative TFEMA populations in the core and corona blocks reasonably well. The conformation of the corona was found to be extended in the QB-47 sample, which contained META units and had therefore high charge density in the corona. Correspondingly, the conformation of the corona was found to be collapsed in the other block copolymer samples (B-20 and B-47), which contained non-quaternized DMAEMA units and had therefore low charge density at the applied conditions with unadjusted pH.

In addition to the experiments described in Table 4, some of the PDMAEMA-PTFEMA copolymers were studied also at lower, 0.005 w/v-% (50 ppm) concentration by DLS. The copolymers were assembled to aqueous nanoparticles through solvent exchange from acetone (method B* was applied), after which the pH of the solution was adjusted either with HCl or NaOH. The DLS results of this solution series are presented in Table 5. The solution series presented in Table 5 was further used in surface experiments described in Chapter 7.

The B-47 results in Table 5 show that the D_H of the nanoparticles almost doubled from 41 nm to 77 nm when the pH was lowered from 9 to 3. The B-47 corona blocks had a low charge density at pH 9 whereas they had a high charge density at pH 3. The particles were expected to be kinetically trapped, and therefore the change in D_H is not expected to derive from changes in the aggregation number, as the pH adjustment was done as the final step, after the nanoparticles were formed. Rather, the change is expected to derive from the significant extension of the corona chains with increasing charge density. This observation is consistent with ^{19}F NMR results of the copolymers (Table 4).

* See chapter 2, experimental

Table 5. The DLS results of the PDMAEMA-PTFEMA nanoparticles prepared with solvent exchange (method B). The polymer concentration was 0.005 w/v-% and NaCl concentration was 0.01 M.^V

Sample		D_H (nm) (DLS) ^a
<i>Statistical copolymer</i>		
C-51	pH 3	Unimers – the C-51 particles disaggregated when the pH was lowered
	pH 6.5	64
	pH 9	Precipitated
<i>Block copolymers</i>		
B-20	pH 6.5	82
B-47	pH 3	77
	pH 6.5	64
	pH 9	41
B-77	pH 6.5	60

^a Relative standard deviation was < 8 % for the nanoparticle hydrodynamic diameters.

As the aqueous solutions described in Table 4 were visible in ^{19}F NMR, the copolymers in Table 4 have potential as ^{19}F magnetic resonance imaging (MRI) agents.¹⁰³⁻¹⁰⁷ The polymers could potentially be incorporated e.g. within therapeutic particles or cells, and could subsequently be tracked *in vivo* in a non-invasive manner by ^{19}F MRI. In the method, a ^{19}F image is superimposed on a familiar ^1H density image, revealing the location of the fluorinated compounds. ^{19}F is an attractive tracking nucleus for MRI due to its high sensitivity and the absence of a confounding ^{19}F background signal within the body.

In ^{19}F MRI utilizing spin-echo pulse sequence, the most effective imaging agents will have short T_1 relaxation times, long T_2 relaxation times and high fluorine contents.¹⁰⁸ ^{19}F MRI intensities of phantom images were measured from the Table 4 solutions.^{IV} It was observed, that increasing the fluorine content of the polymer on one hand increased the image intensity by adding more ^{19}F nuclei to the image, but on the other hand resulted in increased association, which at some point started to decrease the image intensity as the T_2 shortened. Only water-solvated polymer chains (i.e. statistical copolymers and block copolymer coronas) were detectable in the ^{19}F MRI with the pulse sequence that was applied. The T_2 of the ^{19}F nuclei in the solid nanoparticle cores were so short that in practice the core nuclei did not contribute to the images.

7 ULTRA-THIN LAYERS OF AMPHIPHILIC POLYELECTROLYTES AS SURFACE WETTABILITY MODIFIERS^{III, V}

A major objective in this thesis was to apply amphiphilic polymers on hydrophilic substrates as ultra-thin layers from aqueous medium, in order to achieve a change in the wetting properties of the substrate. In order to study the potential of the synthesized cationic amphiphilic polyelectrolytes as surface wettability modifiers, they were applied on silica, mica or cellulose fiber substrates (cellulosic filter paper) from aqueous solutions. All the applied substrates have a negative character in water over a wide solution pH range.

7.1 Structure and wettability of the PDMAEMA-PMMA and PDMAEMA-PBMA copolymer layers on silica^{III}

The synthesized PDMAEMA-PMMA and PDMAEMA-PBMA copolymers (presented in Table 1) were applied on silica substrates from 1 w/v-% aqueous solutions containing 0.0001 M NaCl. The solutions were presented in Table 3. According to the solution studies, the copolymer samples formed unimeric, equilibrium micelle or kinetically trapped nanoparticle structures in these conditions, depending on the polymer. The copolymers were applied on silica by either spin coating or adsorption. The obtained surface structures were studied with AFM and indicative wetting properties with static contact angle measurements.

On spin-coated samples, the obtained polymer layer thicknesses were 10-30 nm, as measured by AFM with scratch method, indicating that the layers were thicker than monolayers. The static contact angles on these surfaces were below 20°, indicating highly hydrophilic behavior. This can be attributed to the fact that only the lowest layer of polymer chains was attached to the substrate through electrostatic interactions and the uppermost chains were free to dissolve in the measurement droplet, since all the PDMAEMA-PMMA and PDMAEMA-PBMA samples were directly soluble in water. From this result the obvious conclusion can be drawn, that in case water-soluble

polymers are used in surface wettability modification, a monolayer must be obtained in order to get layers that are stable when in contact with water.

In order to obtain monolayer samples from the spin-coated surfaces, the surfaces were rinsed thoroughly with water.* After rinsing and drying, only those polymer chains that were attached to the substrate were expected to remain on the surface. When the contact angles were measured on these surfaces, less hydrophilic values were obtained, indicating successful wettability modification. The AFM image of the obtained B5(QD₆₆B₇₆) surface layer is presented as an example (Figure 5, left). The aggregates visible in the surface are expected to derive from the kinetically trapped nanoparticles present in the aqueous solution of B5(QD₆₆B₇₆) (see Figure 4). The contact angle on the surface was 82°.

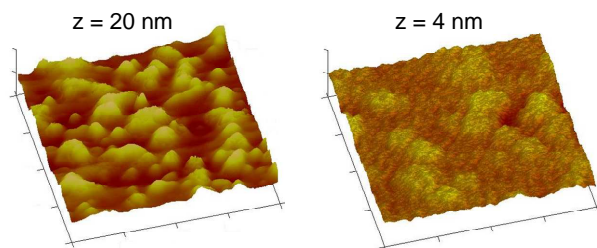


Figure 5. AFM topographic images of B5(QD₆₆B₇₆) surface layers on silica. Left: 1×1 μm², surface prepared by spin coating (after rinsing and drying). Right: 1×1 μm², surface prepared by adsorption (after rinsing and drying).^{III}

The surface layers prepared by adsorption were mainly featureless. The B5(QD₆₆B₇₆) surface was an exception; it had a structure of 100-200 nm wide and 2-6 nm high aggregates separated by smooth areas (Figure 5, right). These aggregates are again expected derive from the aqueous nanoparticles of B5(QD₆₆B₇₆). In general, the adsorbed surfaces were significantly thinner than the spin-coated surfaces, with thicknesses clearly below 10 nm. It can be expected that the polymer layers were monolayers irreversibly attached to the substrate, since the surfaces were thoroughly

* Rinsed surfaces were not prepared from all the spin-coated samples, but from an example set consisting of samples B5(QD₆₆B₇₆) and C1(QD₆₀M₆₂).

rinsed after preparation. Contact angles between 30°-60° were measured on the adsorbed surfaces, depending on the adsorbed polymer. The contact angle of the adsorbed B5(QD₆₆B₇₆) surface presented in Figure 5 was 58°.

From Figure 5 it can be observed, that the structures of the B5(QD₆₆B₇₆) surface layers prepared by spin coating and adsorption differed significantly from each other. Both surfaces consisted of aggregates, but the surface prepared by spin coating was significantly rougher with greater aggregate height and density. The differences are expected to derive from the conditions of preparation: in the adsorption process the surface formation depends on the equilibrium formed on the solid-liquid interface, whereas spin-coating is a forced process.

The contact angle on the spin-coated surface B5(QD₆₆B₇₆) was 82° whereas on adsorbed surface it was 58°. It can be concluded, that the obtained level of wettability was dependent not only on the applied polymer but also on the surface preparation method and on the resulting surface structure.

7.2 Structure and wettability of the PDMAEMA-PTFEMA copolymer layers on mica^v

The synthesized PDMAEMA-PTFEMA copolymers (presented in Table 2) were applied on mica substrates from 0.005 w/v-% aqueous solutions containing 0.01 M NaCl. The solutions were presented in Table 5, and majority of them consisted of kinetically trapped nanoparticles. The statistical copolymer C-51 was an exception; when the pH was lowered to 3, the polymer dissolved as unimers.

The copolymers were applied on mica by adsorption. After adsorption, the surfaces were rinsed with water and dried under N₂ flow. The structure of the formed polymer layers was studied with AFM and the obtained surface wetting properties were studied with dynamic contact angle measurements. The layers were studied both without annealing and after annealing at 150°C. The samples C-51 and B-47 were studied as a

function of adsorption pH in order to evaluate the effect of polymer charge density on the properties of the layers.

The AFM images of the obtained surface layers are presented in Figure 6. As the polymer layers observed in the images were able to withstand desorption during rinsing, it can be expected that their adsorption process was irreversible. In the majority of the non-annealed layers in Figure 6, nanoscale particles were observed in the AFM images. The particles are expected to directly derive from the solution nanoparticles. Accordingly, the non-annealed C-51 surface layer adsorbed at pH 3 was rather featureless, as the adsorbing species was unimeric. After annealing, the surfaces had flattened and the nanoparticles had spread significantly.

The wetting properties (i.e. advancing and receding contact angles) of the surfaces are presented in Table 6. The surfaces can be divided to three different groups based on their structures observed in the AFM images, including featureless surfaces, surfaces with partial nanoparticle coverage and surfaces with high nanoparticle coverage. The wetting properties of these groups are discussed below separately.

Table 6. Advancing/receding water contact angles of PDMAEMA-PTFEMA layers on mica. Notation $<< 10^\circ$ indicates contact angle close to 0° .^V

Sample		contact angle ^a (non-annealed)	contact angle ^a (annealed)
<i>Statistical copolymer</i>			
C-51	pH 3	81° / 39°	85° / 40°
	pH 6.5	100° / $<<10^\circ$	84° / 42°
<i>Block copolymers</i>			
B-20	pH 6.5	47° / $<20^\circ$	63° / 22°
B-47	pH 3	60° / $<20^\circ$	71° / 32°
	pH 6.5	64° / $<20^\circ$	73° / 32°
	pH 9	80° / $<20^\circ$	90° / 24°
B-77	pH 6.5	82° / $<<10^\circ$	96° / 63°

^a standard deviation $< 5^\circ$.

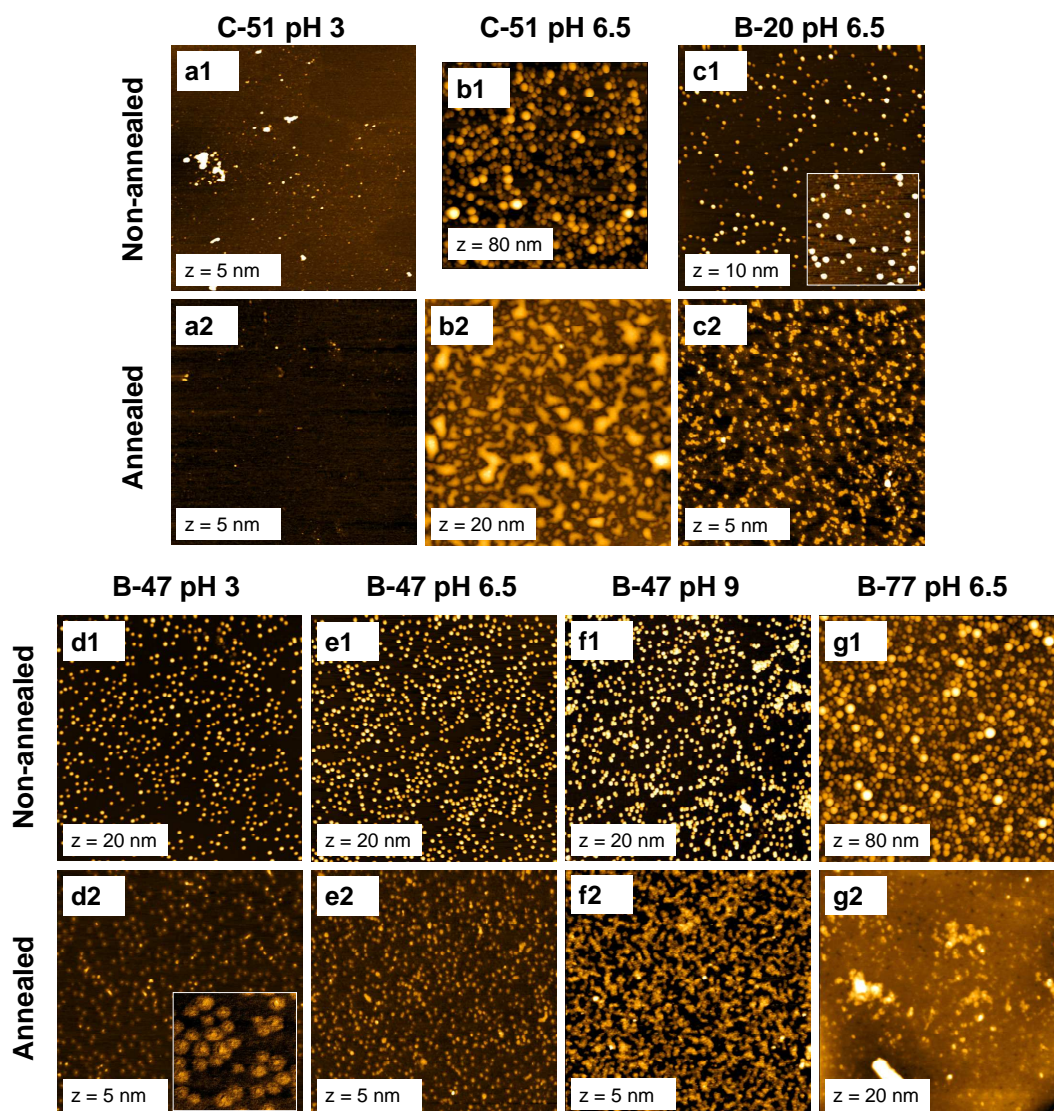


Figure 6. AFM topographic images of PDMAEMA-PTFEMA copolymer layers on mica. Image b1 is $2.5 \times 2.5 \mu\text{m}^2$, other images are $3 \times 3 \mu\text{m}^2$. Inset of c1 shows $1 \times 1 \mu\text{m}^2$ enlargement ($z = 2 \text{ nm}$). Inset of d2 shows a $0.7 \times 0.7 \mu\text{m}^2$ phase contrast image.^V

Featureless surfaces. The C-51 surfaces adsorbed at pH 3 were rather featureless, both before and after annealing (a1 and a2 in Figure 6). Some aggregates were observed on the non-annealed surface. The flat structure of the surfaces was attributed to the fact that the adsorbing species was unimeric. Both the advancing and receding contact angles of these surfaces were relatively high, ca. $80^{\circ}/40^{\circ}$ both before and after annealing (Table 6). This behavior was likely a combined effect of the relatively low hydrophilicity and high homogeneity and flatness of the surface. The C-51 pH 3 results demonstrate that when the statistical copolymer was adsorbed as a homogeneous layer, no annealing was necessary to obtain significant hydrophobization.

Surfaces with partial nanoparticle coverage. The B-20 and B-47 block copolymer surfaces consisted of a polymeric layer partially covering the mica substrate (c1-f1 and c2-f2 in Figure 6). Before annealing, these surfaces consisted of an array of particles divided by flat areas. After annealing the particles flattened and spread significantly. The formation of these surfaces was attributed to the irreversible adsorption of B-20 and B-47 nanoparticles. The particles had relatively large, charged coronas, inducing steric and electrostatic inter-particle repulsions on the surface. According to the random sequential adsorption (RSA) model, such adsorption process is expected to result in fractional surface coverage.^{109, 110} Variation in the adsorption pH affected the size and charge density of the particle coronas, which resulted in variation in the nanoparticle density on the surface, as observed in the pH series of B-47 surfaces (d1-f1 and d2-f2 in Figure 6).

The surfaces with partial coverage had rather large contact angle hysteresis (B-20 and B-47 in Table 6). The advancing contact angles on the non-annealed surfaces increased with increasing amount of particles on the surface, which at least to some extent could be attributed to the hydrophilic mica substrate becoming increasingly covered. The receding contact angles on the non-annealed surfaces were always low (below 20°). This behavior could correspondingly, at least to some extent, be attributed to pinning of the receding droplet line on the hydrophilic areas of uncovered mica. Annealing increased both the advancing and receding contact angles, which could be attributed to the mica

substrate becoming further more covered, and also potentially to the hydrophobic blocks reorganizing from the cores of the particles towards the uppermost surface layer.

Surfaces with high nanoparticle coverage. The C-51 and B-77 surfaces consisted of a polymer layer fully covering the substrate (b1, b2, g1 and g2 in Figure 6). Before annealing, the surfaces were rough with particles of various sizes visible in the AFM images. After annealing the surfaces flattened significantly. The high nanoparticle coverage when compared to B-20 and B-47 samples (discussed above) was expected to be a combined result of increased corona hydrophobicity, decreased corona charge density, and decreased corona size of the adsorbing nanoparticles, which have reduced the inter-particle repulsions and allowed more efficient packing on the surface.

The wetting behavior on the annealed surfaces was expected to a large extent reflect the intrinsic wetting behavior of the polymers, though the roughness could also have an effect as the surfaces were not perfectly smooth. The potential hydrophobicity of the annealed B-77 block copolymer surfaces was expected to be similar to the hydrophobicity of TFEMA homopolymer. The contact angles measured on the annealed B-77 surface (96°/63°) were slightly lower than values measured by Honda et al.⁷⁹ on PTFEMA homopolymer surface (102°/84°). This could indicate that the uppermost layer of the annealed B-77 surface still contained some DMAEMA units.

The wetting behavior of the non-annealed B-77 and C-51 (pH 6.5) surfaces was more complicated, with a high level of contact angle hysteresis. It has been observed previously, that rough surface structure in nanometer¹¹¹ or micrometer scale^{76, 77} can lead to high contact angle hysteresis. This type of behavior has been connected to surfaces, where the measurement droplet is able to wet the roughness features thoroughly. The low receding contact angles on such surfaces have been attributed to the entrapment of water during the receding stage within the roughness features through the capillary effect.

The static contact angles of B-77 and C-51 (pH 6.5) surface layers were also measured. The measured contact angles were rather close to each other on all the surfaces, within 75° - 85°, including both the non-annealed and the annealed surfaces. This demonstrates how inadequately the static contact angle measurements can describe the wettability of this type of surfaces.* The wettability of the non-annealed B-77 and C-51 (pH 6.5) surfaces was actually highly different from the wettability of the annealed surfaces. When the non-annealed surfaces were in contact with water (e.g. if the surface was immersed in water and then withdrawn), continuous water films were formed on the surfaces, due to the poor ability of the surfaces to dewet. On the contrary, when the annealed surfaces were in contact with water, distinct water droplets were formed on the surfaces.

7.3 PDMAEMA-TFEMA copolymers on cellulose fiber substrates^V

A set of contact angle experiments were conducted on cellulosic filter paper surfaces, in order to test the properties of the polymers when adsorbed on cellulosic surfaces, which bear a wide range of applications ranging from papermaking to textile industry. Whatman 3 filter paper, that was applied, consists of mainly (over 98 %) α -cellulose, and can therefore be used as a model for cellulose based materials. Cellulose substrates are anionic with low charge density, and cationic polyelectrolytes have been shown to adsorb on them.¹¹²⁻¹¹⁵

When those nanoparticles that provided high contact angles on mica were adsorbed on cellulose fiber substrates from 0.05 w/v-% solutions and annealed (B-77 and C-51 at pH 6.5), highly hydrophobic surfaces were obtained, with advancing contact angles around 160° (Figure 7). The receding stage of the droplets did not follow a well-defined path; some parts of the droplets receded already above 120°, indicating highly hydrophobic behavior, whereas other parts had receding contact angles close to 0°. The wetting behavior of the modified filter papers likely arises from the combination of the inherent

* For this reason, the wetting results of AS graft copolymers in chapter 3 and PDMAEMA-PMMA and PDMAEMA-PBMA copolymers in chapter 7.1 are only indicative.

roughness of the filter paper and of the hydrophobization of paper fibers by the polymer treatment.^{32, 116}

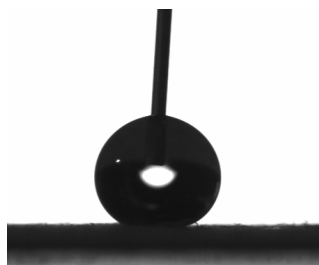


Figure 7. The measurement of the advancing contact angle on cellulosic filter paper treated with 0.05 w/v-% B-77 solution, after annealing. The advancing contact angle is ca. 160°.^v

8 CONCLUSIONS

This thesis described a method for modifying the wetting properties of various hydrophilic substrates with a minimal amount of amphiphilic polymer that is applied from an easily applicable solvent, water.

Majority of the experiments were conducted with amphiphilic polyelectrolytes. The polyelectrolytes had either statistical or block copolymer structure and they were synthesized by atom transfer radical polymerization (ATRP). Two series of polymers were synthesized. The first one consisted of copolymers with either DMAEMA or METAI as the hydrophilic monomer and either MMA or BMA as the hydrophobic monomer (PDMAEMA-PMMA and PDMAEMA-PBMA copolymers). The second series consisted of copolymers with either DMAEMA or METAI as the hydrophilic monomer, and TFEMA as the hydrophobic monomer (PDMAEMA-PTFEMA copolymers). Polymers with low polydispersities and controllable molecular weights and compositions were obtained.

Solution properties of the synthesized amphiphilic polyelectrolytes were studied in aqueous medium. The copolymers were either dissolved directly in water or assembled to aqueous nanoparticles through solvent exchange. The obtained solution structures were studied at varying conditions with e.g. dynamic light scattering, ^1H NMR spectroscopy and surface tension measurements. Unimeric, equilibrium micelle or kinetically trapped nanoparticle structures were observed, depending on the polymer, solution ionic strength and solution pH.

The aqueous conformations of the PDMAEMA-PTFEMA copolymers were studied by ^{19}F NMR relaxation time measurements at varying solution conditions. The longer the spin-lattice (T_1) and spin-spin (T_2) relaxation times were, the more extended the aqueous conformation of the polymer was expected to be. The shortest ^{19}F relaxation times were obtained from TFEMA units assembled to solid nanoparticle cores. The longest relaxation times were obtained from TFEMA units within water-solvated statistical

copolymers with low TFEMA contents and high charge densities. The potential of the PDMAEMA-PTFEMA copolymers as ^{19}F magnetic resonance imaging (MRI) agents was investigated.

The copolymers were applied on hydrophilic substrates from aqueous medium as ultra-thin layers. The effect of the thin polymer layer on surface wettability was studied by contact angle measurements, and the obtained surface structures were studied by AFM. The PDMAEMA-PMMA and PDMAEMA-PBMA copolymers were either spin-coated or adsorbed on silica. Wetting properties of the obtained layers were indicatively determined by static contact angle measurements. Alongside with the polymer composition, the surface preparation method was found to have an effect on the surface layer structure and wettability. The PDMAEMA-PTFEMA copolymers were adsorbed on mica and cellulose fiber substrates. Wetting properties of the obtained layers were determined by dynamic contact angle measurements. A range of wettability levels were measured, with advancing contact angles up to 100° on inherently flat surfaces (mica) and up to 160° on inherently rough surfaces (cellulose fiber substrate). The receding contact angles on mica varied from $\sim 0^\circ$ to 63° . The surface layer structures, e.g., whether the substrate was fully or only partly covered by the polymer, were studied on mica by AFM. The results could be correlated to the wetting properties.

In addition to the studies with amphiphilic polyelectrolytes, carbohydrate based polymers were studied for their potential in a similar wettability modification. The studied polymers were starch graft copolymers and glycopolymers with various sugars as side groups.

The starch graft copolymers consisted of acetylated starch oligomer as backbone, to which PMMA was grafted by ATRP. Graft copolymers with varying graft lengths and densities were prepared in a controlled manner. The polymers were spin-coated on silica from aqueous dispersions and THF solutions. A range of wettability levels were indicatively observed by static contact angle measurements.

The glycopolymers were synthesized with a route involving a combination of catalytic chain transfer polymerization (CCTP) to obtain the polymer backbone and Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) to obtain the sugar-functionalized side chains. The adsorption of cellobiose functionalized polymers on cellulose model surfaces from aqueous solutions was studied. The polymers were found not to adsorb on the substrates, possibly because they had quite low degrees of polymerization. However, mannose and galactose functionalized polymers were found to be recognized by various lectins, which indicated their potential in biological applications.

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ISBN 978-952-60-3397-6
ISBN 978-952-60-3398-3 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)